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and

Three-Hour Air Toxics Monitoring Program

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1989 NONMETHANE ORGANIC COMPOUND MONITORING PROGRAM AND THREE-HOUR AIR TOXICS MONITORING PROGRAM

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SYMBOLS AND ABBREVIATIONS

AC, or A.C.	area counts, generated from a gas chromatograph
ADELTA	absolute value of DELTA
ADIF	absolute value of DIF
ADIFF	absolute value of DIFF
AIRS	Aerometric Information Retrieval System
ALCA	Alpine, CA - AIRS No. 29-510-0072
a.m.	ante meridiem
APDIFF	absolute value of PDIFF
APDIF	absolute value of PDIF
APR	April
AREAL	Atmospheric Research and Exposure Assessment Laboratory
Aug	August
BACA	Bakersfield, CA - AIRS No. 06-029-0004
Bldg.	building
BMTX	Beaumont, TX - AIRS No. 48-245-0009
C3IL	Chicago, Illinois - AIRS No. 17-031-0042
C6IL	Chicago, Illinois - AIRS No. 17-031-0063
Cal., or Calib.	calibration
cm	centimeter
DELTA	Radian NMOC concentration - QAD NMOC concentration, ppmC; Radian NMOC concentration - ASRL concentration, ppmC; or AREAL NMOC concentration - QAD NMOC concentration, ppmC
DIF	(NMOC concentration for the second channel) - (NMOC concentration for the first channel
DIFF	measured NMOC concentration - calculated NMOC concentration ppmC for in-house quality control samples
DLTX	Dallas, TX - AIRS No. 48-113-0069
Dup.	duplicate
e	base of natural logarithm, 2.71828...
ECD	electron capture detector
ELCA	El Cajon, CA - AIRS No. 06-073-0003
ELTX	El Paso, TX - AIRS No. 48-141-0037
EPA	United States Environmental Protection Agency

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SYMBOLS AND ABBREVIATIONS (continued)

F	Friday
FID	flame ionization detector
FECA	Fremont, CA - AIRS No. 06-001-1001
GC/ECD	gas chromatography electron capture detection
GC/FID	gas chromatography flame ionization detection
GC/MD	gas chromatography multidetection
GC/MS	gas chromatography mass spectrometry
GRMI	Grand Rapids, MI - AIRS No. 26-081-0020
H	Thursday
H1TX	Houston, TX - AIRS No. 48-201-1034
Hg	mercury
i.d.	inside diameter
ID	identification
INST.	instrument
Jul	July
Jun	June
L	liter
LBCA	Long Beach, CA - AIRS No. 06-037-4002
Lpm	liters per minute
LXKY	Lexington, KY - AIRS No. 21-067-0012
m	meter
M	Monday
M1NY	New York, NY - AIRS No. 36-061-0056
MAX	maximum
MGAL	Montgomery, AL - AIRS No. 01-101-0008
MID	multiple ion detection
MIN	minimum
min.	minute
mL	milliliter
mm	millimeter
MNY	New York, NY - AIRS No. 36-061-0010
MU	mean of ln(NMOC)

(Continued)

SYMBOLS AND ABBREVIATIONS (continued)

NC	North Carolina
NIST	National Institute of Standards and Technology
NMOC	Nonmethane organic compound
NOx	oxides of nitrogen
NWNJ	Newark, NJ - AIRS No. 34-013-011
Oct	October
o.d.	outside diameter
Off.	Office
PCDIFF	percent difference = DIFF/calculated NMOC concentration x 100, for in-house QC samples
PDELTA	$\frac{\text{DELTA}}{[(\text{Radian NMOC concentration + QAD NMOC concentration})/2]} \times 100$; $\frac{\text{DELTA}}{[(\text{Radian NMOC concentration + AREAL NMOC concentration})/2]} \times 100$; or, $\frac{\text{DELTA}}{[(\text{AREAL NMOC concentration + QAD NMOC concentration})/2]} \times 100$
PDFID	preconcentration, direct flame ionization detection
PDIF	DIF/([(NMOC concentration, 1st channel) + (NMOC concentration, 2nd channel)]/2) x 100
PLNJ	Plainfield, NJ - AIRS No. 34-035-1001
p.m.	post meridiem
ppb	parts per billion
ppbv	parts per billion by volume
ppm	parts per million
ppmC	parts per million by volume as carbon
ppmv	parts per million by volume
psi	pounds (force) per square inch
psig	pounds (force) per square inch gauge
QA	quality assurance
QAD	Quality Assurance Division (EPA)
QAPP	Quality Assurance Project Plan
QC	quality control
RAO	Radian analysis order: RAO = 1 for the local ambient duplicate sample analyzed first by Radian; RAO = 2 for the local ambient duplicate sample analyzed first by EPA
RT	retention time
RTP	Research Triangle Park

(Continued)

S2MO	St. Louis, MO - AIRS No. 29-510-0072
SAROAD	Storage and Retrieval of Aerometric Data
Sep	September
SOP	standard operating procedure
SOx	oxides of sulfur
SRM	Standard Reference Material
SIGMA	standard deviation of ln(NMOC)
STD. DEV., SD	standard deviation
T	Tuesday
UATMP	Urban Air Toxics Monitoring Program
U.S.	United States
UTM	Universal Transverse Mercator
W	Wednesday
°C	degrees Celsius
°F	degrees Fahrenheit
%CV	percent coefficient of variation

1.0 SUMMARY AND CONCLUSIONS

In certain areas of the country where the National Ambient Air Quality Standard (NAAQS) for ozone is being exceeded, additional measurements of ambient nonmethane organic compounds (NMOC) are needed to assist the affected states in developing revised ozone control strategies. Because of previous difficulty in obtaining accurate NMOC measurements, the U.S. Environmental Protection Agency (EPA) has provided monitoring and analytical assistance to these states through Radian Corporation. This assistance began in 1984 and continues through the 1989 NMOC Monitoring Program.

Between June 5 and September 29, 1989, Radian analyzed 1,956 ambient air samples, including 194 duplicate samples, collected in SUMMA® polished stainless steel canisters at 23 sites. These NMOC analyses were performed by the cryogenic preconcentration, direct flame ionization detection (PDFID) method.[1] Based on the 1984 through 1988 studies, the method was shown to be precise, accurate, and cost effective relative to the capillary column gas chromatographic, flame ionization detection (GC/FID) method (see Appendix B). The 1989 study confirmed these findings and supported the conclusion that the PDFID method is the method of choice to measure NMOC concentration in ambient air.

In 1986 specific toxic compounds, primarily aromatics and halocarbons, were also determined in the ambient air samples used for the NMOC analyses. In 1987 Radian Corporation developed a gas chromatographic multidetector (GC/MD) method to determine the concentration of 38 selected toxic organic compounds in ambient air. In 1988, air toxic analyses were conducted by GC/MD on ambient air samples taken at 13 sites at which NMOC samples were taken. In 1989, air toxic analyses were conducted on ambient air samples taken at seven sites at which NMOC samples were taken. These samples were called 3-hour air toxics samples because the sampling period was three hours, from 6:00 a.m. to 9:00 a.m. The 1989 Urban Air Toxics Monitoring Program (UATMP) began in January 1989 at 13 urban sites and extended through December 1989. The samples from the latter program were 24-hour integrated ambient air samples and are referred to as UATMP samples throughout this report.

The Final Report for the 1989 Nonmethane Organic Compound and Three-Hour Air Toxics Monitoring program are included in Sections 1.0 through

10.0. Sections 1.0 through 6.0 report the data, procedures, and assessment of the NMOC portion of the monitoring program. Sections 7.0 through 9.0 report the data, procedures, and assessment of the 3-hour air toxics portion of the monitoring program. Section 10.0 lists references.

The sampling sites for the 1989 NMOC Monitoring Program are listed in Appendix A. Appendix A also gives the EPA Regions for each site, the Radian Site Code, the Storage and Retrieval of Aerometric Data (SAROAD) numbers, the Aerometric Information Retrieval System (AIRS) numbers, and whether or not 3-hour air toxics analyses were performed on selected ambient air samples from the site.

Appendix B contains the detailed instructions on the Cryogenic Preconcentration and Direct Flame Ionization Detection (PDFID) method. Appendix C lists the 1989 NMOC Monitoring Program Site Data. Appendix D lists the 1989 NMOC Monitoring Program Invalidated and Missing Samples information. Appendix E gives PDFID Integrator Programming Instructions. Appendix F gives 1989 NMOC Daily Calibration Data. Appendix G gives 1989 In-House Quality Control Samples, and Appendix H gives Multiple Detector Speciated Three-Hour Site Data Summaries.

The UATMP data and results will be reported under separate cover in a final report for the UATMP.

1.1 NMOC MONITORING PROGRAM

1.1.1 Introduction and Data Summary

Table 1-1 gives details of the sample completeness results. Percent completeness, a quality measure is shown in Table 1-1. Completeness, which ratios the number of valid samples to the number of scheduled samples, averaged 95.5% in 1989 compared to 93.4% in 1988, 95.0% in 1987, 96.8% in 1986, 95.8% in 1985, and 90.6% in 1984. Percent completeness for 1989 ranged from 86.81 at S3CA (AIRS No. 66-067-0010, Sacramento, CA) to 101.10 for ELTX (AIRS No. 48-141-0037, El Paso, TX). During the last week of the 1989 NMOC Monitoring Program, the ELTX site had one more cleaned canister than was needed to complete its scheduled samples, so an extra duplicate was collected.

TABLE 1-1. 1989 COMPLETENESS RESULTS

Radian Site Code Complete	Scheduled Sampling Days	Total Scheduled Duplicate Samples	Total Scheduled Samples	Total Valid Duplicate Samples	Total Valid Samples	Percent
ALCA	83	8	91	11	89	97.80
BACA	83	8	91	10	83	91.21
BMTX	83	8	91	10	90	98.90
C3IL	83	8	91	8	84	92.31
C6IL	83	8	91	7	85	93.41
DLTX	83	8	91	8	91	100.00
ELCA	83	8	91	7	85	93.41
ELTX	83	8	91	8	92	101.10
FECA	83	8	91	8	87	95.60
GRMI	83	8	91	7	88	96.70
H1TX	82	8	90	9	83	92.22
LBCA	67	8	75	7	71	94.67
LXKY	83	8	91	9	91	100.00
M1NY	82	8	90	9	89	98.89
MGAL	83	8	91	8	86	94.51
NMY	83	8	91	8	85	93.41
NWNJ	83	8	91	8	88	96.70
PLNJ	83	8	91	10	87	95.60
RLNC	83	8	91	7	90	98.90
RSCA	59	7	66	9	59	89.39
S2MO	82	8	90	8	88	97.78
S3CA	83	8	91	10	79	86.81
S4CA	83	8	91	8	86	94.51
Overall	1866	183	2049	194	1956	95.46

Statistics for the NMOC concentrations in parts per million carbon (ppmC) by volume are listed in Table 1-2. In Table 1-2, the sites are divided into "Morning Sites," "Late Morning Sites," and "Above-300-m-Altitude Sites." The Morning Sites are those that collected samples from 6:00 a.m. to 9:00 a.m.; Late Morning Sites sampled from 9:00 a.m. to noon; the Above-300-m-Altitude Sites sampled from 6:00 a.m. to 9:00 a.m. at an altitude above 300 meters.

The sites were separated into these classifications because experience has shown[3] the average NMOC concentrations to be different for the three groups. The overall mean NMOC concentration for the Morning Sites was 0.577 ppmC, while for the Late Morning Sites, the mean was 0.158 ppmC. The mean for the Above-300-m-Altitude Site was 0.267 ppmC.

1.1.2 Calibration and Drift

Each Radian PDFID channel was calibrated twice daily, using propane standards referenced to the National Institute of Science and Technology (NIST) Reference Material No. 1666B propane. Daily, before zero and calibration checks were performed, the analytical systems were purged with cleaned, dried air that had been humidified. Zero readings were determined with cleaned, dried air. Daily percent drift of the calibration factor ranged from -4.5% to +4.5%, averaging -0.375 percent. The absolute value of the percent drift of the daily calibration factors ranged from zero to 4.5%, averaging 0.61 percent.

1.1.3 Precision

Analytical precision was determined by repeated analyses of 156 site samples. Percent differences between the second and the first analysis averaged -0.019 percent. The average of the absolute values of the percent difference was 8.2% with a standard deviation of 12.1. The analytical precision includes the variability between Radian channels and within Radian channels. The data quality objective for this measurement as published in the 1989 Quality Assurance Project Plan (QAPP)[2] was 9.8%, based on previous NMOC program experience[3] with this measurement.

Overall precision, including sampling and analysis variability, was determined by analysis of 181 duplicate site samples, simultaneously collected in two canisters from a common sampling system. Percent difference for Radian's analyses of the duplicates averaged 4.2 percent. The average

TABLE 1-2. 1989 NMOC SITE STATISTICS

Radian Site Code	NMOC, ppmC Minimum	Median	Mean	Maximum	Standard Deviation	Skewness	Kurtosis
Morning Sites (Sampling 6:00 to 9:00 a.m., local time)							
BACA	0.150	0.799	0.809	2.499	0.409	0.917	2.185
BMTX	0.220	0.655	0.830	4.047	0.631	2.880	10.367
C6IL	0.126	0.764	0.851	2.663	0.506	1.233	2.013
DLTX	0.114	0.421	0.474	1.612	0.285	1.548	3.111
ELCA	0.088	0.305	0.452	1.733	0.366	1.644	2.260
ELTX	0.093	0.381	0.498	2.442	0.402	2.375	6.917
FECA	0.124	0.371	0.519	2.491	0.411	2.068	5.795
GRMI	0.203	0.517	0.641	1.880	0.387	1.234	0.739
H1TX	0.180	0.632	0.791	2.614	0.479	1.251	1.639
LBCA	0.242	0.697	0.881	2.855	0.573	1.606	1.922
LXKY	0.082	0.270	0.377	1.796	0.342	2.547	6.574
M1NY	0.211	0.527	0.601	2.043	0.336	1.935	5.180
MGAL	0.087	0.192	0.221	1.133	0.156	4.299	21.667
MNY	0.127	0.515	0.555	1.609	0.286	1.222	1.819
NWNJ	0.158	0.519	0.652	3.693	0.539	2.944	11.375
PLNJ	0.073	0.407	0.529	1.796	0.384	1.354	1.316
RLNC	0.137	0.137	0.162	0.551	0.162	1.368	1.916
RSCA	0.210	1.113	1.224	3.993	0.796	1.278	1.666
S2MO	0.187	0.607	0.747	5.013	0.640	3.941	21.229
S3CA	0.075	0.205	0.310	2.452	0.340	3.920	19.325
S4CA	0.061	0.179	0.262	1.534	0.266	3.192	11.112
Overall	0.043	0.434	0.577	5.013	0.493	2.461	10.334
Late Morning Site (Sampling 9:00 a.m. to noon, local time)							
ALCA	0.037	0.117	0.158	0.867	0.151	3.560	12.838
Above-300-m-Altitude Site (Sampling 6:00 to 9:00 a.m., local time)							
C3IL	0.042	0.228	0.267	0.954	0.172	1.481	2.721

absolute percent difference was 10.6% with a standard deviation of 14.2. The data quality objective for this measurement was 12.2%, based on previous experience.[2]

1.1.4 Accuracy

Because the NMOC measurements encompass a range of mixtures of unknown compounds, it was not possible to define absolute accuracy. Instead, accuracy was determined relative to propane standards with internal and external audit samples.

Accuracy was monitored internally throughout the program by the use of in-house propane standards. Four days per week an in-house propane quality control (QC) sample was prepared with a flow dilution apparatus and analyzed by the PDFID method. The propane used to prepare the in-house QC standards was certified by the EPA Quality Assurance Division (QAD) and was referenced to NIST No. 1666B.

Figures 1-1 through 1-4 show the in-house quality control results for Radian Channels A, B, C, and D. Measured propane values are plotted against calculated propane standards. Table 1-3 shows the linear regression parameters for the Radian in-house quality control data. Daily quality control samples of propane were mixed from a propane standard certified by EPA-QAD and referenced to NIST propane Standard No. 1666B. The regression used the propane concentration calculated from the mixing operation as the independent variable and concentration measured by each Radian channel as the dependent variable. The concentration range of the in-house quality control samples was 0.020 to 18.000 ppmC. Table 1-3 indicates excellent quality control for each channel since, as expected, the intercepts are all near zero, and the slopes and coefficients of correlation are all near 1.0.

External propane audit samples were provided by EPA-QAD. The propane samples were referenced to NIST propane Standard No. 1666B. Table 1-4 summarizes the percent bias of the Radian channels and the EPA Atmospheric Research and Exposure Assessment Laboratory (AREAL) channel relative to the EPA-QAD channel. The audit samples were given Radian ID Numbers upon receipt. Radian ID No. 1004 was received in May 1989, and the other two audit samples were received in September 1989. The average percent bias for the Radian

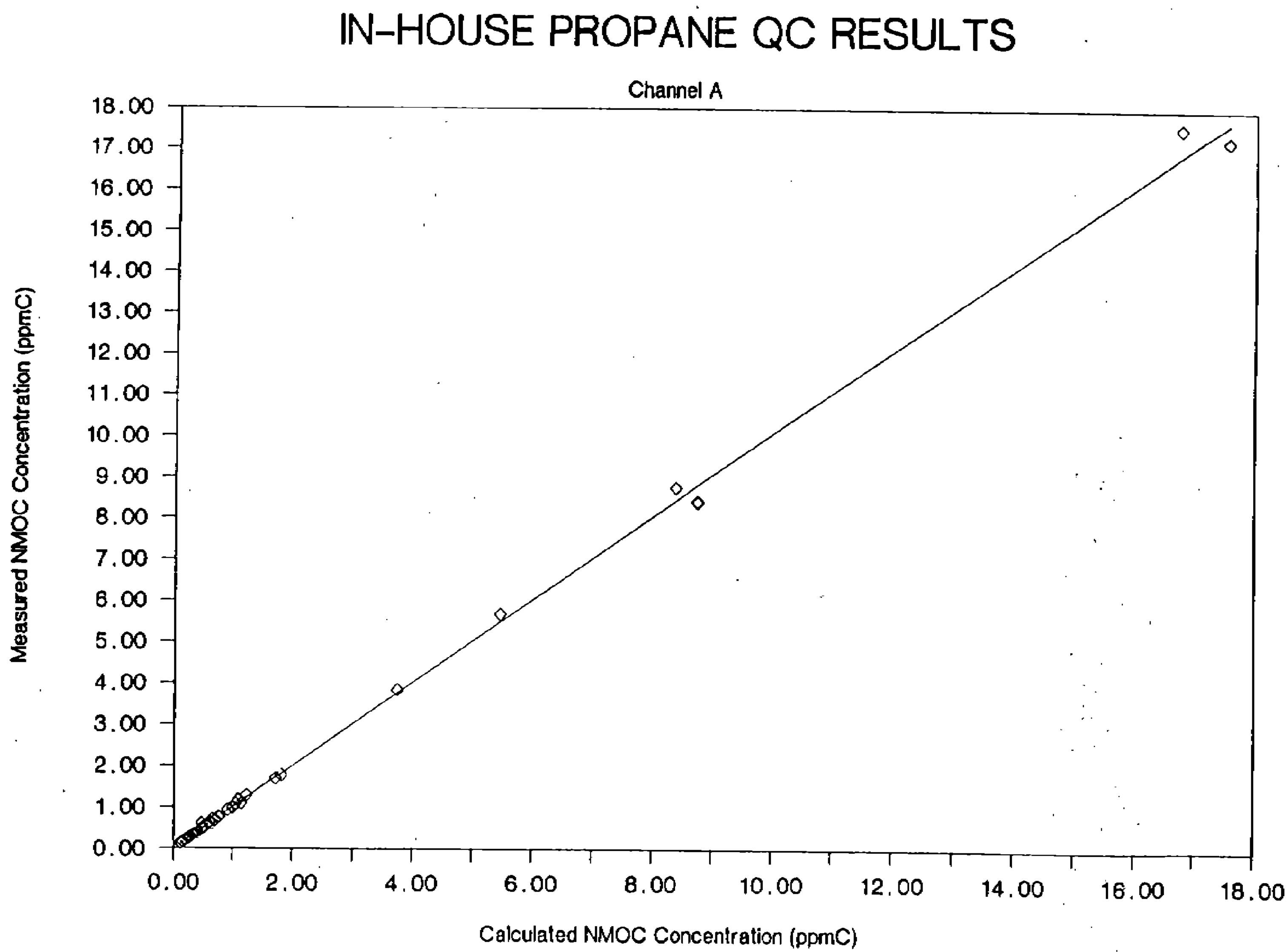


Figure 1-1. In-house quality control results, Channel A.

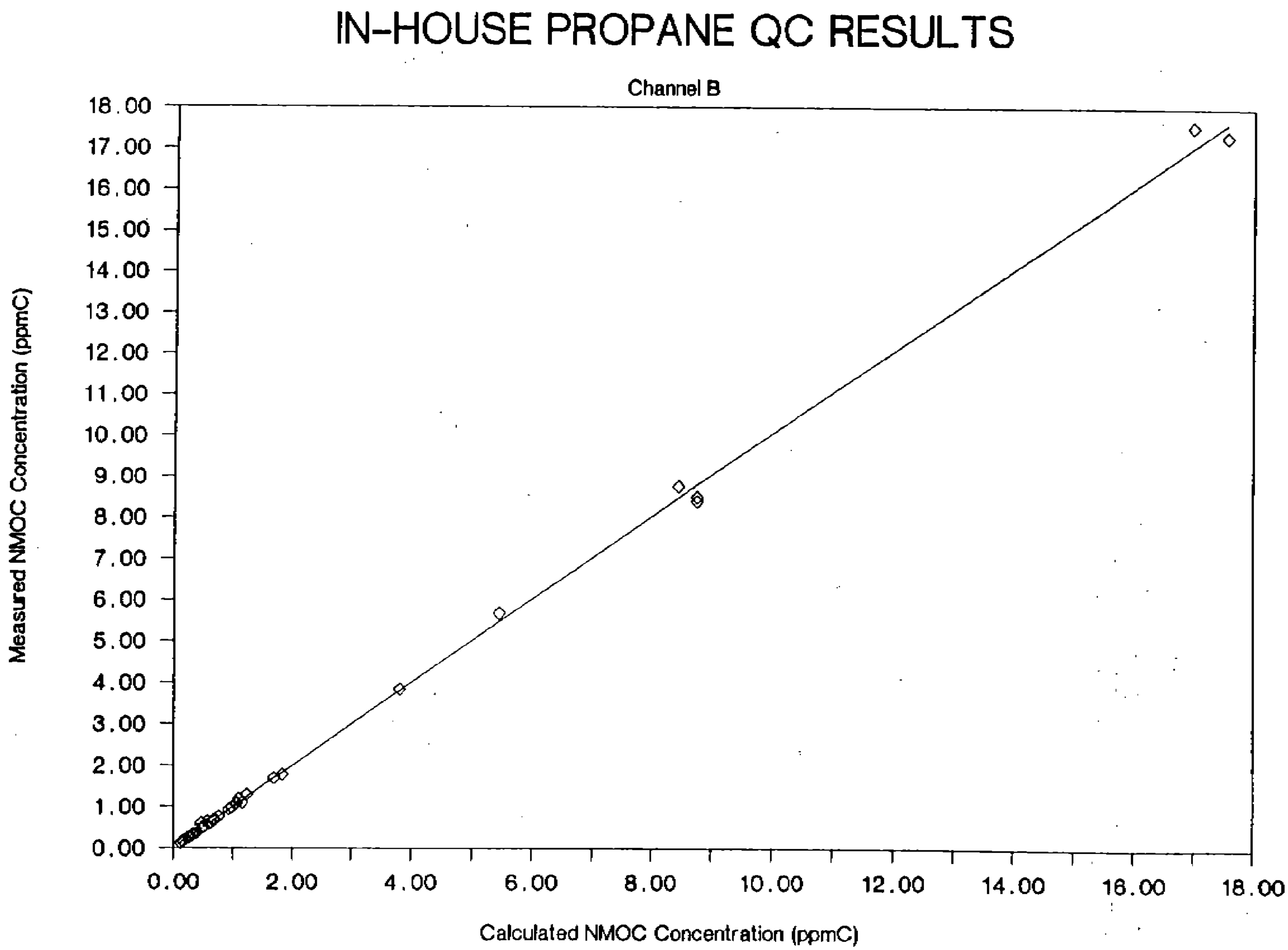


Figure 1-2. In-house quality control results, Channel B.

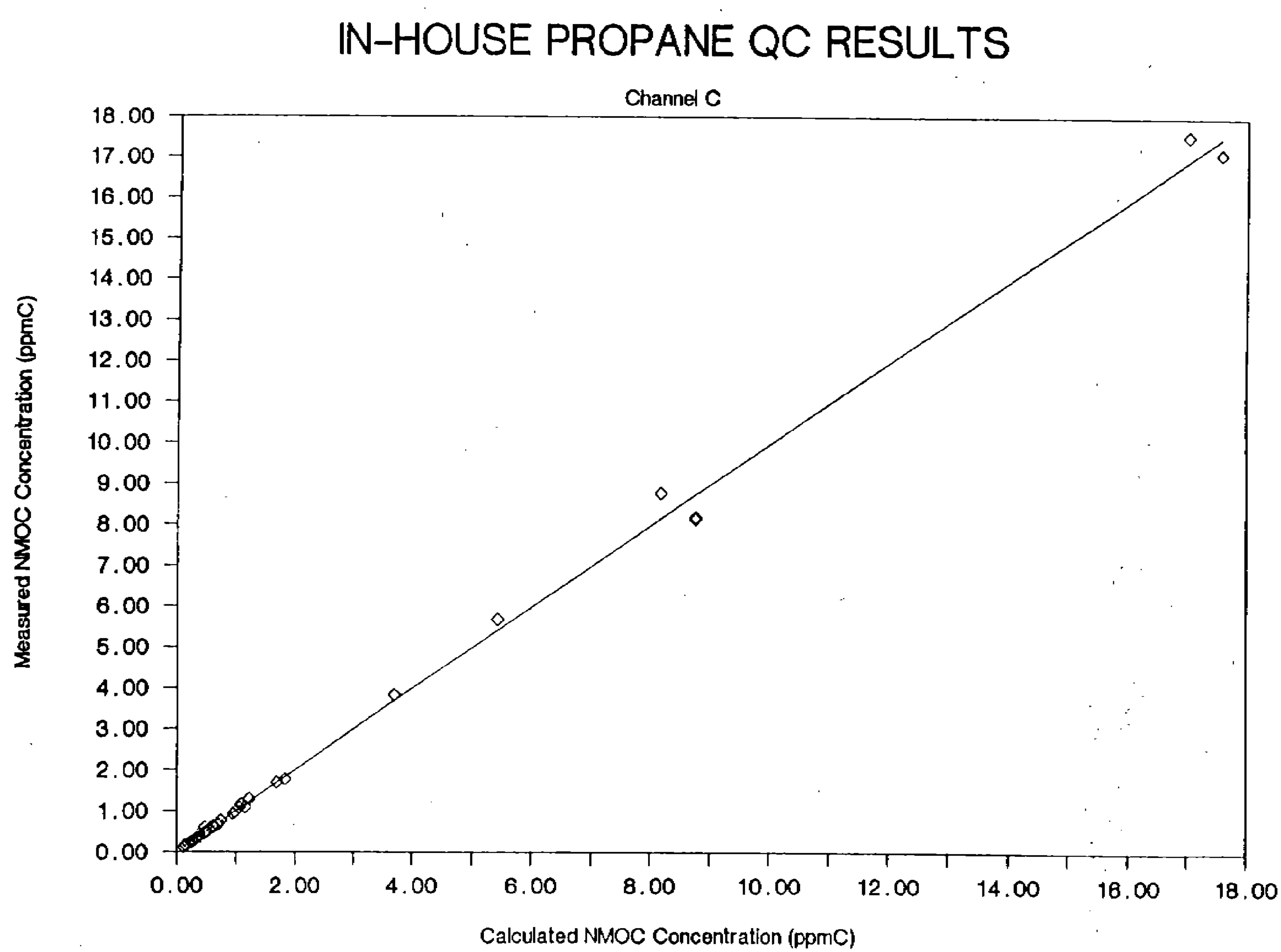


Figure 1-3. In-house quality control results, Channel C.

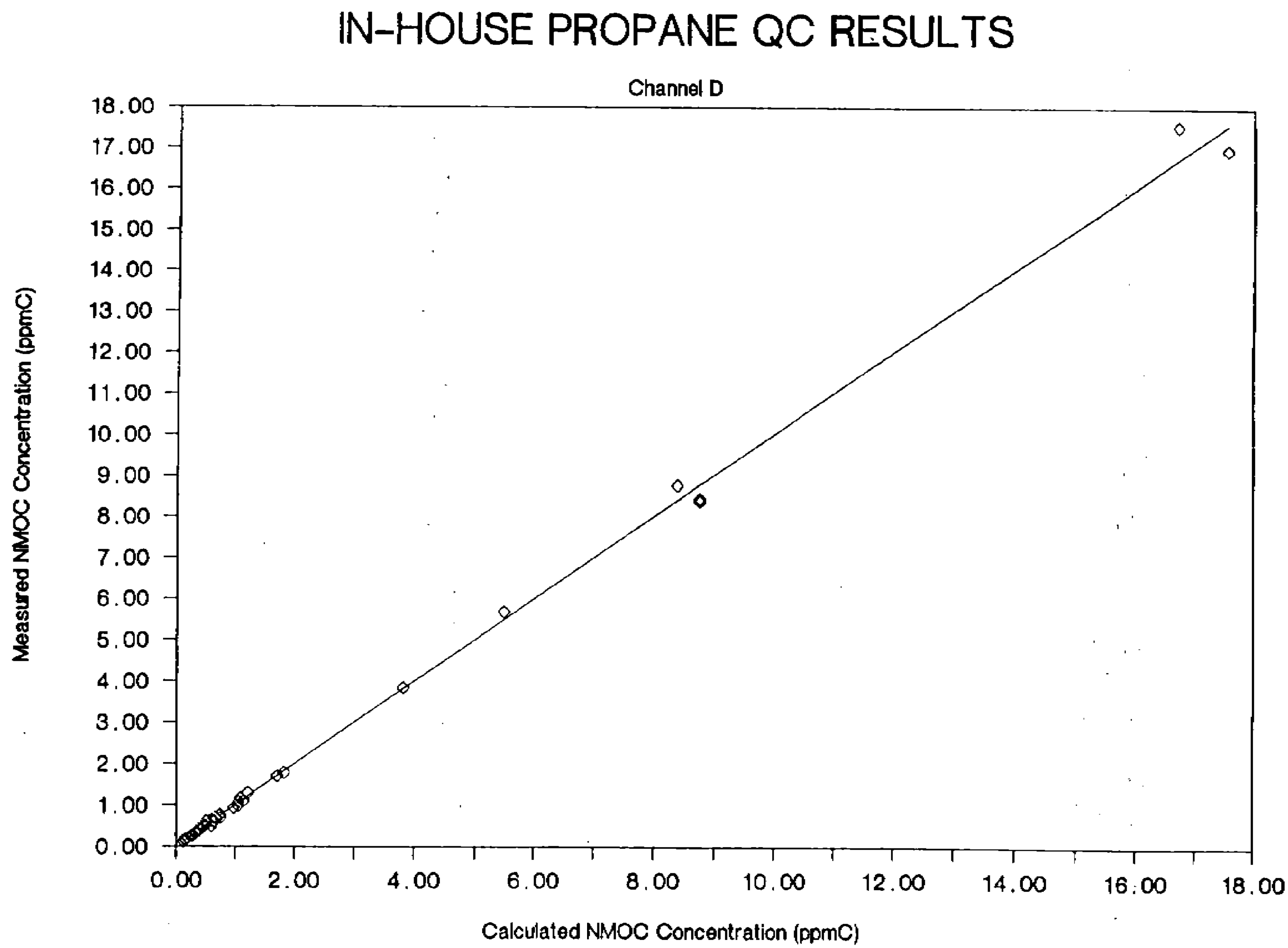


Figure 1-4. In-house quality control results, Channel D.

TABLE 1-3. LINEAR REGRESSION PARAMETERS FOR IN-HOUSE QUALITY CONTROL DATA

Radian Channel	Cases	Intercept	Slope	Coefficient of Correlation
A	51	-0.000182	1.007578	0.999184
B	51	0.005195	1.004650	0.999457
C	51	0.010023	0.997043	0.998786
D	51	0.001783	1.002389	0.998910

TABLE 1-4. AUDIT SAMPLE RESULTS, PERCENT BIAS[a]

Radian ID Number	Channels A Percent Bias	B Percent Bias	C Percent Bias	D Percent Bias	Radian Percent Bias
1005	0.00	-1.13	-1.04	-1.04	
1006	-0.96	-3.23	1.05	0.99	
1647	3.30	5.50	3.85	2.75	
1648	0.86	1.26	0.93	1.26	
1969	2.21	4.70	0.41	-0.69	
2290	-2.40	-3.41	1.01	-5.18	
3020	1.72	-0.69	-0.86	-3.78	
3021	-3.26	-1.68	-10.15	-3.16	
Average	0.78	0.16	0.80	-1.11	-0.34
Std. Dev.	2.24	3.39	4.14	2.75	3.22

[a]Percent Bias = [(Measured NMOC - QAD NMOC) / QAD NMOC] x 100.

channels was 0.84%, ranging from 0.30% for Channel B to 1.29% for Channel C. Absolute percent biases are listed in Table 1-5 and range from 1.84% for Channel A to 2.70% for Channel B, averaging 2.33% overall for the Radian channels.

1.1.5 Other Quality Assurance Measurements

The results of other quality assurance measurements are discussed below. Canister cleanup studies established that there was little carryover of NMOC from one sample to the next, using the canister cleanup apparatus and procedure developed for this study. In 206 separate determinations, percent cleanup averaged 99.742%, ranging from 92.12% to 100 percent. Cleanup was defined in terms of the percent of the NMOC concentration that was removed in the cleanup cycle. Figure 1-5 shows a between-laboratory comparison of site sample analyses involving Radian channels and the EPA-QAD channel for the PDFID method. Figure 1-6 shows comparisons of EPA-ASRL and EPA-QAD channels. Table 1-6 gives the orthogonal regression parameters, assuming a linear relationship, for Figures 1-5 and 1-6 and other possible comparisons. The results show good agreement because the intercepts are very close to zero, the slopes are within 10% of 1.0, and the coefficients of correlation are within 3% of 1.0. Approximately 14.6% of the NMOC data base was validated by checking data transcriptions from original data sheets for 36 entries per sample. The errors found equal a data base error rate of 0.369 percent. The data validation included 100% of the reported NMOC concentration values. All errors that were found were corrected.

1.2 THREE-HOUR AIR TOXICS MONITORING PROGRAM

At seven sites, 3-hour NMOC samples were speciated by a GC/MD analytical system for 38 UATMP target compounds for a total of 64 NMOC ambient air samples. After NMOC analysis, the NMOC sample canisters were bled to atmospheric pressure, stored at least 18 hours for equilibration, and then analyzed by GC/MD. Duplicate samples were collected at all seven of the sites simultaneously and analyzed individually by GC/MD. Replicate analyses were performed on one duplicate sample per site. A total of 78 GC/MD analyses were performed, including duplicate samples and replicate analyses.

TABLE 1-5. AUDIT SAMPLE RESULTS, ABSOLUTE PERCENT BIAS

Radian ID Number	Channels A Percent Bias	B Percent Bias	C Percent Bias	D Percent Bias	Radian Absolute Percent Bias
1005	0.00	1.13	1.04	1.04	
1006	0.96	3.24	1.06	0.99	
1647	3.30	5.50	3.85	2.75	
1648	0.86	1.26	0.93	1.26	
1969	2.21	4.70	0.41	0.69	
2290	2.40	3.41	1.01	5.18	
3020	1.72	0.69	0.86	3.78	
3021	3.26	1.68	10.15	3.16	
Average	1.84	2.70	2.41	2.35776	2.32761
Std. Dev.	1.18	1.79	3.30	1.62150	2.12701

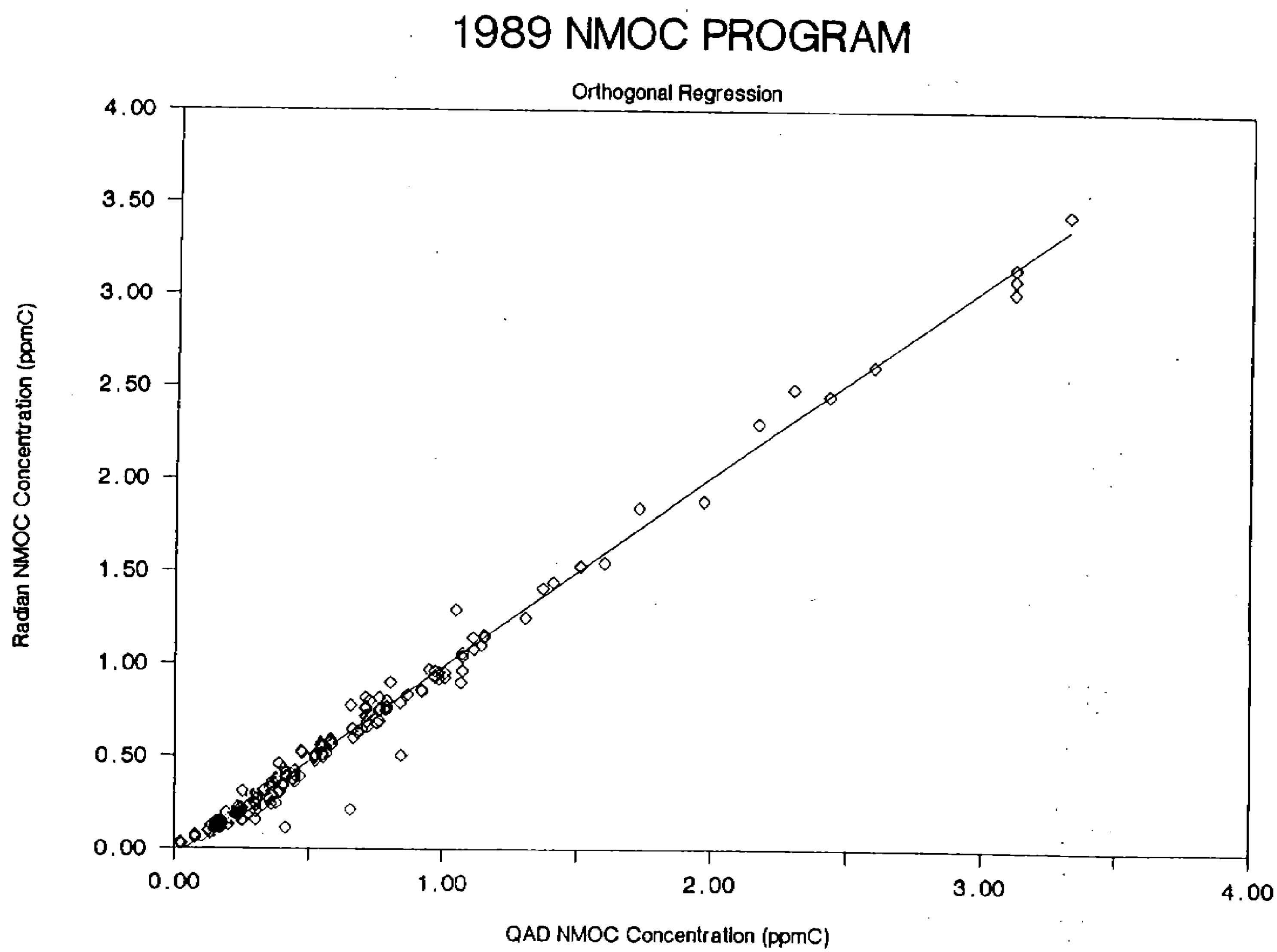


Figure 1-5. Orthogonal regression comparing QAD with Radian NMOC analyses.

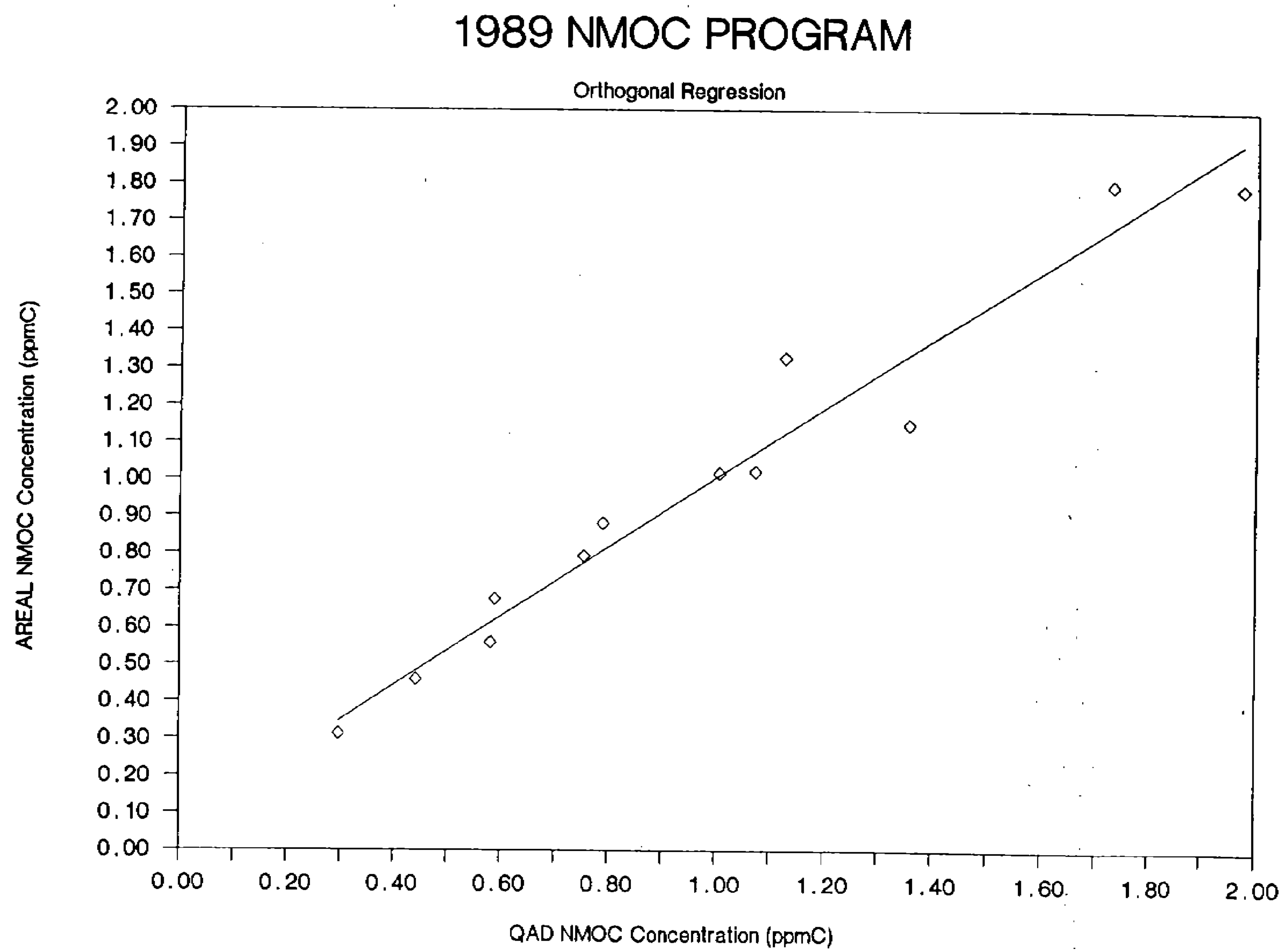


Figure 1-6. Orthogonal regression comparing QAD with AREAL NMOC analyses.

TABLE 1-6. ORTHOGONAL REGRESSION PARAMETERS FOR COMPARATIVE ANALYSES OF SITE SAMPLES

Channel Pair (X-Y)	Cases	Intercept	Slope	Coefficient of Correlation
QAD-Radian	202	-0.038190	1.025019	0.995887
Radian-QAD	202	0.037260	0.975590	0.995887
AREAL-Radian	20	-0.136310	1.098092	0.995908
Radian-AREAL	20	0.124140	0.910670	0.995908
QAD-AREAL	12	0.069707	0.933637	0.975807
AREAL-QAD	12	-0.074660	1.071079	0.975807

1.2.1 Overall Data Summary

Twenty-seven target compounds were identified in the 78 analyses. Benzene, m/p-xylene, toluene, ethylbenzene, styrene/o-xylene, carbon tetrachloride, and 1,1,1-trichloroethane were the most frequently identified compounds. Concentrations of the target compounds identified ranged from 0.01 ppbv for 1,1,2-trichloroethane to 88.90 ppbv for m/p-xylene. The overall average concentration of the target compounds identified was 2.28 ppbv.

1.2.2 Site Results

Overall site mean concentrations ranged from 0.92 ppbv for C3IL to 5.34 ppbv for C6IL for the target compounds identified. These data are presented in Section 7.0.

1.2.3 Gas Chromatography/Mass Spectrometry Confirmation Results

Fourteen 3-hour air toxics ambient air samples were analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) for compound identification confirmation of the GC/MD analyses. The GC/MS analyses were performed after the GC/MD analyses. The GC/MS analyses confirmed 93.9% of the GC/MD analyses.

For the 3-hour air toxics samples the negative GC/MD-positive GC/MS analyses were 3.57 percent. The positive GC/MD-negative GC/MS analyses were 2.52 percent.

1.2.4 Precision

Sampling and analytical precision of 3-hour air toxics samples was estimated by analyzing duplicate samples. In terms of overall average absolute percent difference, the sampling and analysis precision was 8.72 percent.

Analytical precision was estimated by repeated analyses of seven duplicate samples. The analytical precision measured by the overall average absolute percent difference was 9.12 percent. Both the sampling and analytical precision results are excellent in view of the concentration range found in this study.

The data analyses showed that both for the duplicate and replicate results, the imprecision was significantly higher at concentrations less than 2 ppbv. Both the duplicate sample and repeated analyses results are discussed in Section 8.0.

1.2.5 External Audit

UATMP External Audit Sample No. 3 was received from the EPA-QAD and analyzed prior to the analyses of the 3-hour air toxics samples. The sample was analyzed by both the GC/MD and the GC/MS analytical systems. An average bias of 0.84% was found for the GC/MD analyses and an average bias of -20.5% was found for the GC/MS analyses. In view of the fact that the GC/MS analyses were used as a qualitative screening tool for compound identification confirmation (and not for quantitation), these are excellent results and well within the data quality objectives of the program.

2.0 NMOC DATA SUMMARY

This section presents the data summary for the 1989 NMOC Monitoring Program conducted during June, July, August, and September. Daily NMOC concentrations and other pertinent monitoring data are given by site in Appendix C. The majority of the data presented in this section summarize the NMOC concentrations measured for samples collected at 23 sites throughout the continental United States. Sites were selected in urban and/or industrial locations; they are described in Appendix A. The site codes for the 1989 NMOC Monitoring Program are listed in Appendix A and are used throughout the report to identify the sites. Samples were collected in 6-liter (L) stainless steel canisters by local site operators trained by Radian Corporation personnel. The sampling procedure was described in detailed written instructions and given to the site operators. The sampling procedure instructions also appear in Section 3.1.2. Analytical concentration measurements of NMOC were made in the Radian Corporation Research Triangle Park (North Carolina) laboratory according to the PDFID method TO-12.[1] The complete procedure is described in Appendix B.

The concentration of oxides of nitrogen (NO_x), site temperature, barometric pressure, wind direction, and weather conditions were provided on the field sampling forms by site personnel at the time of sampling. These data were recorded in the 1989 NMOC data base, but are not presented in this report because they were not measured by Radian equipment or personnel, nor were the data subjected to project quality assurance procedures.

Table 2-1 lists the NMOC Monitoring Program completeness results by site code. The scheduling of sample days and the scheduling of duplicate analyses is given in the QAPP.[2] One site, ELTX (El Paso, TX), produced over 100% completeness by taking an unscheduled duplicate in addition to all other scheduled samples. For the remainder of the 1989 NMOC sites, completeness was over 80%, and generally very near to 100 percent. A complete listing of invalid samples and the reasons for the invalidation are given in Appendix D.

Overall completeness figures for the 1989 NMOC Program show 95.5% complete. This compares with 93.4% in 1988, 95.0% complete in 1987, 96.8% complete in 1986, 95.8% complete in 1985 and 90.6% complete in 1984.[2,3,4,5]

TABLE 2-1. 1989 COMPLETENESS RESULTS

Radian Site Code Complete	Scheduled Sampling Days	Total Scheduled Duplicate Samples	Total Scheduled Samples	Total Valid Duplicate Samples	Total Valid Samples	Percent
ALCA	83	8	91	11	89	97.80
BACA	83	8	91	10	83	91.21
BMTX	83	8	91	10	90	98.90
C3IL	83	8	91	8	84	92.31
C6IL	83	8	91	7	85	93.41
DLTX	83	8	91	8	91	100.00
ELCA	83	8	91	7	85	93.41
ELTX	83	8	91	8	92	101.10
FECA	83	8	91	8	87	95.60
GRMI	83	8	91	7	88	96.70
HITX	82	8	90	9	83	92.22
LBCA	67	8	75	7	71	94.67
LXKY	83	8	91	9	91	100.00
M1NY	82	8	90	9	89	98.89
MGAL	83	8	91	8	86	94.51
NMY	83	8	91	8	85	93.41
NWNJ	83	8	91	8	88	96.70
PLNJ	83	8	91	10	87	95.60
RLNC	83	8	91	7	90	98.90
RSCA	59	7	66	9	59	89.39
S2MO	82	8	90	8	88	97.78
S3CA	83	8	91	10	79	86.81
S4CA	83	8	91	8	86	94.51
Overall	1866	183	2049	194	1956	95.46

Completeness was defined as the percentage of samples, scheduled in the QAPP,[1] that were collected and analyzed as valid samples, beginning with the first valid sample and ending with the last scheduled sample.

Table 2-2 summarizes statistics by sites into three classifications, Morning Site, Late Morning Site, and Above-300-m-Altitude site. "Morning Sites" were those where an integrated sample was collected from 6:00 a.m. to 9:00 a.m. "Late Morning Site" collected samples 9:00 a.m. to noon. The "Above 300-m-Altitude Site" collected ambient air samples from 6:00 a.m. to 9:00 a.m. at an altitude above 300 meters from ground level. Morning and Late Morning Site samples were collected at 3 to 10 meters above ground level. The subclassifications of the NMOC monitoring sites were made because the mean NMOC values were expected[3] to be different in the Morning and Late Morning Sites, and at the higher elevations above ground level. It is not known whether the difference between the Morning Sites and the Late Morning Sites is because of their locations, because of the difference in time of the collection of the sample, or both.

The overall average of the Morning Site NMOC concentration is seen to be 0.577 ppmC, while the Late Morning Site NMOC concentration average is 0.158 ppmC, about 27% of the morning concentration average. The higher altitude site averaged 0.267 ppmC, only 46% of the morning concentration average. The averages given here are not intended to be characteristic of all possible sites, sampling times, or altitudes. The averages pertain only to the sites for the 1989 Monitoring Program.

In Table 2-2, the means are the arithmetic averages of the NMOC concentrations at each site. The numbers given for standard deviation, skewness, and kurtosis are the second, third, and fourth moments, respectively about the arithmetic means. A skewness value greater than zero applies to distributions having a longer tail to the right. A distribution that is normally distributed would have a kurtosis of 3.0. A distribution more peaked (or pointed) than a normal distribution, having the same variance, would have a kurtosis greater than 3.0.

NMOC monitoring data can be better characterized by a lognormal distribution than by a normal distribution, following the findings of previous years.[3,4,5,6,7] Table 2-3 summarizes the 1989 NMOC data using the definitions

TABLE 2-2. 1989 NMOC SITE STATISTICS

Radian Site Code	NMOC, ppmC Minimum	Median	Mean	Maximum	Standard Deviation	Skewness	Kurtosis
Morning Sites (Sampling 6:00 to 9:00 a.m., local time)							
BACA	0.150	0.799	0.809	2.499	0.409	0.917	2.185
BMTX	0.220	0.655	0.830	4.047	0.631	2.880	10.367
C6IL	0.126	0.764	0.851	2.663	0.506	1.233	2.013
DLTX	0.114	0.421	0.474	1.612	0.285	1.548	3.111
ELCA	0.088	0.305	0.452	1.733	0.366	1.644	2.260
ELTX	0.093	0.381	0.498	2.442	0.402	2.375	6.917
FECA	0.124	0.371	0.519	2.491	0.411	2.068	5.795
GRMI	0.203	0.517	0.641	1.880	0.387	1.234	0.739
H1TX	0.180	0.632	0.791	2.614	0.479	1.251	1.639
LBCA	0.242	0.697	0.881	2.855	0.573	1.606	1.922
LXKY	0.082	0.270	0.377	1.796	0.342	2.547	6.574
M1NY	0.211	0.527	0.601	2.043	0.336	1.935	5.180
MGAL	0.087	0.192	0.221	1.133	0.156	4.299	21.667
MNY	0.127	0.515	0.555	1.609	0.286	1.222	1.819
NWNJ	0.158	0.519	0.652	3.693	0.539	2.944	11.375
PLNJ	0.073	0.407	0.529	1.796	0.384	1.354	1.316
RLNC	0.137	0.137	0.162	0.551	0.162	1.368	1.916
RSCA	0.210	1.113	1.224	3.993	0.796	1.278	1.666
S2MO	0.187	0.607	0.747	5.013	0.640	3.941	21.229
S3CA	0.075	0.205	0.310	2.452	0.340	3.920	19.325
S4CA	0.061	0.179	0.262	1.534	0.266	3.192	11.112
Overall	0.043	0.434	0.577	5.013	0.493	2.461	10.334
Late Morning Site (Sampling 9:00 a.m. to noon, local time)							
ALCA	0.037	0.117	0.158	0.867	0.151	3.560	12.838
Above-300-m-Altitude Site (Sampling 6:00 to 9:00 a.m., local time)							
C3IL	0.042	0.228	0.267	0.954	0.172	1.481	2.721

TABLE 2-3. 1989 NMOC LOGNORMAL STATISTICS

Radian Site Code	Logarithmic Normal Distribution of NMOC						
	Minimum	Mode	Median	Mean	Maximum	MU[a]	SIGMA[b]
Morning Sites (Sampling 6:00 to 9:00 a.m., local time)							
BACA	0.150	0.502	0.799	0.828	2.499	-0.356	0.577
BMTX	0.220	0.486	0.655	0.816	4.047	-0.376	0.588
C6IL	0.126	0.469	0.764	0.871	2.663	-0.344	0.643
DLTX	0.114	0.289	0.421	0.476	1.612	-0.908	0.577
ELCA	0.088	0.206	0.305	0.448	1.733	-1.061	0.719
ELTX	0.093	0.247	0.381	0.494	2.442	-0.936	0.677
FECA	0.124	0.252	0.371	0.514	2.491	-0.903	0.690
GRMI	0.203	0.401	0.517	0.638	1.880	-0.604	0.557
H1TX	0.180	0.468	0.632	0.795	2.614	-0.406	0.594
LBCA	0.242	0.550	0.697	0.871	2.856	-0.292	0.553
LXKY	0.082	0.188	0.270	0.365	1.796	-1.230	0.666
M1NY	0.211	0.419	0.532	0.598	2.043	-0.633	0.487
MGAL	0.087	0.158	0.192	0.216	1.133	-1.636	0.456
MNY	0.127	0.377	0.515	0.559	1.609	-0.713	0.512
NWNJ	0.158	0.357	0.519	0.638	3.693	-0.644	0.622
PLNJ	0.073	0.247	0.407	0.535	1.796	-0.882	0.717
RLNC	0.043	0.087	0.137	0.162	0.551	-2.026	0.644
RSCA	0.210	0.644	1.113	1.243	3.993	-0.002	0.663
S2MO	0.187	0.431	0.607	0.726	5.013	-0.494	0.589
S3CA	0.075	0.143	0.205	0.293	2.452	-1.467	0.689
S4CA	0.061	0.127	0.179	0.249	1.534	-1.615	0.670
Overall	0.043	0.228	0.434	0.583	5.013	-0.853	0.792
Late Morning Site (Sampling 9:00 a.m. to noon, local time)							
ALCA	0.037	0.092	0.117	0.150	0.867	-2.061	0.575
Above-300-m-Altitude Site (Sampling 6:00 to 9:00 a.m., local time)							
C3IL	0.042	0.144	0.228	0.271	0.954	-1.517	0.649

[a]MU is the mean of ln(NMOC). e^{MU} is the geometric mean.

[b]SIGMA is the standard deviation of ln(NMOC). e^{SIGMA} is called the geometric standard deviation.

that characterize a lognormal distribution overall and for each site. MU and SIGMA are the mean and standard deviation, respectively, of the logarithm of NMOC to the Napierian base e. The geometric mean is e raised to the power MU; the geometric standard deviation is e raised to the power SIGMA. The mode is the most frequently occurring logarithm of NMOC value for a continuous probability distribution function.

Information listed in Appendix A includes the location of the site, street address as well as the Universal Transverse Mercator (UTM) coordinates for the site (where available), the site code used throughout this report, the Storage and Retrieval of Aerometric Data (SAROAD) Number, and the Aerometric Information Retrieval System (AIRS) Number. Appendix A gives the AIRS printouts for all the sites that are in the system for 1989.

Appendix C gives the daily NMOC concentration data listed chronologically for the entire sampling season. In addition, figures are given for each site in which NMOC concentrations in ppmC are plotted versus the 1989 Julian date on which the sample was taken. Data tables for each site include the following:

- calendar date sampled;
- Julian date samples;
- weekday sample (M, T, W, H, F);
- sample ID number, assigned consecutively upon receipt of the sample;
- sample canister number;
- Radian analysis channel;
- NMOC concentration in ppmC, determined by Radian;
- NMOC concentration in ppmC, determined by U.S. EPA, Quality Assurance Division; and
- NMOC concentration in ppmC, determined by U. S. EPA, Atmospheric Research and Exposure Assessment Laboratory.

Appendix D lists invalidated or missing samples. Table D-1 lists these data chronologically, while Table D-2 groups the listings by site code. For each sample, the tables list the site code, the date of the missing or invalid sample, a brief description of the possible cause of the invalid or missing sample, and the assigned cause for the failure.

3.0 NMOC TECHNICAL NOTES

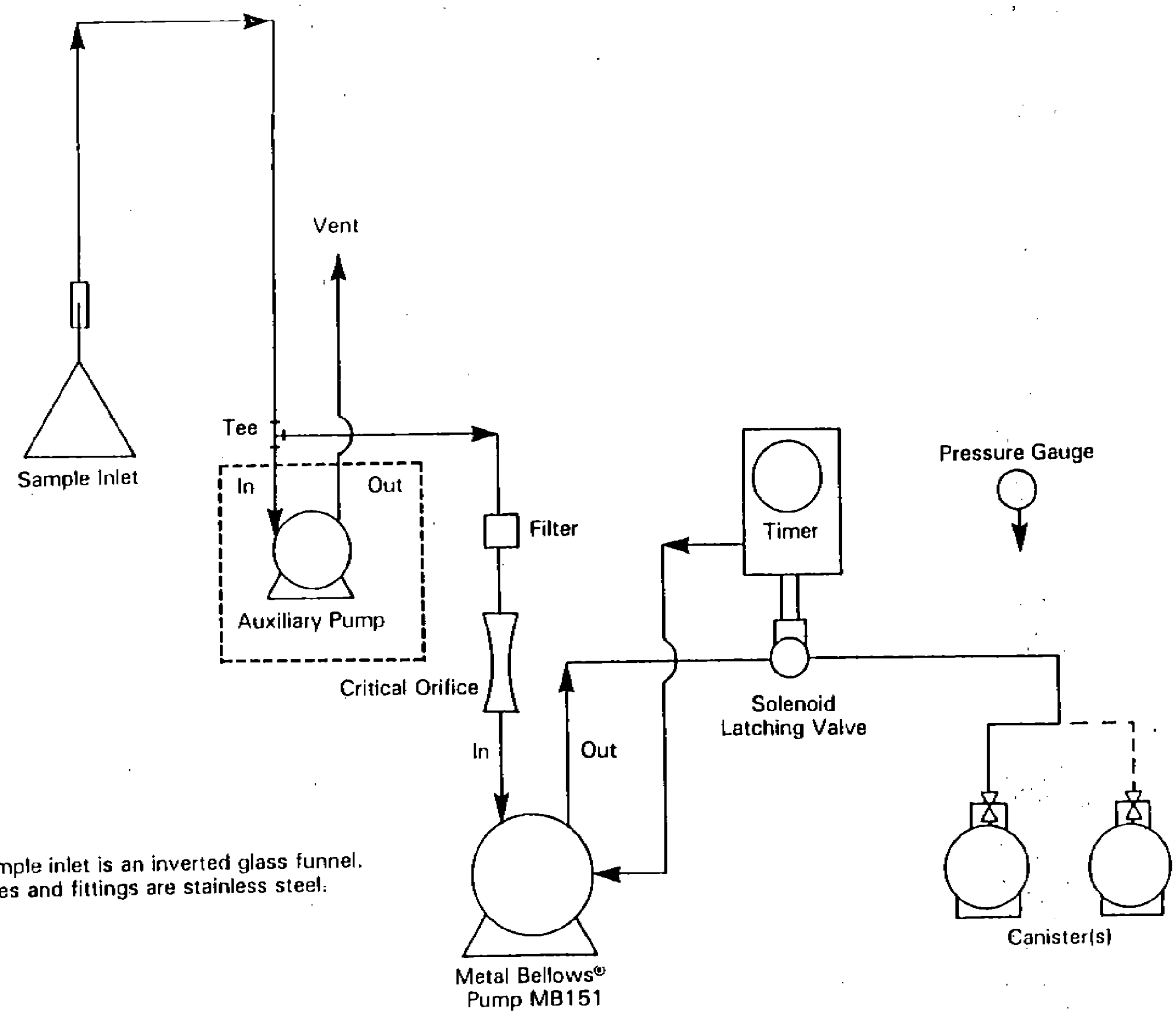
This section summarizes descriptions of the installation and operation of the field sampling equipment, a summary of the analytical equipment and procedures for NMOC measurement, and a description of the canister cleanup equipment and procedures.

3.1 NMOC FIELD SAMPLING EQUIPMENT

The field sampling equipment used to collect ambient air samples for NMOC measurement is relatively simple to operate. Ambient air is drawn through a sintered stainless steel filter (2 micron) and critical orifice by a Metal Bellows® pump and delivered to a SUMMA® canister. The sampler components are made of nonbiasing stainless steel. Figure 3-1 is a schematic diagram of the NMOC sampling system.

3.1.1 Installation

NMOC sampler installation configurations were site dependent. All field sites were installed by or under the direction of Radian personnel. Installation requirements included a temperature-controlled environment (70° to 86°F), close proximity to the atmosphere to be sampled, and noncontaminating sampler connections. Glass and/or gas-chromatographic-grade stainless steel tubing are the preferred materials of construction for all connections contacting the sample. Typical sampler installations involved three configurations including direct connections to a ventilated glass manifold, a slipstream connection prior to the station NO_x analyzer with a bypass pump, or collocated NMOC and NO_x sample inlet lines. For sites where the distance between the sample inlet and the stainless steel post was greater than 8 feet, an auxiliary pump, as shown in Figure 3-1, was used. The auxiliary pump helps ensure that the air in the sample line is representative of the ambient air. The critical orifice was sized to maintain a constant flow rate and to fill a 6-L stainless steel canister from the 5 mm Hg vacuum to about 15 psig in 3 hours. When duplicate samples were taken, the critical orifice used for single sample collection was replaced with an orifice sized to fill two canisters during the 3-hour sampling period.



* Sample inlet is an inverted glass funnel.
Lines and fittings are stainless steel.

Figure 3-1. Sampling system for collecting 3-hour integrated ambient air samples.

3.1.2 Operation

Presampling

The following instructions pertain to the sampling operation prior to collection of the field sample.

1. Verify timer program (see timer instructions). Set to MANUAL position to leak check sampling system. Once the system passes the leak check, turn timer to AUTO position.

2. With no canisters connected to the sampling system, turn the timer switch to the MANUAL position.

3. Disconnect the sample inlet from the top of the orifice/filter assembly mounted on the pump inlet. Connect the rotameter to the top of the orifice/filter assembly. Tighten Swagelok® (1/4") fitting securely with a wrench. Do not overtighten.

4. Turn timer switch ON. Do not turn the power off and on rapidly. Wait 20 seconds between cycles to prevent premature timer/solenoid failure. The pump should run and the latching valve should open (audible click with 2 to 5 seconds delay). Verify that the rotameter reading is approximately the same (±15%) as the reading obtained during installation as recommended on the orifice tag. If the rotameter reading is not correct, see the troubleshooting instructions.

5. Allow the pump to run for at least 20 seconds, then press the timer OFF button.

6. Connect a cleaned, evacuated canister to the sampling system. If duplicate samples are to be collected, remove the plug from the second port of the tee and connect a second canister to the sampling system. Remove the orifice assembly marked with an "S," denoting a single orifice. Install the orifice assembly marked with a "D," denoting a double orifice. Replace the filter holder on the "D" orifice. After obtaining scheduled duplicate samples, replace the plug and the "S" orifice assembly to return to single sample collection status.

7. With the pump off, open completely the valve on the canister (or on one of the canisters if two are connected) and verify that no flow is registered on the rotameter. If any flow is detected by the rotameter, immediately close the canister valve and see the troubleshooting instructions.

8. If no flow is observed, disconnect the rotameter and reconnect the inlet sample line to the filter assembly. If two canisters are connected, completely open the valve on the second canister.

9. Reverify that the canister valve(s) is (are) completely open and the timer is properly set for sampling from 6 a.m. to 9 a.m. the next weekday. Set timer to AUTO mode.

10. Reset the elapsed time counter.

Postsampling

The instructions that follow outline the NMOC postsampling operation procedures in the field.

1. Close the canister valve(s) firmly. Disconnect the canister(s) from the sampling system.

2. Connect the pressure gauge to the canister inlet and open the canister valve. Record the canister pressure on the field sampling data form. Close the canister valve and remove the pressure gauge. Repeat pressure measurement for second canister if collecting a duplicate sample. If the pressure reading is not at least 11 psig, see the troubleshooting instructions.

3. Fill in the required information on the NMOC SAMPLING FIELD DATA FORM. PLEASE PRESS HARD AND WRITE WITH A BALLPOINT PEN; YOU ARE MAKING THREE COPIES. (see Figure 3-2).

4. Verify elapsed time counter reading equals 3 hours.

5. Verify that the timer shows the correct time setting. If not, note that fact on the sample form along with any information pertaining to the possible cause. Reset the timer to the correct time, if necessary.

6. Verify that the canister valves are closed firmly. Do not overtighten them. Put the protective cap(s) on the valve(s) and prepare the canister(s) for shipment to Radian, RTP.

3.1.3 Troubleshooting Instructions

A list of troubleshooting instructions was given to each field site during the site installation and operator training. Typical problems encountered with the field sampling apparatus included: loose fittings, misprogrammed timer, or clogged orifices. To minimize downtime, field site operators were encouraged to relay sampling problems to the Radian laboratory daily, by telephone. Most sampling problems were addressed promptly through these telephone discussions.

RADIAN CORPORATION

NMOC SAMPLING FIELD DATA FORM

Site Code : ______________ SAROAD # : __ __-__ __ __ __ __-__ __ __ __-__ __ __

Site Location : City: ______________ State: ______________

Sample Collection Date : ______________ Sampling Period : ______________

Operator : ______________

Final Canister Pressure (psig) : ______________

Sample Canister Number : ______________ Side : ______________

Sample Duplicate for this Date : Yes ☐ No ☐

If yes, Duplicate Canister Number : ______________

NOx Analyzer Operating? Yes ☐ No ☐

If yes, Average Reading (ppmv as NOx) : ______________

Average Wind Speed : ______________ Average Wind Direction : ______________

Rotameter Indicated Flow Rate : ______________ Orifice Number : ______________

Average Barometric Pressure (mm Hg or inches Hg) : ______________

Ambient Temperature (°F) : ______________ Relative Humidity : ______________

THC Model (if available) : ______________ Average THC : ______________

Sky/Weather Conditions : ______________

____

Site Conditions/Remarks : ______________

____

____

Canister Number : ______________

Initial Canister Vacuum : ______________

____

Received By : ______________

Date : ______________

Sample Validity : ______________

If Invalid, Reason : ______________

____

3881189R

Figure 3-2. NMOC Sampling field data form.

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3.1.4 Sampler Performance for 1989

The NMOC sampler was modified in 1989 to improve performance. This modification involved replacing the mechanical timer previously used with an electronic version. The electronic timer improves sample integration. An elapsed time counter was added to the sampler to verify sample duration. This modified system was used during the 1989 program. In addition, all sampler orifice(s) and canisters were subjected to a preseason QC check to ensure field performance. All orifices were checked against the rotameter enclosed in each sampling kit, and referenced to a transfer standard (bubble flowmeter). Prior to field installation, all samplers were operated in the laboratory to establish an expected final pressure range for the canister samples. Two single orifices and one double orifice were tested for each sampler kit.

Due to the preseason checks and modifications, the NMOC sampler performance was improved for the 1989 sampling season. This assessment is based on the consistency of the final sample pressures on a site-specific basis (see Section 4.6). The sampler performance in terms of successful sample collection (i.e., completeness) was comparable to previous years. Overall completeness from all sites averaged 95.5 percent. The site-specific completeness ranged from 86.5% for S3CA to 101.1% for ELTX.

Invalidated or missing samples were primarily due to the operator or the site rather than to equipment. Completeness can be improved at certain sites through greater attention to sampling procedure, and by ensuring that trained site personnel are available. Those samples that were invalidated due to equipment failure were assigned to three major categories: timer, canister, and miscellaneous.

A total of 93 missing or invalidated samples was recorded in the 1989 NMOC Monitoring Program. There were nine invalidated samples related to timer problems, 12 invalidated samples related to canister problems, and 83 remaining invalidated samples. Appendix D lists a total of 86 invalidated samples. In addition to invalidated samples there were seven missed samples. Missed samples resulted from a number of problems at the site -- the operator was locked out of the sampling station, a site operator was not available on the day the sample was to be collected, etc. Avoidable operator error accounts for 43.0% of invalidated samples. No invalid samples were attributable to timer malfunctions. The operator's failure to open the canister valve accounted for 91.7% of the canister-related invalidated samples, and 8.3% were attributable to canister leaks. Of the remaining 83 invalidated samples, 45.8% were caused by loose or broken sample lines, or leaking solenoid valves; 54.2% were attributable to missed samples, power outages, or consecutive samples collected into the same canister. A listing of invalidated or missing samples is contained, chronologically and by site, in Appendix D.

A further improvement in completeness may be possible as site operators gain familiarity with the electronic timer. Revised sampler operating instructions will focus additional attention on timer programming and operation, and will include a daily checklist to eliminate common operator errors.

3.1.5 Field Documentation

The field sample collection information was documented by the site operator on printed forms. Figure 3-2 is an example NMOC Sampling Field Data Form. Each canister sent to the field was accompanied by this form. The field data form is a multiple part unit. A copy of the field data form was retained by the site operator for the site notebook. Figure 3-3 is the Invalid Sample Form. This form was completed by the site operator to document the reasons for a missed or invalid field sample collections.

3.2 NMOC ANALYSIS

The NMOC analysis equipment and analysis procedure are described in greater detail in Appendix A. A brief description of the equipment and operating procedure used in this study follows.

3.2.1 Instrumentation

Two gas chromatographs were used by Radian. Each was a dual-channel Hewlett-Packard Model 5880 (HP-5880) using flame ionization detection (FID). NMOC instrument Channels A and B refer to the two FIDs on one HP-5880 unit, and Channels C and D refer to the two FIDs on the other HP-5880 unit. These chromatographs were modified to be similar to the prototype unit (EPA-QAD

RADIAN
CORPORATION

V-

NMOC INVALID SAMPLE FORM

Site Code : ________ SAROAD # : __ __ · __ __ __ __ · __ __ __ · __ __ __

City : ________ State : ________

Sample Collection Date : ________ Operator : ________

Sample Canister Number : ________

Sample Duplicate for this Date : Yes ☐ No ☐

If Yes, Duplicate Canister Number : ________

Reason for Invalid or Missed Sample : ________

____

____

Average NOx Analyzer Reading for this Collection Date : ________

Wind Speed : ________ Wind Direction : ________

Average Barometric Pressure (mm Hg or inches Hg) : ________

Ambient Temperature (°F) : ________ Relative Humidity : ________

Sky/Weather Conditions : ________

____

____

Received By : ________

Date : ________

Action Taken : ________

____

Resolution : ________

____

Field Invalid or In-house Invalid

3881188R

Figure 3-3. NMOC Invalid sample form.

cah.175f

instrument), which is described in Appendix B. The EPA-QAD instrument was used as a reference during this program. In addition, an HP-5880 gas chromatograph located at EPA and equipped with a 60 m x 0.32 mm inside diameter (i.d.), DB-1, fused silica capillary column was used as the gas speciation method and as a quality assurance check. This capillary column instrument is called EPA-ASRL channel in subsequent sections of this report.

3.2.2 Hewlett-Packard, Model 5880, Gas Chromatograph Operating Conditions

The sample trap consisted of 30 cm of 1/8-inch outside diameter (o.d.) stainless steel tubing, packed with 60/80 mesh glass beads.

Three support gases were used in this analysis: helium, hydrogen, and hydrocarbon-free air. Details of their use are given below in Table 3-1.

TABLE 3-1. SUPPORT GAS OPERATING CONDITIONS

Purpose	Cylinder Composition	Pressure	Mean Flow Rate[a]
Carrier Gas	Helium	30 psig	29.4 mL/min
FID Air	Hydrocarbon-free air	30 psig	300.1 mL/min
FID Fuel	Hydrogen	32 psig	31.1 mL/min

[a]Flow rates corrected to standard conditions (1 atmosphere pressure, 20°C).

The operating temperatures of the HP-5880 were controlled for the NMOC analysis. The FID and auxiliary area were controlled at 250°C and 90°C, respectively. The oven temperature was programmed from 30°C to 90°C at a rate of 30°C per minute for 4 minutes, holding at 90°C for the fourth minute. Oven and integration parameters were controlled by HP Level 4 programmable integrators. A complete listing of the integrator programming sequence for NMOC measurement by the PDFID method is given in Appendix E.

3.2.3 NMOC Analytical Technique

The modified HP-5880, dual-FID chromatographs were operated during the 1989 study according to a project specific Standard Operating Procedure (SOP).

Further description is given below to help explain the analytical apparatus and procedure.

The six-port valve shown in Figure 3-4 was installed in the auxiliary heated zone of the HP-5880 and was pneumatically actuated using chromatographic valve control signals to apply either compressed air or vacuum to the valve. The sample trap itself was located inside the chromatograph's column oven. A section of 1/16-inch o.d. stainless steel tubing was sized to a length that prevented pressure and flow surges from extinguishing the FID flame. This length was determined experimentally and differs for each chromatograph and for each channel within chromatographs. Although the length of tubing effectively substitutes for the pressure restriction provided by a column, it does not perform the separation function of a column.

During sample trapping, a slight excess of sample gas flow was maintained. A pressure change of 80 mm Hg in a 1.7-L vacuum reservoir was used to gauge and control the volume of sample gas cryogenically trapped. After the trapping cycle was complete, the HP-5880 program shown in Appendix B was initiated. When the program triggered a horn emitting an audible beep, the cryogen was removed from the trap and the oven door was closed. The chromatographic program then assumed control of raising the oven temperature, at the preset rate, to release the trapped sample to the FID, and set up the integration parameters.

3.3 CANISTER CLEANUP SYSTEM

A cleanup cycle consisted of first pulling a vacuum of 5 mm Hg absolute pressure in the canister, followed by pressurizing the canister to 20 psig with cleaned, dried air that had been humidified. This cycle was repeated two more times during the canister cleanup procedure. The cleanness of the canister was qualified by PDFID analysis. Upon meeting the cleanness criterion, the canister was evacuated to 5 mm Hg absolute pressure a fourth time, in preparation for shipment to the site.

3.3.1 Canister Cleanup Equipment

A canister cleanup system was developed and used to prepare sample canisters for reuse after analysis. A diagram of the system is shown in Figure 3-5. An oil-free compressor with a 12-gallon reservoir provided source

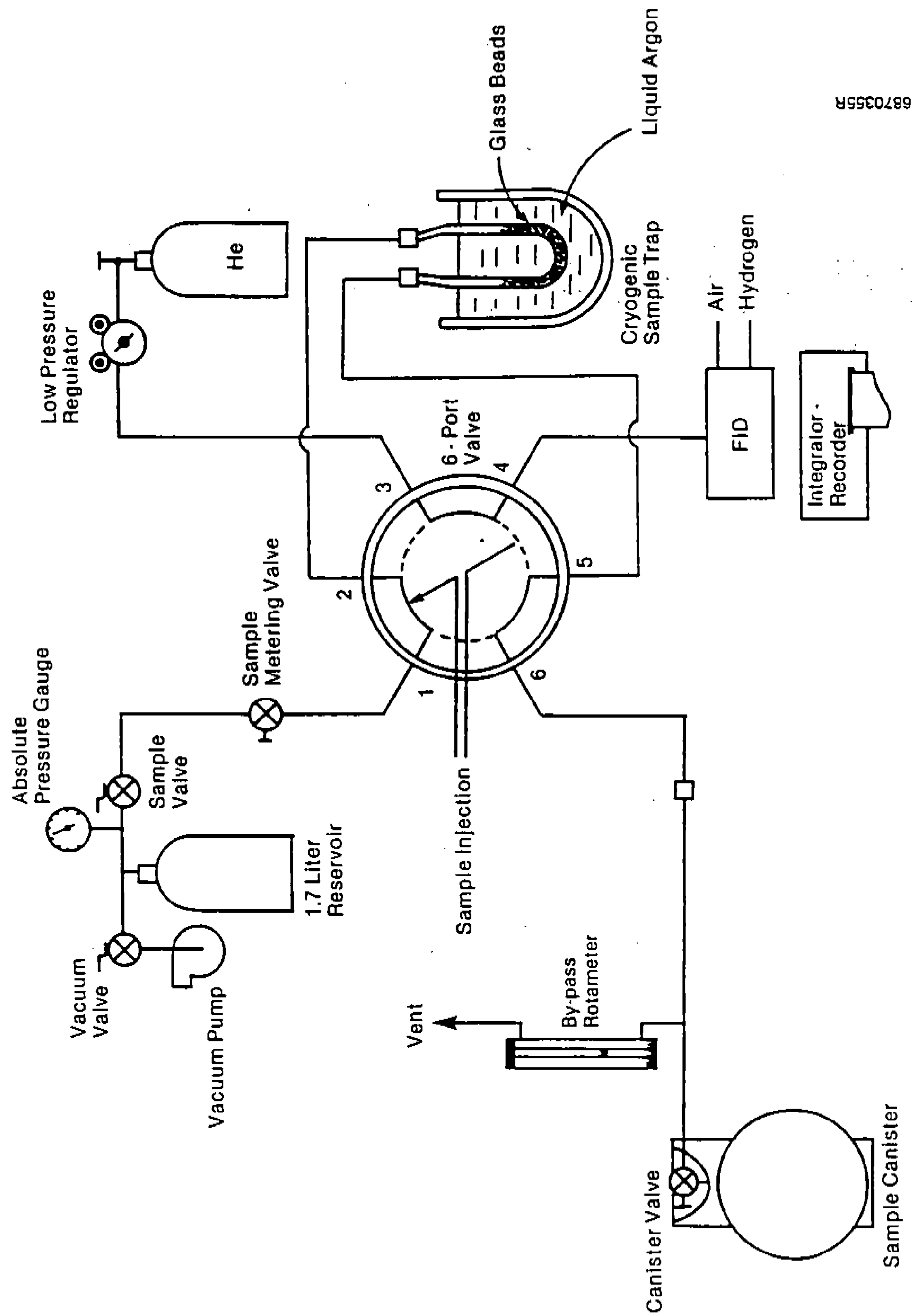
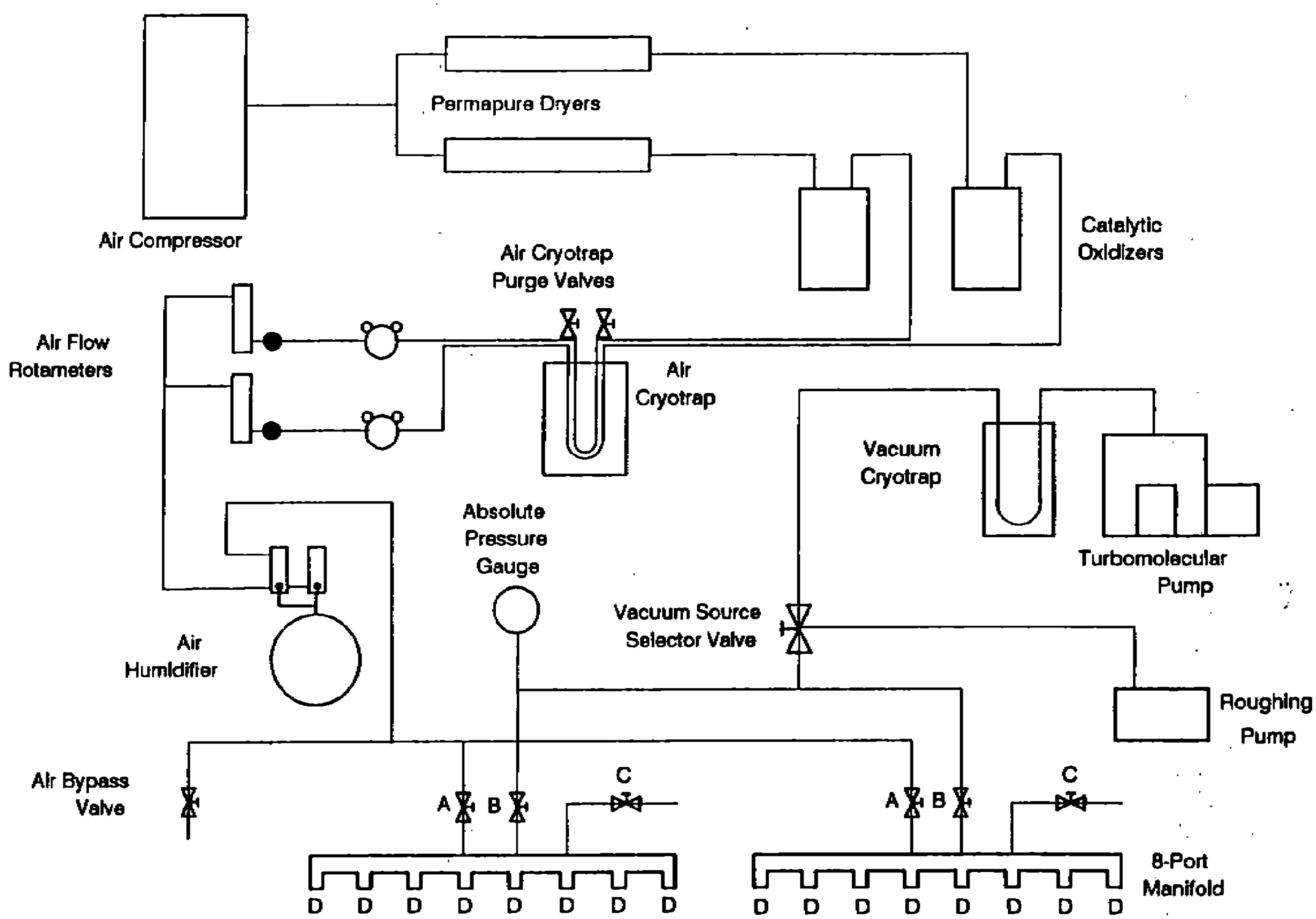


Figure 3-4. NMOC analytical equipment.



A. Manifold Air Pressure Valve
B. Manifold Vacuum Valve
C. Manifold Pressure Release Valve
D. Manifold Port for Connecting Canisters to be Cleaned

Figure 3-5. Canister cleanup apparatus.

2393104R

air for the system. The oil-free compressor was chosen to minimize hydrocarbon contamination. The compressor reservoir was drained of condensed water each morning. A coalescing filter provided water mist and particulate matter removal down to a particle size of one micron. Permeation dryers removed water vapor from the compressor source air. These permeation dryers were followed by moisture indicators to show detectable moisture in the air leaving the dryer. The moisture indicators never showed any water, indicating that the permeation dryers effectively removed all of the water vapor.

Air was then passed through catalytic oxidizers to destroy residual hydrocarbons. The oxidizers were followed by inline filters for secondary particulate matter removal, and by a cryogenic trap to condense any water formed in the catalytic oxidizers and any organic compound not destroyed by the catalytic oxidizer. A single-stage regulator controlled the final air pressure in the canisters and a metering valve was used to control the flow rate at which the canisters were filled during the cleanup cycle. The flow was indicated with a rotameter installed in the clean, dried air line. There was a shutoff valve between the rotameters and the humidifier system. The humidifier system consisted of a SUMMA® treated 6-L canister partially filled with high performance liquid chromatographic-grade (HPLC-grade) water. One flowmeter and flow-control valve routed the cleaned, dried air into the 6-L canister where it was bubbled through the HPLC-grade water. A second flow-control valve and flowmeter allowed air to bypass the canister/bubbler. By setting the flow-control valves separately, the downstream relative humidity was regulated. For the 1989 study, 80% relative humidity was used for canister cleaning. There was another shutoff valve between the humidifier and the 8-port manifold where the canisters were connected for cleanup.

The vacuum system consisted of a Precision Model DD-310 turbomolecular vacuum pump, a cryogenic trap, an absolute pressure gauge, and a bellows valve connected as shown in Figure 3-5. The cryogenic trap prevented the sample canisters from being contaminated by back diffusion of hydrocarbons from the vacuum pump into the cleanup system. There are no oil-free high vacuum pumps currently available at a competitive cost. The bellows valves enabled isolation of the vacuum pump from the system without shutting off the vacuum pump.

3.3.2 Canister Cleanup Procedures

After NMOC analyses were completed, a bank of eight canisters was connected to each manifold shown in Figure 3-5. The valve on each canister was opened, with the shutoff valves and the bellows valves closed. The vacuum pump was started and one of the bellows valves was opened, drawing a vacuum on the canisters connected to the corresponding manifold. After reaching 5 mm Hg absolute pressure as indicated by the absolute pressure gauge, the vacuum was maintained for 30 minutes on the eight canisters connected to the manifold. The bellows valve was then closed and the cleaned, dried air that had been humidified was introduced into the evacuated canisters until the pressure reached 20 psig. The canisters were filled from the clean air system at the rate of 7.0 L/min. This flow rate was recommended by the manufacturer as the highest flow rate at which the catalytic oxidizers could handle elimination of hydrocarbons with a minimum 99.7% efficiency.

When the first manifold had completed the evacuation phase and was being pressurized, the second manifold was then subjected to vacuum by opening its bellows valve. After 30 minutes, the second manifold was isolated from the vacuum and connected to the clean, dried air that had been humidified. The first manifold of canisters was then taken through a second cycle of evacuation and pressurization. Each manifold bank of eight canisters was subjected to three cleanup cycles.

During the third cleanup cycle, the canisters were pressurized to 20 psig with clean, dried air that had been humidified. For each bank of eight canisters, the canister having the highest precleanup NMOC concentration was selected for NMOC analysis to determine potential hydrocarbon residues. If the analysis measured less than 0.030 ppmC, then the eight canisters on the manifold were considered to be clean. Finally the canisters were again evacuated to 5 mm Hg pressure absolute; they were capped under vacuum and then packed in the containers used for shipping to the field sites.

4.0 NMOC QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES

This section details the steps taken in the 1989 NMOC Monitoring Program to ensure that the data taken were of known quality and were well documented. Analysis results are given in terms of precision, completeness, and accuracy. Repeated analyses provided analytical precision. Duplicate samples provided sampling and analysis precision. Completeness was measured in terms of percent of scheduled samples that resulted in valid samples, beginning with the first valid site-specific sample collected and ending with the last scheduled site-specific sample. Accuracy of NMOC concentrations was reported as percent bias of audit samples referenced to an NIST SRM propane by EPA-QAD.

4.1 INTRODUCTION AND CONCLUSIONS

Completeness for the 1989 NMOC study was 95.5 percent. This value indicates that good communication and planning were maintained between the site personnel and the laboratory personnel. Precision for the 1989 NMOC study averaged 14.2% absolute percent difference of repeated analysis and compared to 10.1% for the 1988 study, 9.61% for the 1987 study, 9.01% for the 1986 study, and 10% for the 1985 study. The absolute percent difference in 1989 was higher than in previous years and probably related to the fact that the overall average NMOC concentration for 1989 was lower than in previous years. For smaller values of NMOC concentrations, imprecision increases.

Bias of the Radian channels for the 1989 audit results ranged from +1.3% to +4.5 percent. In 1987 the accuracy determined from the external audit samples ranged from -2.9% to -0.06% and from 1.3% to 4.5% in 1988. In 1986 bias ranged from -0.52% to -3.3% and in 1985 bias ranged from -2.3% to +5.2 percent.

An initial multipoint performance evaluation was done with propane responses for each Radian channel. Twice daily calibration checks and daily in-house propane QC samples monitored instrument and operator performance. Duplicate site samples showed good overall sampling and analysis precision.

Data validation was performed on 14.5% of the 1989 NMOC data base, as described later in this section.

Calibration and drift determinations showed that the instrumentation was stable and that the calibration procedures were consistent. Canister cleanup results showed there was negligible carryover from one sample to the next. In-house QC samples of propane demonstrated that the analytical systems were in control.

Precision, accuracy, and completeness results for 1989 are comparat to results from previous years and indicate that the data quality are good and meet all of the data quality objectives of the QAPP.[2]

4.2 CALIBRATION AND INSTRUMENT PERFORMANCE

Initial performance assessments for NMOC were conducted with propane. Daily calibrations were checked with about 3.0 ppmC propane for the NMOC measurements.

4.2.1 Performance Assessment

An initial performance assessment was done on each Radian channel, using propane certified by EPA-QAD. EPA-QAD referenced the certified propane to an NIST SRM No. 1666B propane. The concentration of the propane used in the performance assessment ranged from 0.117 to 17.559 ppmC. The "zero" value was determined using cleaned, dried air from the canister cleanup system described in Section 3.0. Table 4-1 summarizes the performance assessments below. The FID responses for propane are linear, having coefficients of correlation from 0.999742 to 0.999998. Figures 4-1 through 4-4 show plots of the NMOC performance results for Radian Channels A, B, C, and D, respectively. The plots show the regression line.

4.2.2 Calibration Zero, Span, and Drift

Radian PDFID channels were tested twice daily for zero and span. Zero readings were measured using cleaned, dried air. The zero air was supplied by the same system that cleans air for the canister cleanup system. Span readings used a mixture of about 3.0 ppmC propane in dry air. Calibration factors were calculated from the span and zero readings for each Radian channel. Initial calibration factors were determined in the morning before any site samples were analyzed and final calibration factors were determir in the afternoon after all the ambient air samples had been analyzed. Per

TABLE 4-1. 1989 PERFORMANCE ASSESSMENT SUMMARY, RADIAN CHANNELS

Radian Channel	Cases	Linear Regression Results[a] Intercept	Slope	Coefficient of Correlation
A	5	1.0327	3283.350	0.999998
B	5	5.0703	3245.779	0.999944
C	5	-0.6076	3270.644	0.999916
D	5	0.4108	3271.665	0.999742

[a]Figures 4-1 through 4-4 plot propane area counts vs. concentration in ppmC.

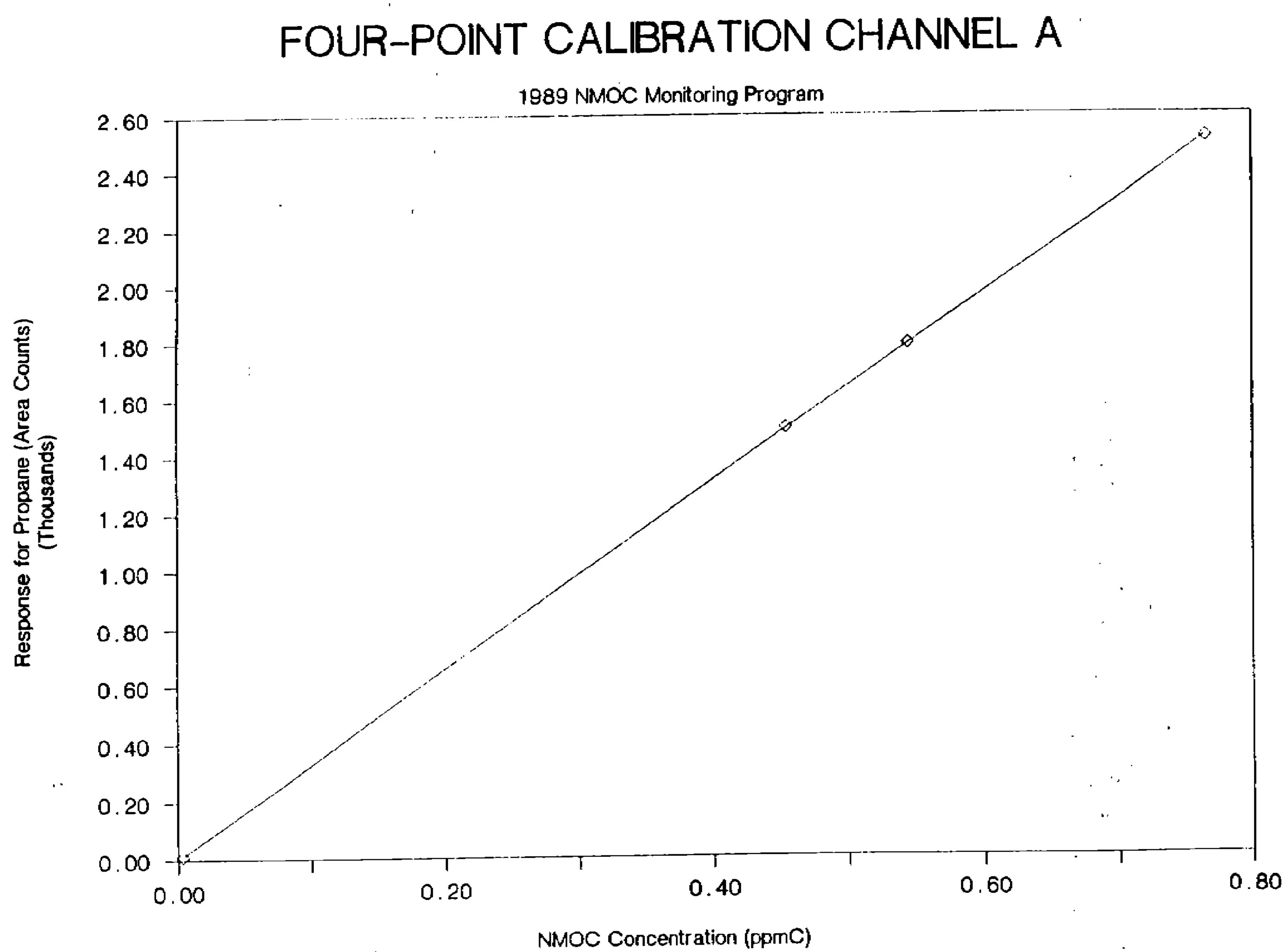


Figure 4-1. NMOC performance results, Channel A.

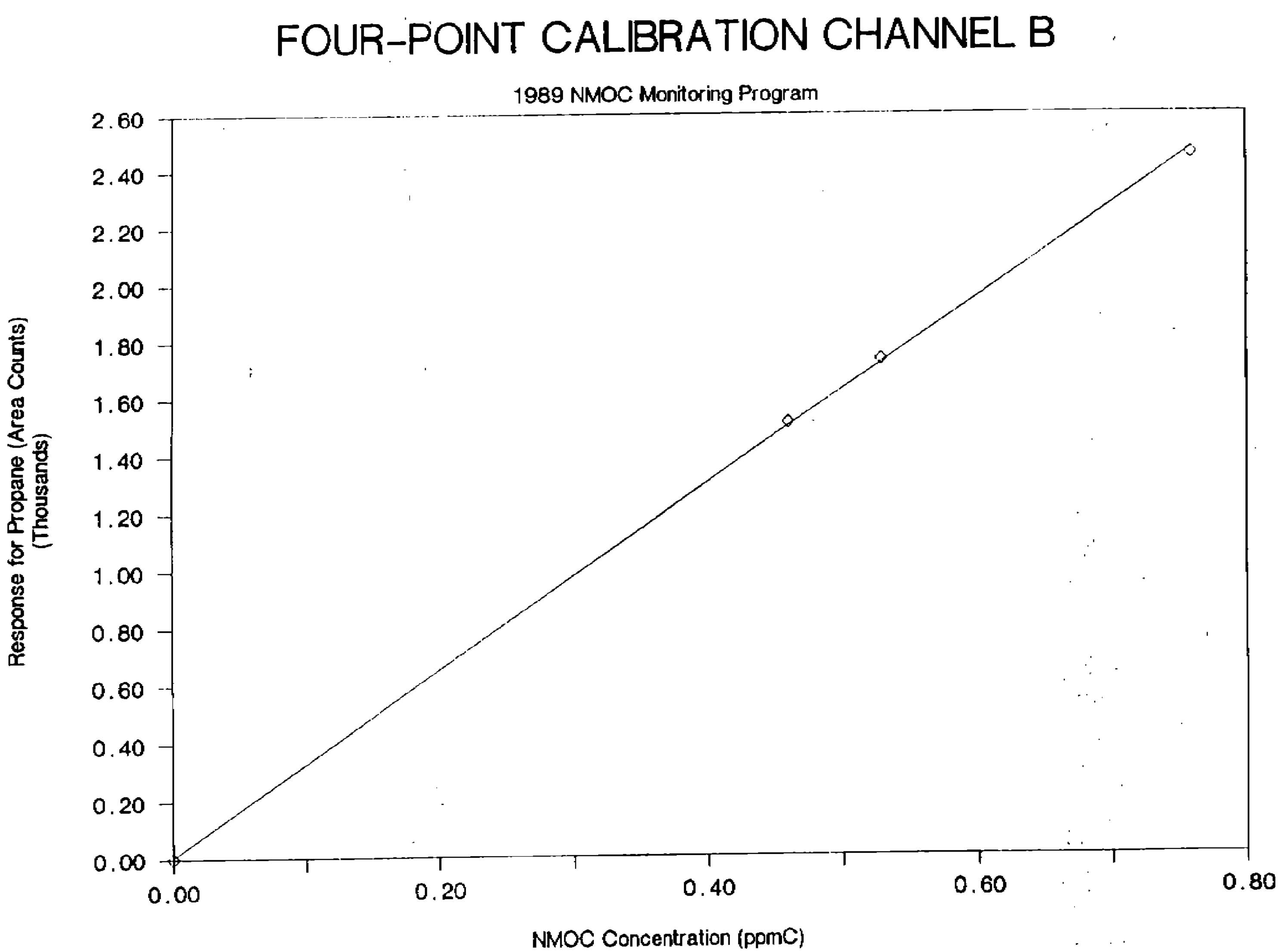


Figure 4-2. NMOC performance results, Channel B.

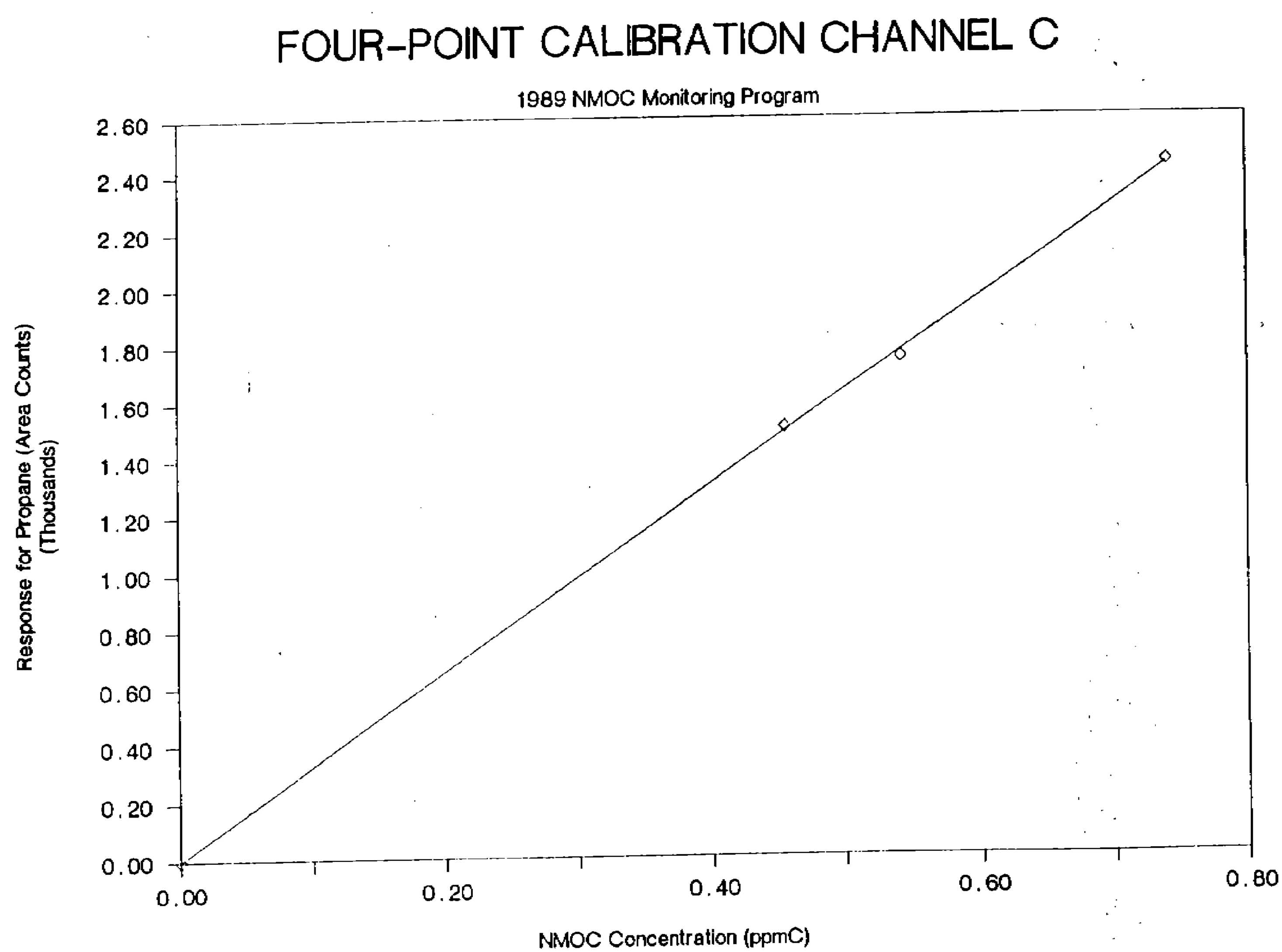


Figure 4-3. NMOC performance results, Channel C.

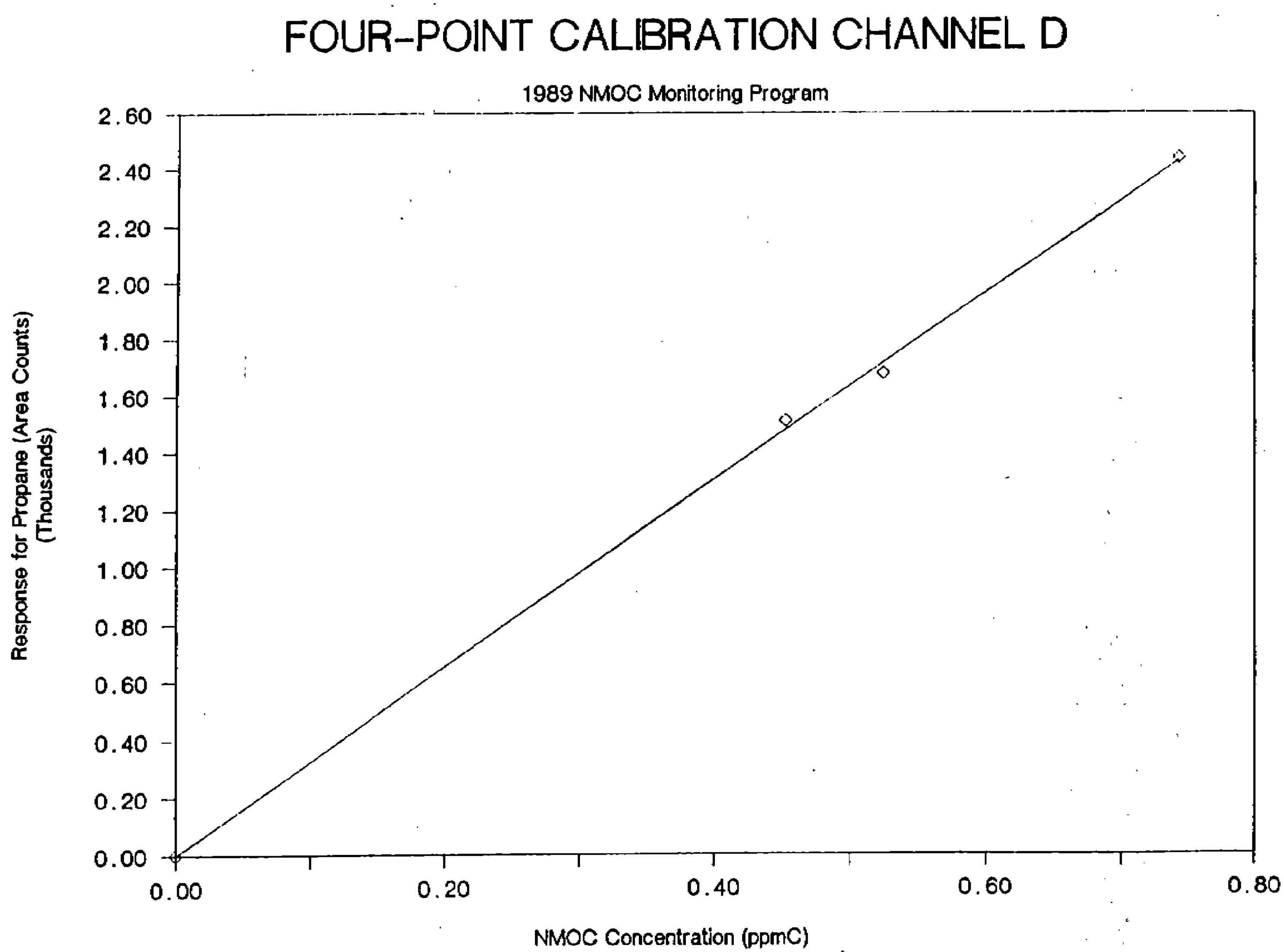


Figure 4-4. NMOC performance results, Channel D.

calibration factor drifts were determined based on the initial calibration factor. The data for zeros, calibration factors, and calibration factor drifts are given in Appendix F for each Radian channel and each calendar day of the analysis season. Figures 4-5 through 4-8 show plots for daily calibration zeros for Radian Channels A, B, C, and D. Figures 4-9 through 4-12 show the daily calibration span data as a function of the 1989 Julian date. Figures 4-13 through 4-16 show daily percent drift figures for the 1989 Julian dates. Inspection of the percent drift figures shows that the maximum percent drift was 4.54. The average absolute % drift ranged from 0.483 for Channel A to 0.673 for Channel D.

4.2.3 Calibration Drift

Summary calibration factor drift data are given in Table 4-2. The table presents calibration factor drift, percent calibration factor drift, and absolute percent calibration factor drift. Calibration factors were calculated from an analysis of a propane-air mixture whose concentration was known and was referenced by the EPA-QAD to an NIST SRM No. 1666B propane reference standard as follows:

$$\text{calibration factor} = \frac{\text{concentration of propane standard (ppm)} \times 3 \text{ ppmC/ppm}}{\text{(propane standard response (area counts) - zero response (area counts))}}$$

Daily calibration factors ranged from 0.000293 ppmC/area count to 0.000334 ppmC/area count, depending on the channel. Maxima, minima, and mean values are given in Table 4-2 for calibration factor drift and percent calibration factor drift. If drift and percent drift are random variables and normally distributed, the mean values would be expected to be zero. The means shown in Table 4-2 for the drift and percent drift are approximately zero, showing little bias overall, or for any channel. The overall mean values shown in Table 4-2 were weighted according to the number of calibration drift data for each channel. The last two columns of Table 4-2 show the means and standard deviations of the absolute percent calibration factor drifts. The fact that the standard deviations are the same order of magnitude as the means indicates that the mean calibration factor drifts are not significantly different from zero.

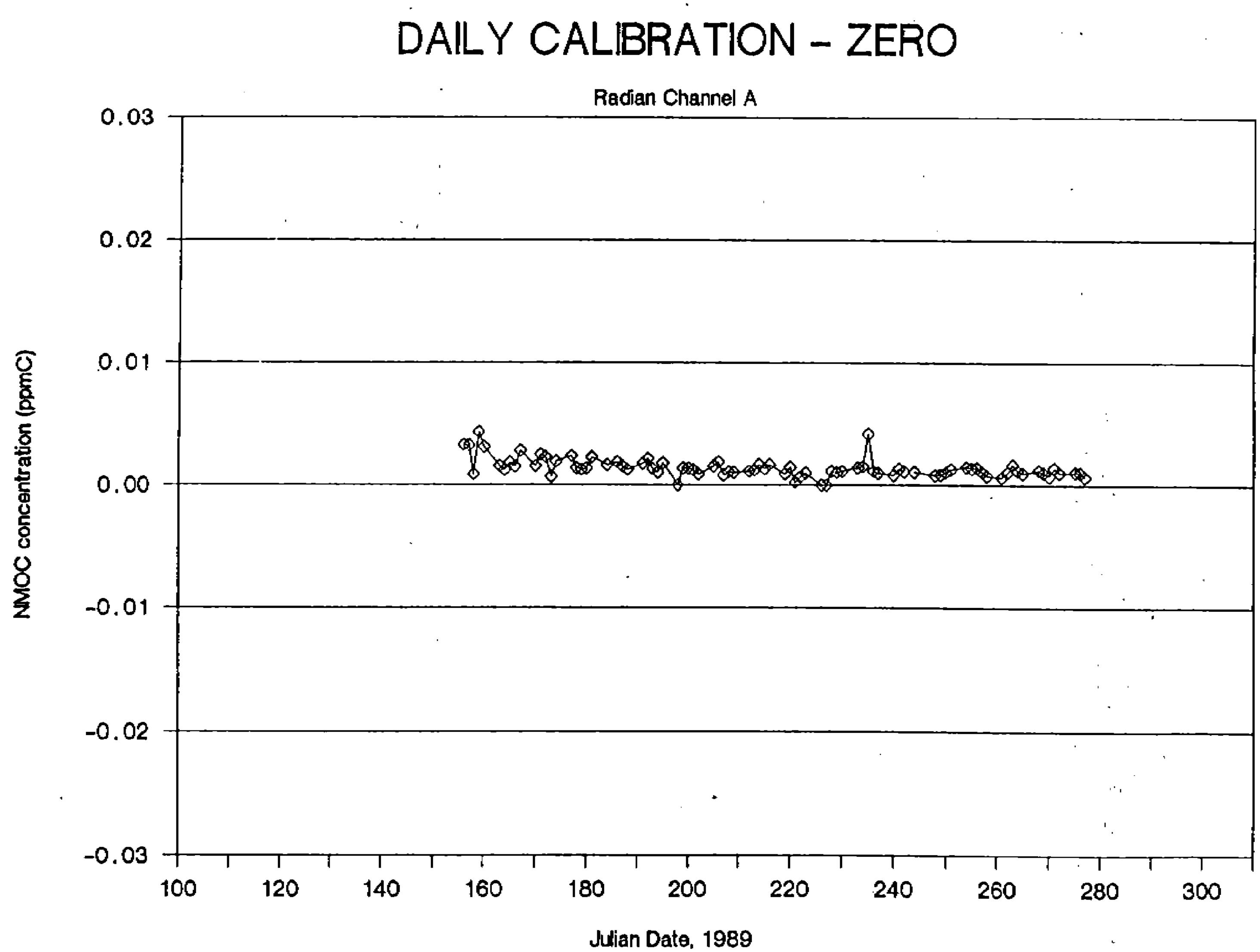


Figure 4-5. Daily calibration zero, Channel A.

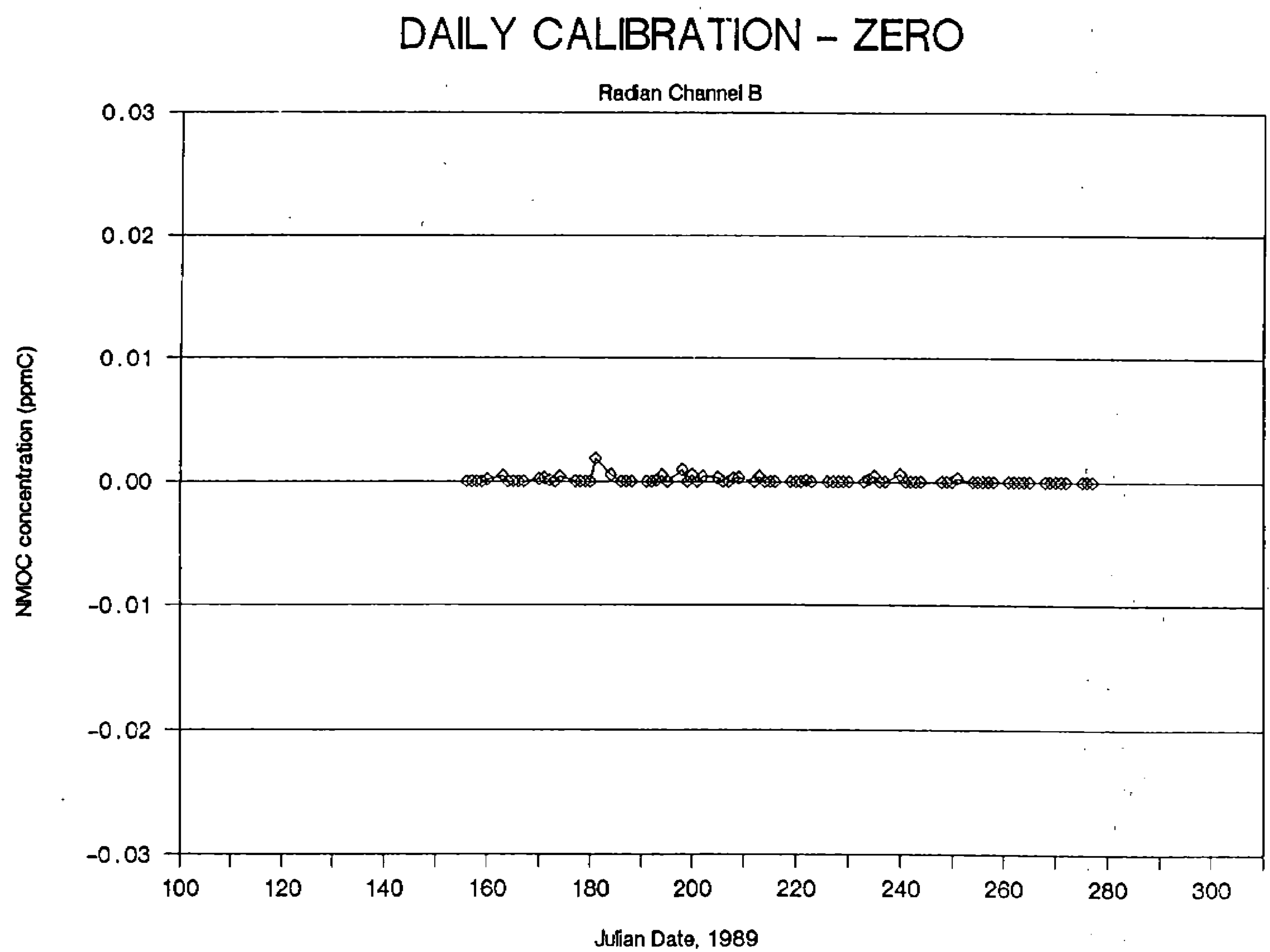


Figure 4-6. Daily calibration zero, Channel B.

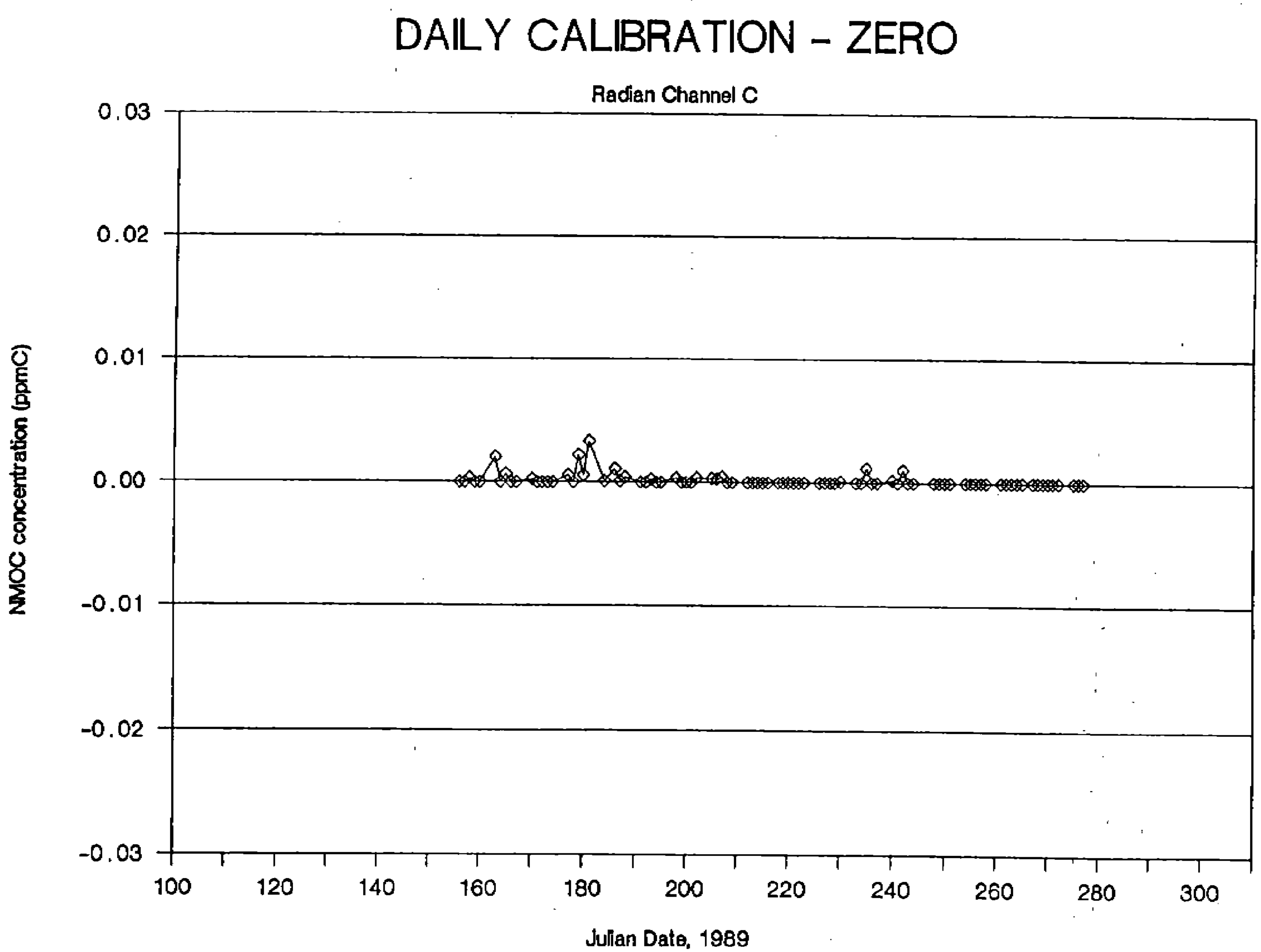


Figure 4-7. Daily calibration zero, Channel C.

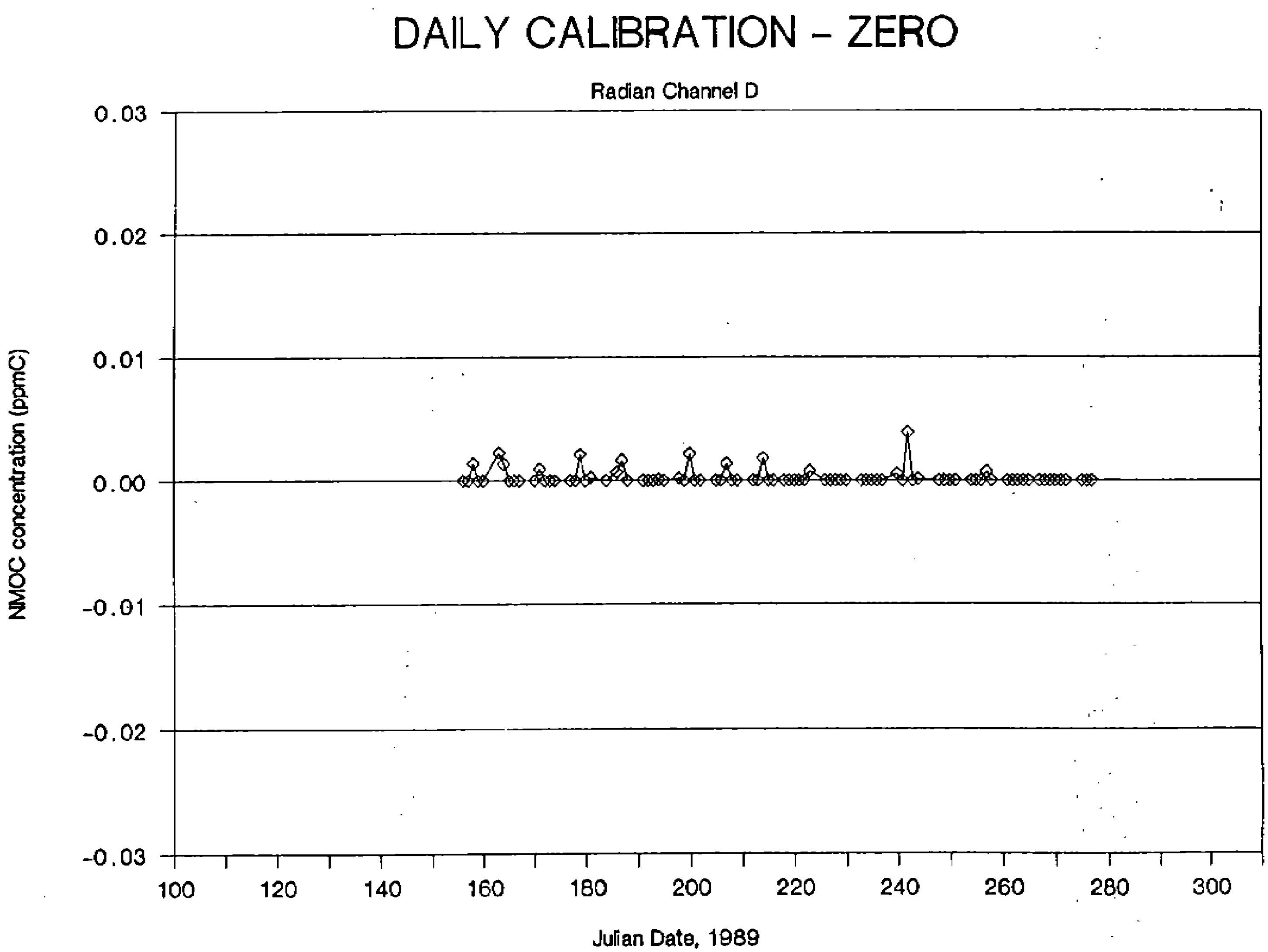


Figure 4-8. Daily calibration zero, Channel D.

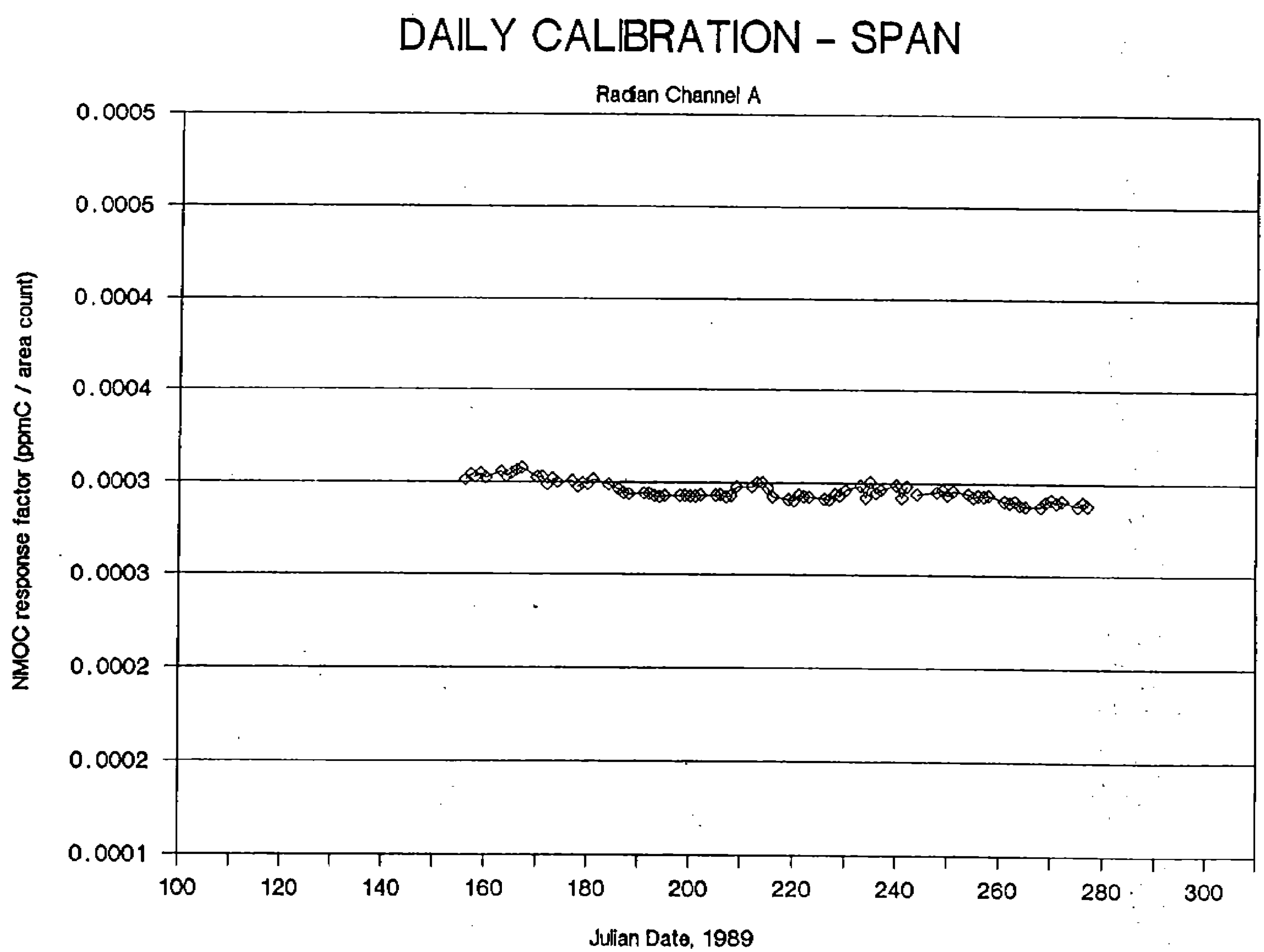


Figure 4-9. Daily calibration span, Channel A.

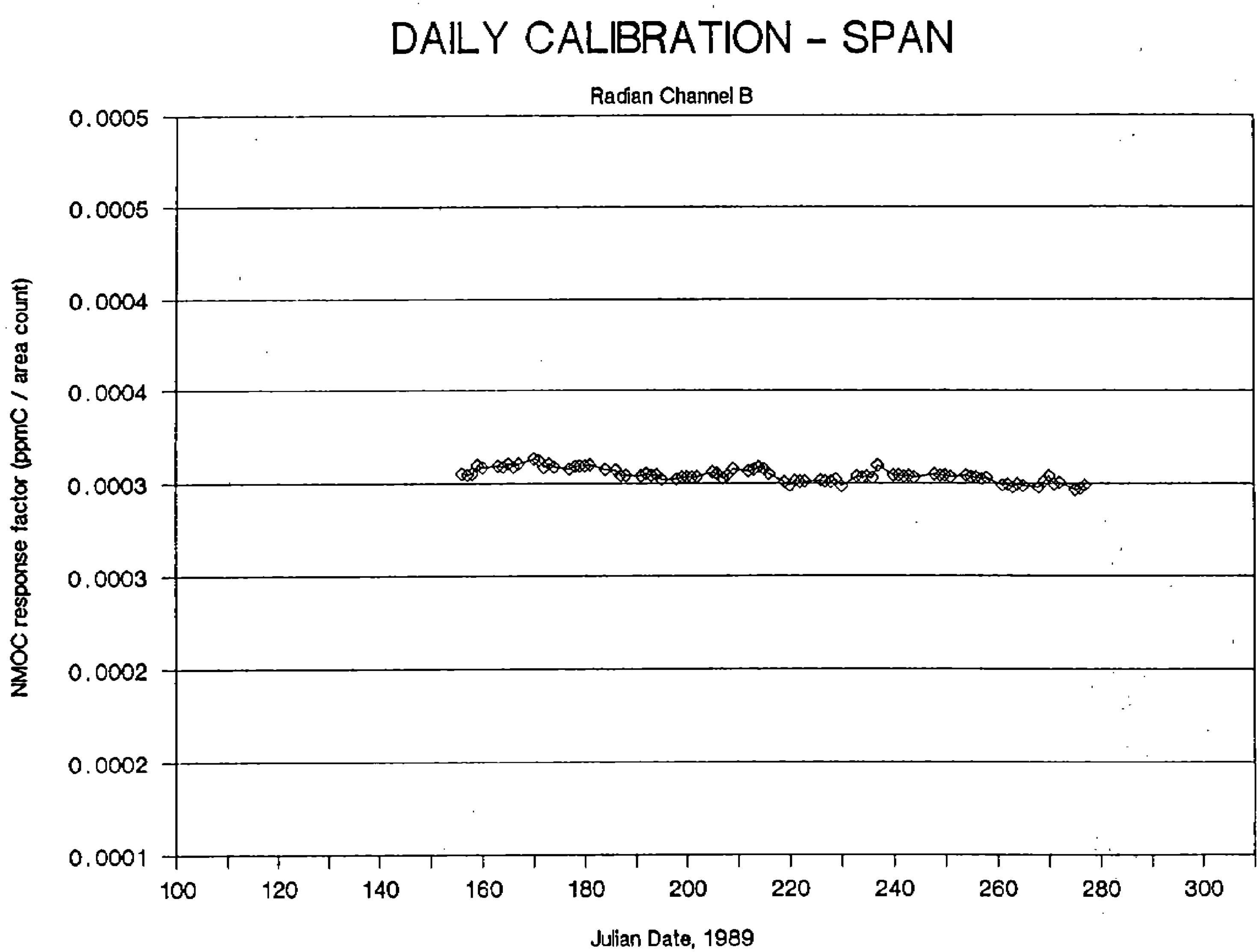


Figure 4-10. Daily calibration span, Channel B.

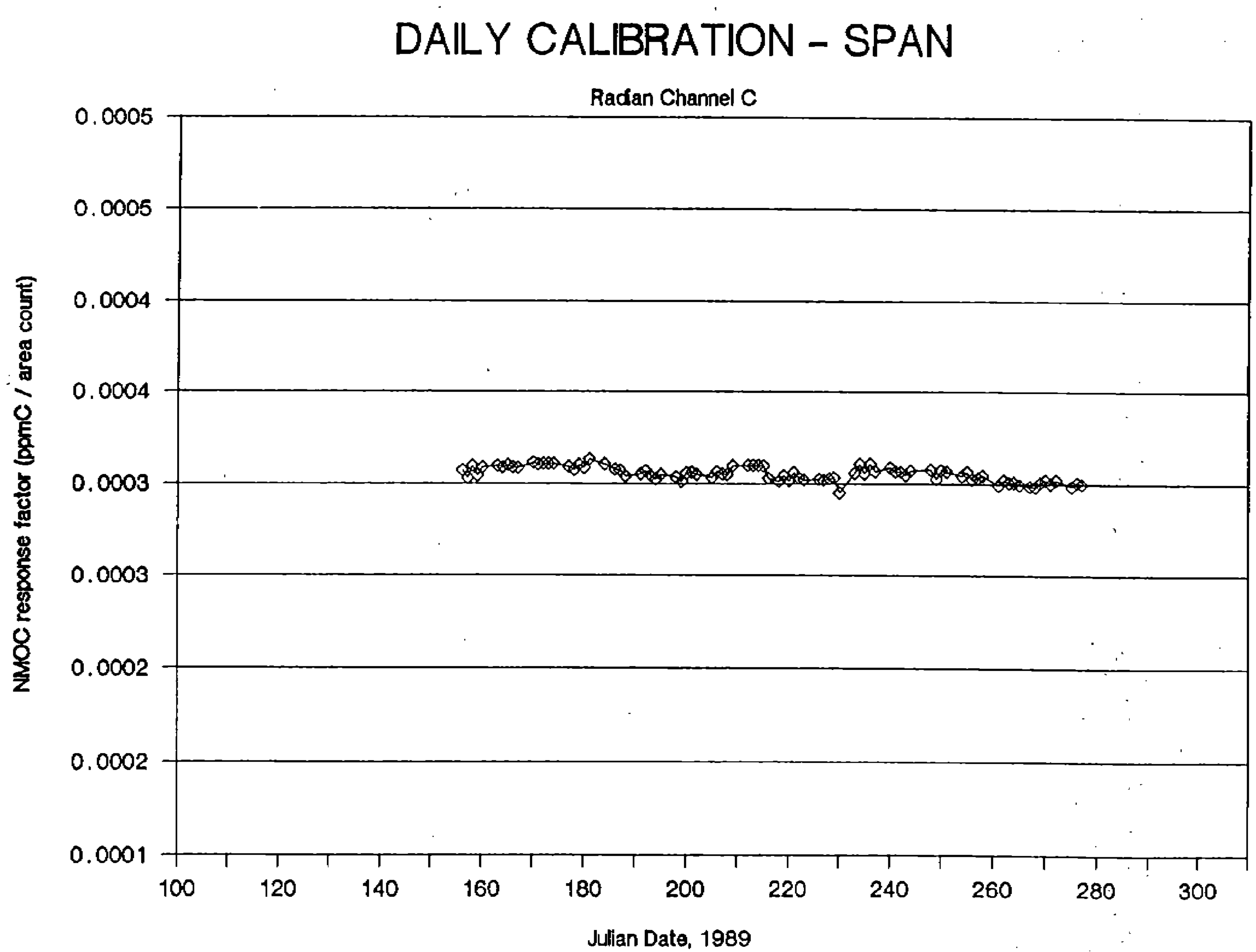


Figure 4-11. Daily calibration span, Channel C.

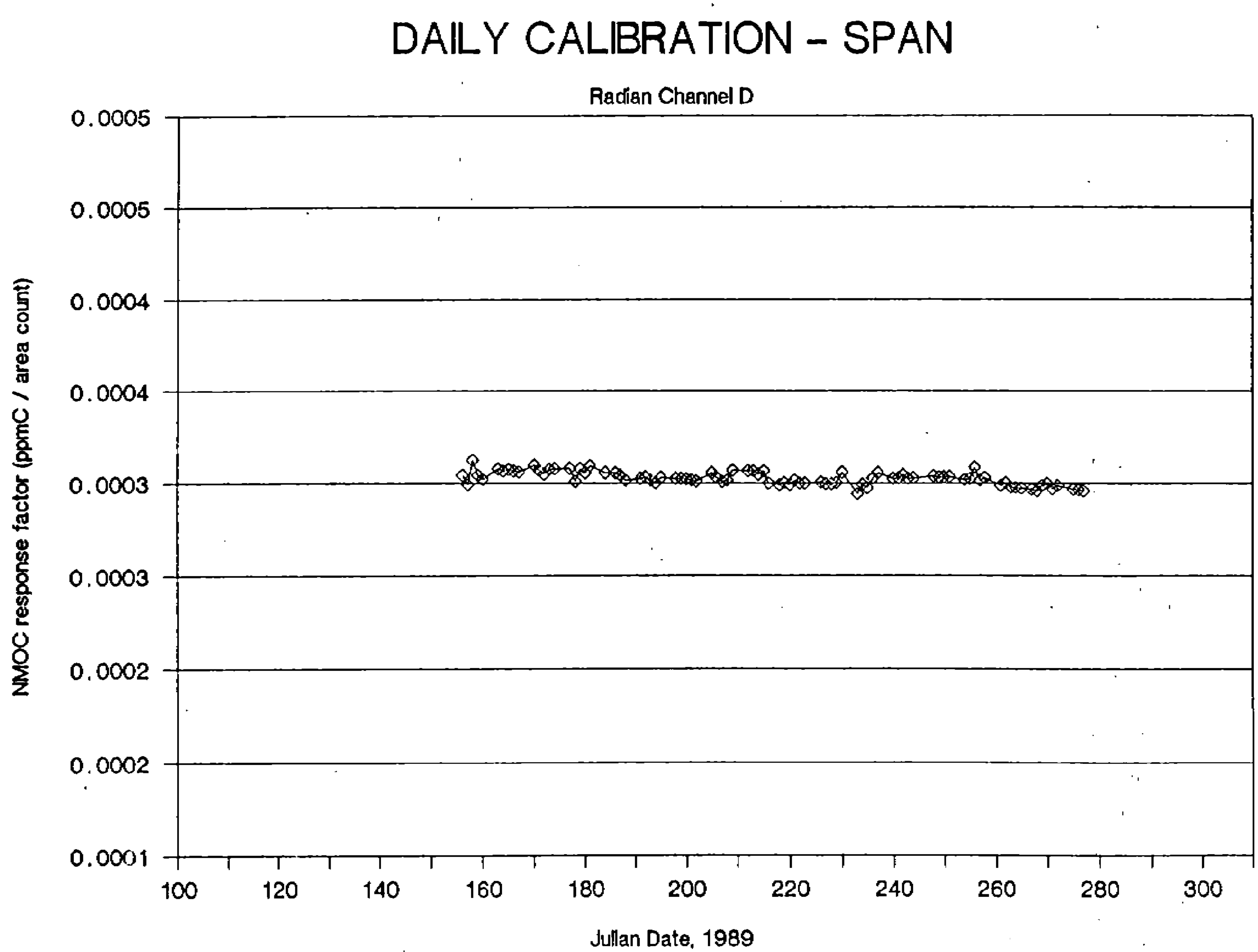


Figure 4-12. Daily calibration span, Channel D

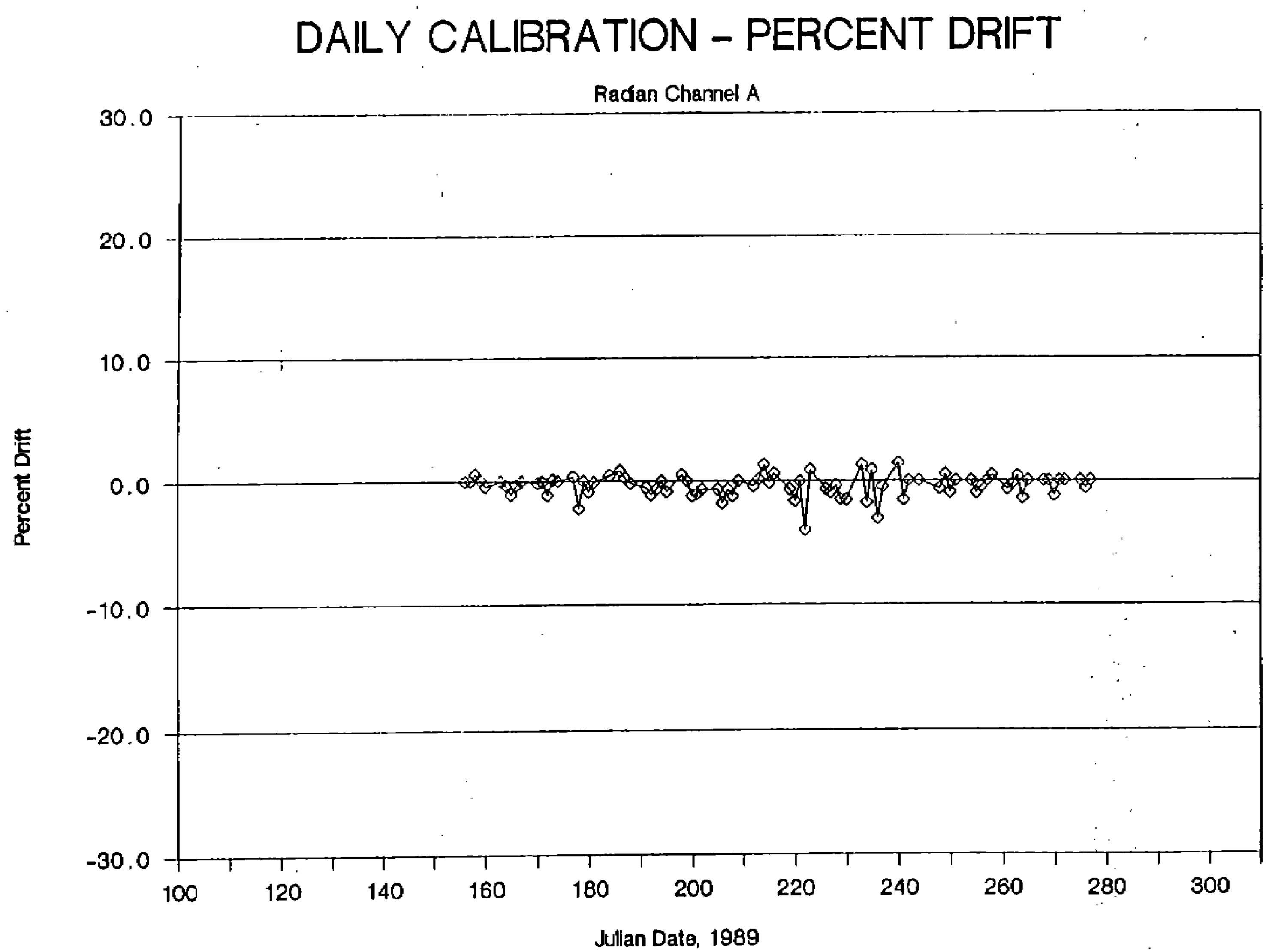


Figure 4-13. Daily calibration percent drift, Channel A.

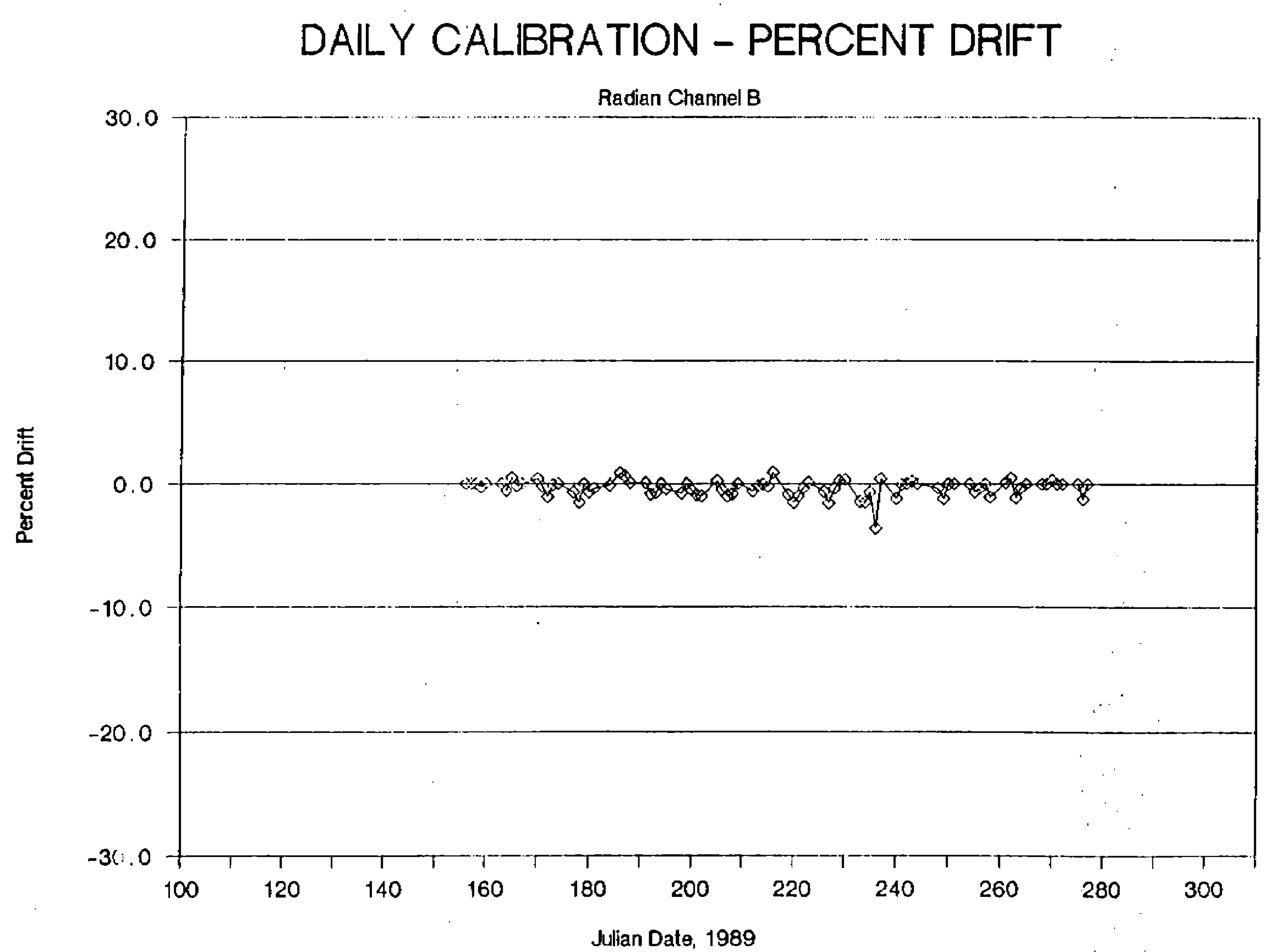


Figure 4-14. Daily calibration percent drift, Channel B.

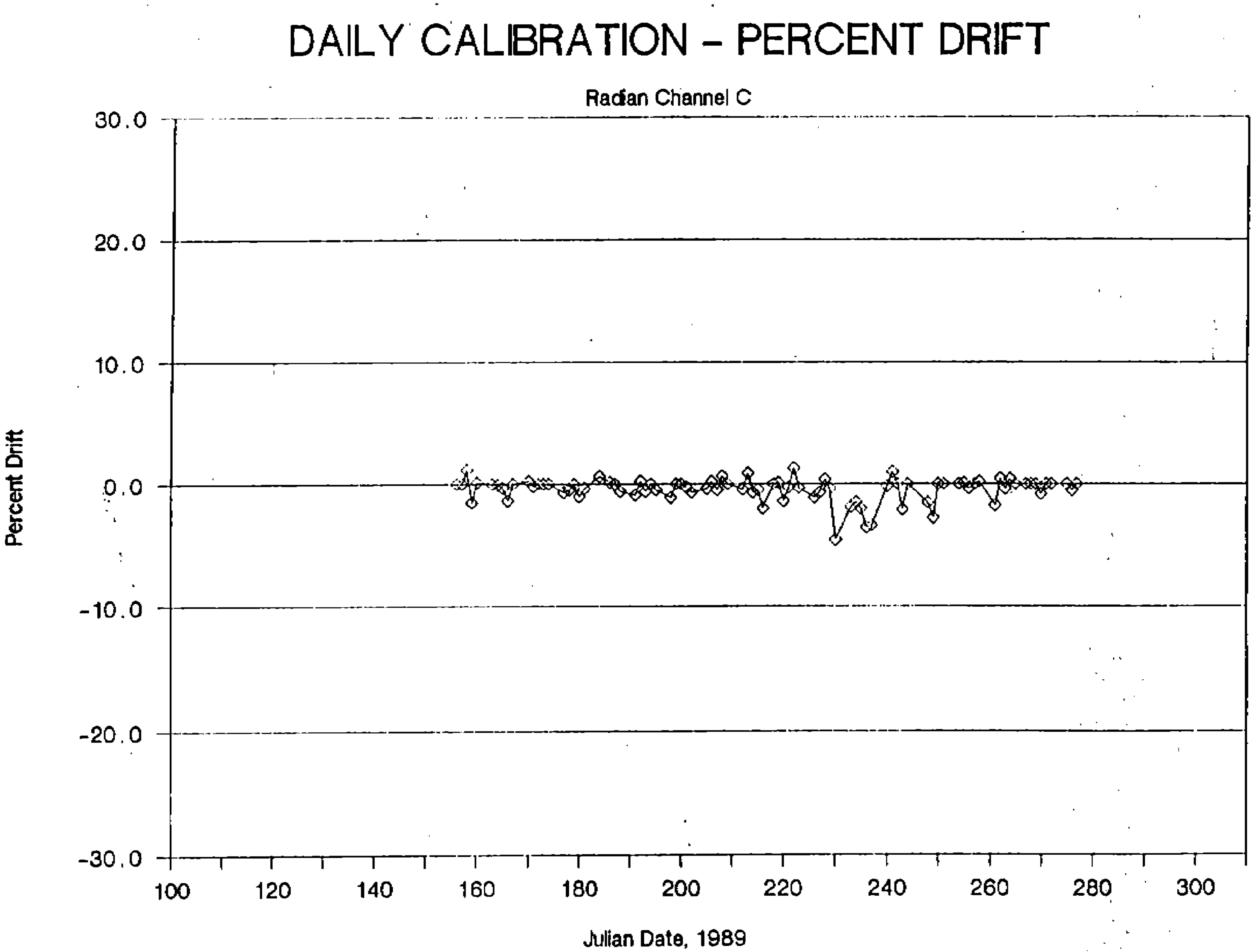


Figure 4-15. Daily calibration percent drift, Channel C.

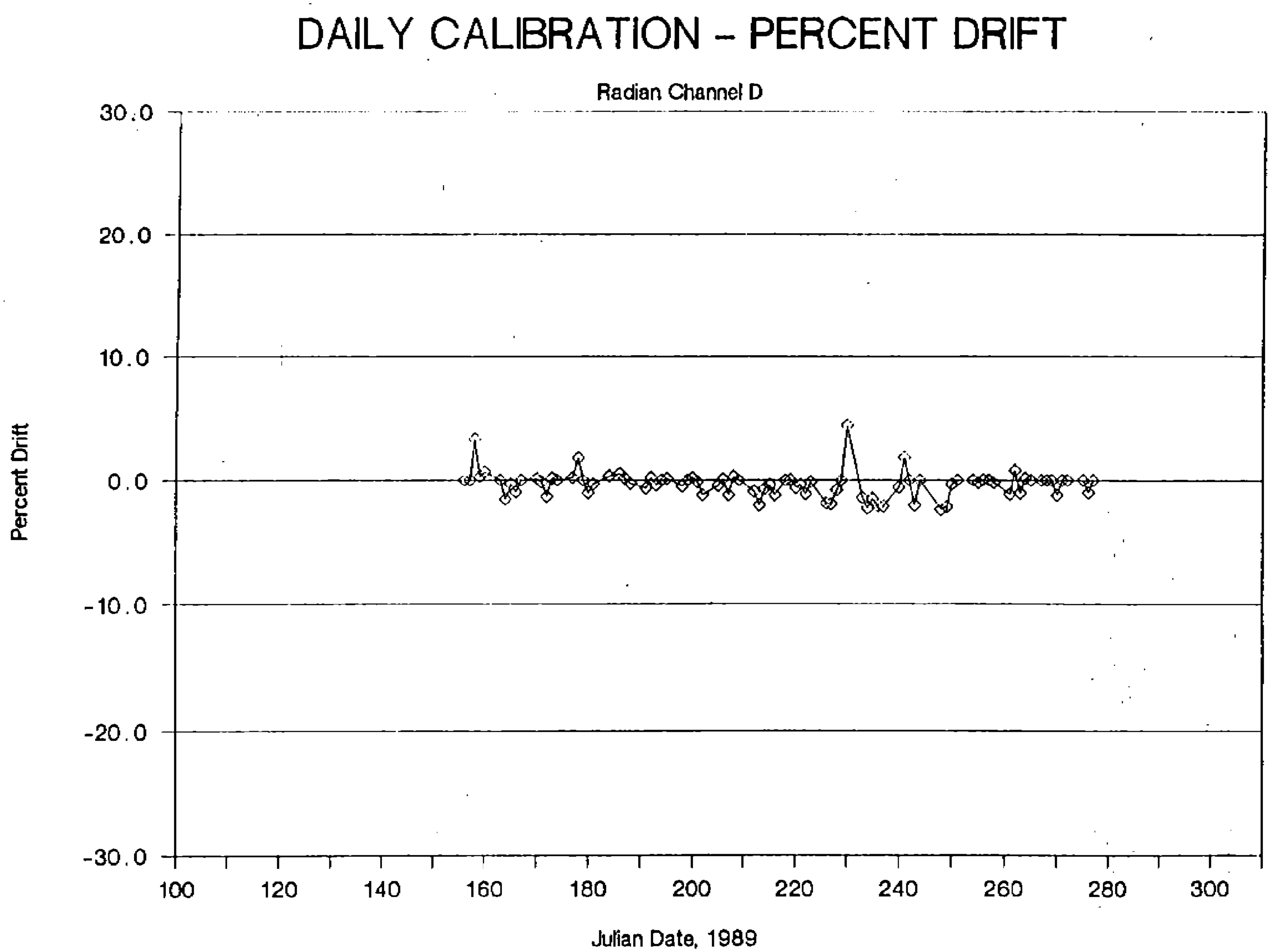


Figure 4-16. Daily calibration percent drift, Channel D.

TABLE 4-2. SUMMARY NMOC CALIBRATION FACTOR DRIFT RESULTS

Radian Channel	Cases	Calibration Factor Drift ppmC/Area Count x 10^{+6}			Percent Factor Drift			Absolute Percent Factor Drift	
		Min	Mean	Max	Min	Mean	Max	Mean	Standard Deviation
A	86	-12	-1	4	-3.9604	-0.3954	1.4164	0.6458	0.7021
B	86	-11	-1	3	-3.6005	-0.3484	0.9255	0.4836	0.5683
C	88	-13	-1	4	-4.5410	-0.4395	1.2395	0.6244	0.8575
D	88	-7	-1	14	-2.3572	-0.3167	4.4605	0.6725	0.8509
Overall	348	-13	-1	14	-4.5410	-0.3750	4.4605	0.6071	0.7764

cah.171f

cah.171f

Calibration factor drift was defined as final calibration factor for the day, minus initial calibration factor. Percent calibration factor drift was defined as the calibration factor drift divided by the initial calibration factor, expressed as a percentage. The absolute percent calibration factor drift is a measure of the calibration drift variability and averaged 0.607% overall. The mean absolute percent calibration drift ranged from 0.484% for Radian Channel B to 0.673% for Radian Channel D.

4.3 IN-HOUSE QC SAMPLES

In-house quality control samples were prepared daily except for one day during the week on which duplicate local ambient samples were collected for "round-robin" analyses. The local ambient samples were analyzed not only by all Radian PDFID channels, but by the EPA-QAD instrument. Local ambient sample results are presented and discussed in Section 4.4.4. In-house quality control samples were prepared by diluting dry propane with cleaned, dried air using calibrated flowmeters. The propane used for the in-house quality control samples was certified by the EPA-QAD against an NIST Reference Standard. The concentration of the in-house standard ranged from about 0.020 ppmC to 18.000 ppmC, but was set to average near the concentration levels that were being analyzed (0.100 to 3.000 ppmC). The analyst did not know the concentration of the in-house standard prior to analysis.

The daily in-house QC data for each Radian channel are given in Appendix G, and include:

- Calendar date analyzed;
- Julian date for 1989;
- Radian ID Number;
- Calculated NMOC concentration in ppmC;
- Measured NMOC concentration in ppmC;
- Bias (measured NMOC-calculated NMOC); and
- % Bias (Bias * 100 / calculated NMOC).

Measured versus calculated NMOC concentrations in Figures 4-17 through 4-20 show excellent agreement. Table 4-3 summarizes the results of the linear regressions for the Radian in-house quality control data, showing regression intercepts near zero, and slopes and coefficients of correlation all near 1.0.

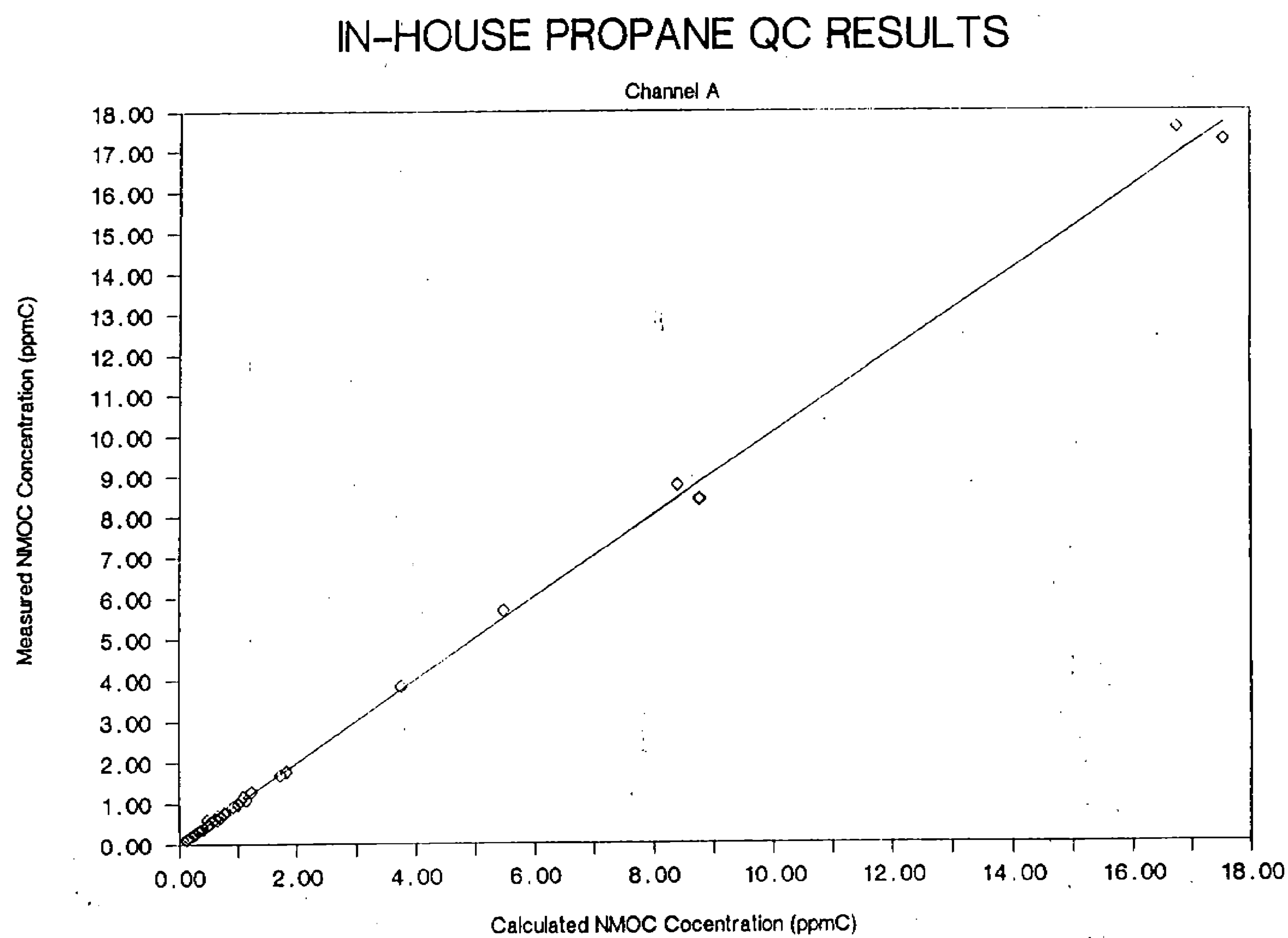


Figure 4-17. In-house quality control results, Channel A.

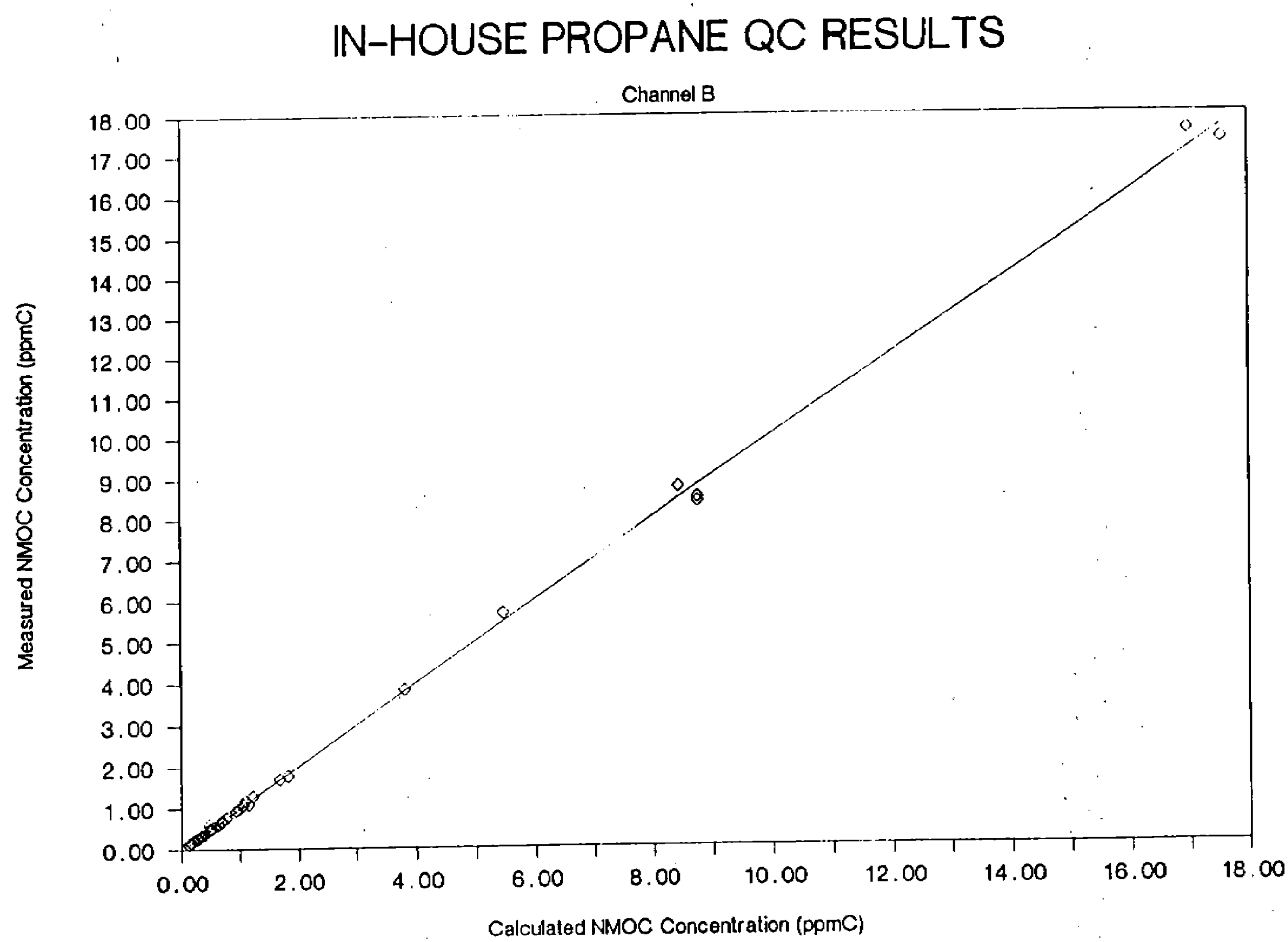


Figure 4-18. In-house quality control results, Channel B.

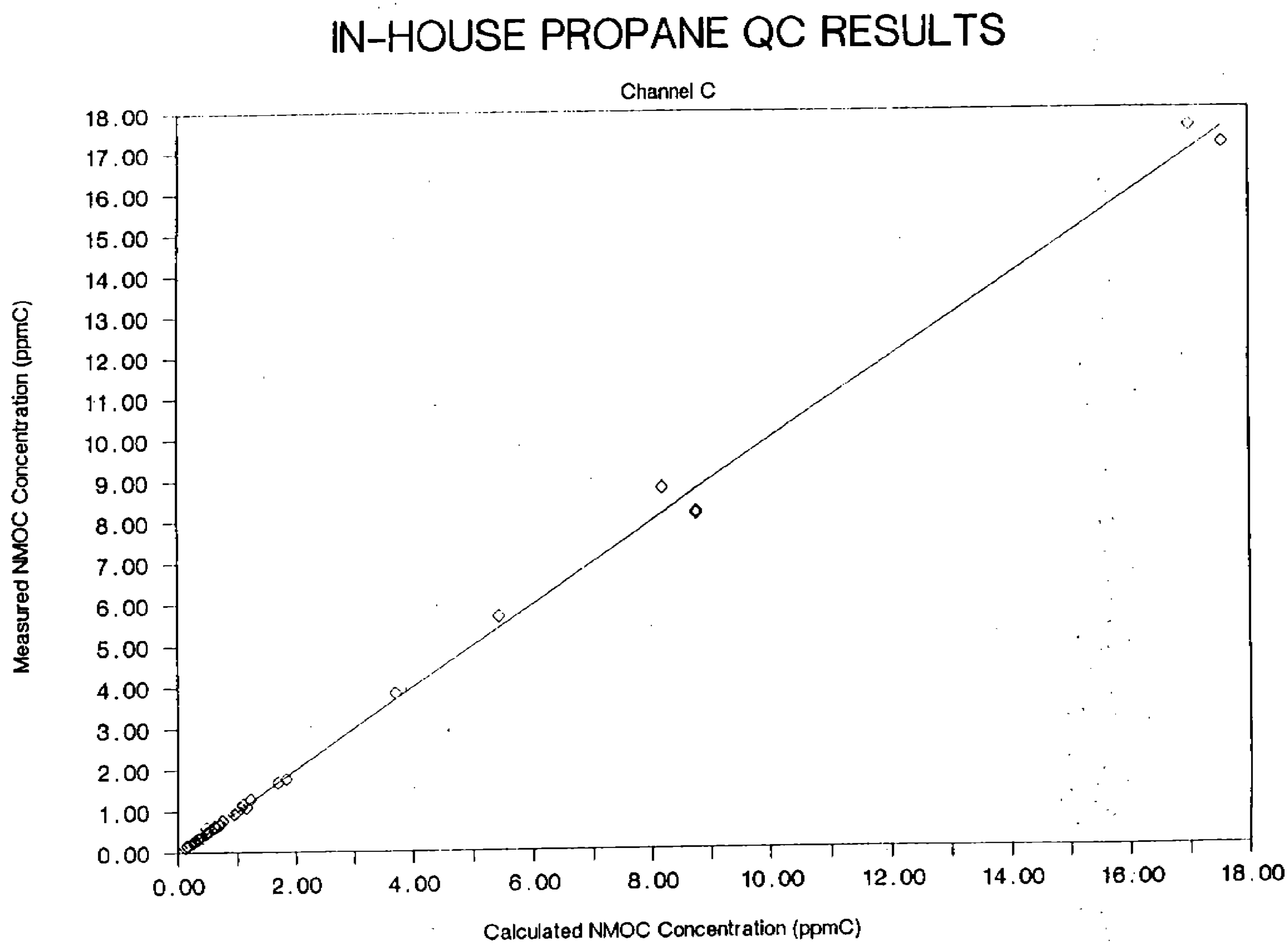


Figure 4-19. In-house quality control results, Channel C.

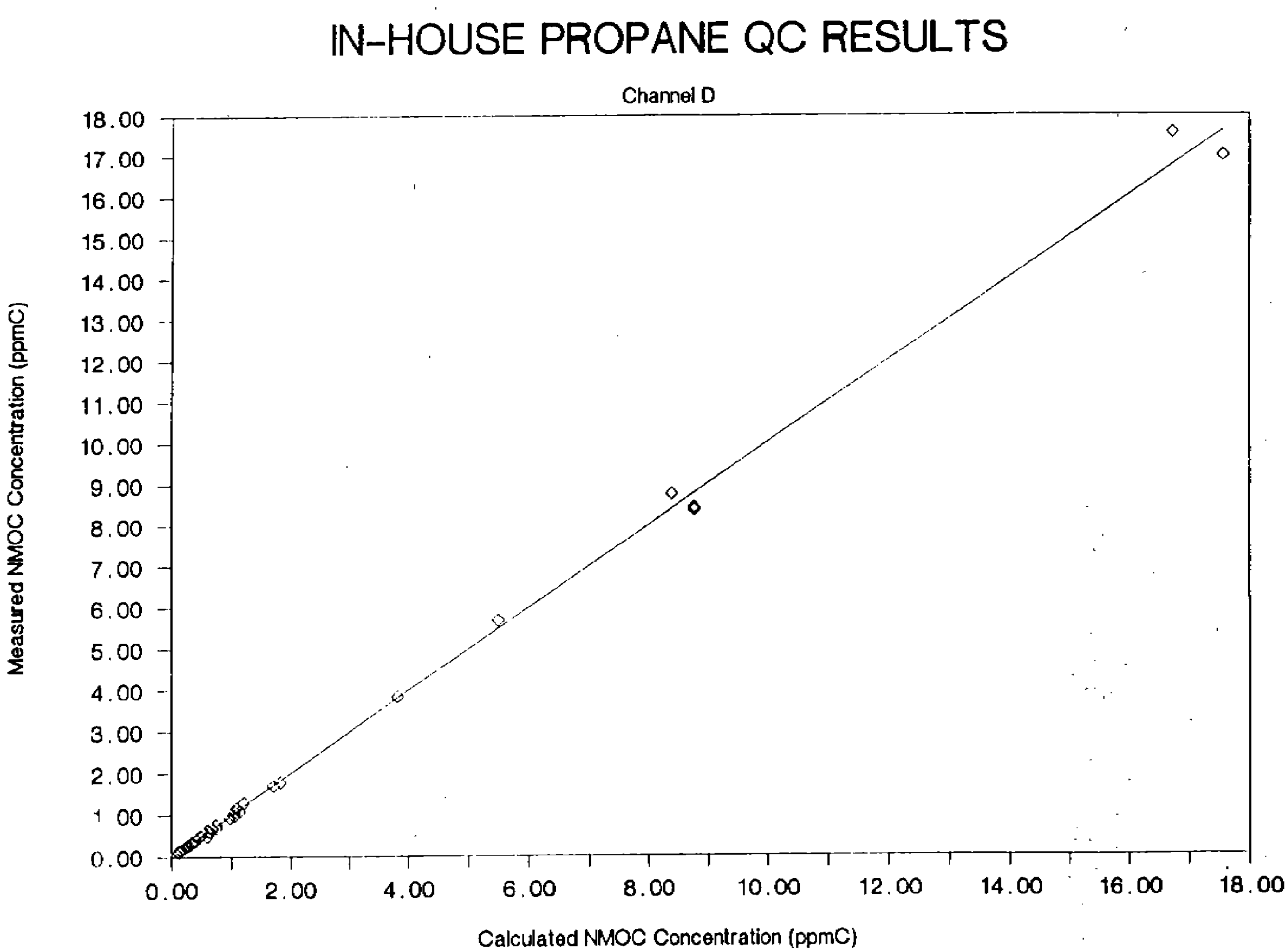


Figure 4-20. In-house quality control results, Channel D.

TABLE 4-3. LINEAR REGRESSION PARAMETERS FOR IN-HOUSE QUALITY CONTROL DATA

Radian Channel	Cases	Intercept	Slope	Coefficient of Correlation
A	51	-0.000182	1.007578	0.999184
B	51	0.005195	1.004650	0.999451
C	51	0.010023	0.997043	0.998786
D	51	0.001783	1.002389	0.998910

Tables 4-4 and 4-5 give statistics for in-house quality control measurements. DIFF is the ppmC difference between the measured and the calculated NMOC concentrations, and PCDIFF is the percentage of the difference relative to the calculated value. Both DIFF and PCDIFF may be considered to be bias terms, assuming that the calculated value is the correct NMOC concentration for the in-house QC sample. Overall, PCDIFF shows a mean bias of +1.27%, and ranges from -18.59% for Channel D to +31.45% for Channel B. ADIFF and APCDIFF, absolute values of DIFF and PCDIFF, respectively, were used as measures of precision. The absolute percent difference ranged from 4.69% for Channel B to 5.46% for Channel D and averaged 5.02 percent. These figures show excellent agreement and consistency for the in-house quality control data and include variability not only in the instrumental analysis but also in the apparatus and method used to generate the QC samples.

Figure 4-21 shows a stem-and-leaf plot of DIFF, the NMOC difference between the calculated and measured in-house quality control samples. The figure shows little skewness, and shows the differences to be approximately normally distributed, which supports the assertion that DIFF is a random variable. The normal distribution of DIFF also implies that there is no significant bias among instrument channels.

4.4 REPEATED ANALYSES

Two types of repeated analyses were conducted in this study. The first type of repeated analysis was conducted primarily to establish precision, and to determine if significant differences in precision existed among Radian (PDFID) channels, the EPA-QAD (PDFID) channel, and the EPA-AREAL (GC/FID) channel. Two samples were selected daily from the received site samples for a second analysis on a Radian channel on the following workday. The second replicate analysis was performed on the day after the first analysis to allow time for the ambient air sample in the canister to equilibrate between analyses. At the beginning of the first analysis, the pressure in the canister is typically about 15 psig. At the beginning of the second analysis, the canister pressure is typically 9 psig.

TABLE 4-4. IN-HOUSE QUALITY CONTROL STATISTICS, BY RADIAN CHANNEL

Channel	Statistics	Variables DIFF[a]	ADIFF[b]	PCDIFF[c]	APCDIFF[d]
A	Cases	50	50	50	50
	Minimum	-0.366000	0.000000	-10.345000	0.000000
	Maximum	0.794000	0.794000	28.390000	28.389830
	Mean	0.014020	0.069708	1.024200	4.698099
	Std. Dev.	0.157111	0.141160	6.701800	4.843689
	Std. Error	0.022219	0.019963	0.947778	2.846198
	Skewness	2.131025	3.391473	1.641115	2.846198
	Kurtosis	11.872723	12.754924	4.359463	10.374671
B	Cases	50	50	50	50
	Minimum	-0.363000	0.000000	-11.077000	0.000000
	Maximum	0.582000	0.582000	31.453000	31.453360
	Mean	0.013920	0.061368	1.560380	4.919399
	Std. Dev.	0.127542	0.112348	7.485092	5.815267
	Std. Error	0.01037	0.015888	1.058552	0.822403
	Skewness	1.322336	2.897890	1.696878	2.664036
	Kurtosis	8.400402	8.709848	4.414086	7.989274
C	Cases	50	50	50	50
	Minimum	-0.624000	0.000000	-9.677000	0.000000
	Maximum	0.590000	0.624000	28.936000	28.936170
	Mean	0.004480	0.084248	1.320620	5.000242
	Std. Dev.	0.187379	0.166999	7.300220	5.436925
	Std. Error	0.026499	0.023617	1.032407	0.768897
	Skewness	-0.425886	2.450505	1.588367	2.604469
	Kurtosis	5.955488	4.513826	3.862143	8.131657
D	Cases	50	50	50	50
	Minimum	-0.566000	0.000000	-18.593000	0.000000
	Maximum	0.845000	0.845000	25.828000	25.827810
	Mean	0.006260	0.079188	1.207040	5.458642
	Std. Dev.	0.177757	0.158869	7.722464	5.542515
	Std. Error	0.025139	0.022467	1.092121	0.783830
	Skewness	1.321056	3.244163	0.841692	1.956190
	Kurtosis	10.808134	10.828937	2.023071	3.797688

[a]DIFF = Measured NMOC concentration - Calculated NMOC concentration, ppmC.

[b]ADIFF = Absolute value of DIFF.

[c]PCDIFF = DIFF/calculated NMOC concentration x 100.

[d]APCDIFF = Absolute value of PCDIFF.

TABLE 4-5. OVERALL IN-HOUSE QUALITY CONTROL STATISTICS

Statistics	DIFF[a]	ADIFF[b]	PCDIFF[c]	APCDIFF[d]
Cases	200	200	200	200
Minimum	-0.624000	0.000000	-18.593000	0.000000
Maximum	0.845000	0.845000	31.453000	31.453360
Mean	0.009670	0.073628	1.278060	5.019096
Std. Dev.	0.162874	0.145512	7.259442	5.387349
Std. Error	0.011517	0.010289	0.513320	0.380943
Skewness	0.864308	3.068350	1.417151	2.508747
Kurtosis	9.773681	9.571014	3.620947	7.379894

[a]DIFF = Measured NMOC concentration - Calculated NMOC concentration, ppmC.

[b]ADIFF = Absolute value of DIFF.

[c]PCDIFF = DIFF/calculated NMOC concentration x 100.

[d]APCDIFF = Absolute value of PCDIFF.

-56		6666
-38		9999
-33		6666
-11		1
-6		3
-5		8543
-4		99320
-3		98776 411
-2		99765 44442
-1	H	99999 86644 32221 11100
-0	M	99999 99999 88887 77665 44444 33333 32211 111
0		00000 01112 22234 5689
1		00001 22222 33333 35555 799
2	H	01124 44456 899
3		06999 999
4		03788 889
5		027
6		7
7		17
8		11114
8		5
9		8
10		3
13		46
14		56
19		2
22		34
25		2
31		8
37		2
38		3
56		4
58		2
59		0
79		4
84		5

	DIFF. ppmC
Cases	200
Minimum	-0.566
Maximum	0.845
Mean	0.007
Standard Deviation	0.167
Standard Error	0.012
Skewness	0.708
Kurtosis	9.041
Lower Hinge (H)	-0.014
Median (M)	0.000
Upper Hinge (H)	0.026

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Figure 4-21. Stem-and-leaf plot of in-house quality control differences.

The QAPP[2] specified which Radian channels were selected for the repeated analyses, so that all combinations of channel pairs, i.e., A-A, B-B, B-C, A-D, etc., would be selected randomly. The EPA-QAD and the EPA-AREAL channels randomly repeated analyses of the site samples already analyzed once by Radian. Shortly after the beginning of the 1988 NMOC Monitoring Program, the decision was made by Radian and the EPA to do repeated analyses only on duplicate samples, and to have the second analysis, not only on the day after the first analysis, but also on the same Radian channel as the first analysis. The purpose of the latter specification on replicate analyses was to avoid any bias that may be caused by a different analysis channel. None of the site samples selected for repeated analyses by Radian channels was analyzed a third time by an EPA channel.

All replicate analyses were performed on duplicate samples, but not all the analyses on duplicate samples were replicated. Each analysis consisted of two or three consecutive injections from a canister that was connected to the GC. After the first analysis, the canister valve was closed. the canister was disconnected from the GC, and the canister was stored at laboratory temperature overnight. The second replicate analysis on the sample in the canister was performed on the next day, or the following Monday if the first analysis was on Friday. Replicate analyses were performed on the same analytical channel, i.e., Radian Channel A, B, C, or D, for a given duplicate sample. By conducting repeated analyses of the duplicate samples it was possible to investigate the relative magnitude of the duplicate sampling precision and the analytical precision. The results for this investigation are given in Section 4.5.3.

The second type of comparative analysis was done on local ambient samples collected by EPA-QAD personnel in Raleigh, in Research Triangle Park, or near Research Triangle Park, North Carolina. These samples were taken once weekly in duplicate at an initial pressure of about 35 psig. Each local ambient sample, called a round-robin sample, was analyzed by all four Radian channels and the EPA-QAD channel. One of the duplicate round-robin samples was analyzed first in the Radian laboratory while the other duplicate round-robin sample was analyzed first in the EPA laboratories. Upon completion of the analyses, the laboratories exchanged canisters and analyzed the other duplicate sample on all channels. The purposes of these studies were:

- to determine if the order of analysis by one laboratory or channel made a significant difference in the measured NMOC value;
- to compare the precision of all the channels;
- to compare the PDFID method of analysis with the GC/FID speciated method of analysis; and
- to compare the results among Radian channels.

4.4.1 Site Sample Results

Figure 4-22 compares the EPA-QAD analyses with Radian analyses of the same site samples. Figure 4-23 compares the EPA-AREAL analyses with Radian analyses. Figure 4-24 compares AREAL analyses with QAD analyses. Orthogonal regression parameters for the three data sets are summarized in Table 4-6.

Summary statistics of the comparative analyses for Radian channels versus the EPA-QAD channel are given in Table 4-7. The table gives DIFF, the difference between the Radian NMOC concentration and the QAD NMOC concentration in ppmC; and PDIFF, the percent difference relative to the mean of the Radian and QAD analyses. ADIFF and APDIFF are the absolute values of DIFF and PDIFF, respectively. The mean percent difference shows Radian NMOC concentrations to average 11.11% higher than the QAD NMOC concentration. This is an average bias figure for the Radian analyses relative to a mean NMOC concentration. The average absolute percent difference is 13.92, which is a measure of the precision.

In 1985, the mean percent difference showed Radian NMOC concentrations to average 0.49% higher than QAD, and 3.77 lower in 1986. In 1987, the mean percent differences showed Radian concentrations to average 4.48% lower than the QAD NMOC concentration. In 1988, the difference was shown to be 1.674 percent. The average absolute percent difference was 10.5% in 1985, 14.8% in 1986, 14.07% in 1987 and 11.76% in 1988. The agreement among the precision results is good, and shows that the instruments and operating procedures were consistent for those years.

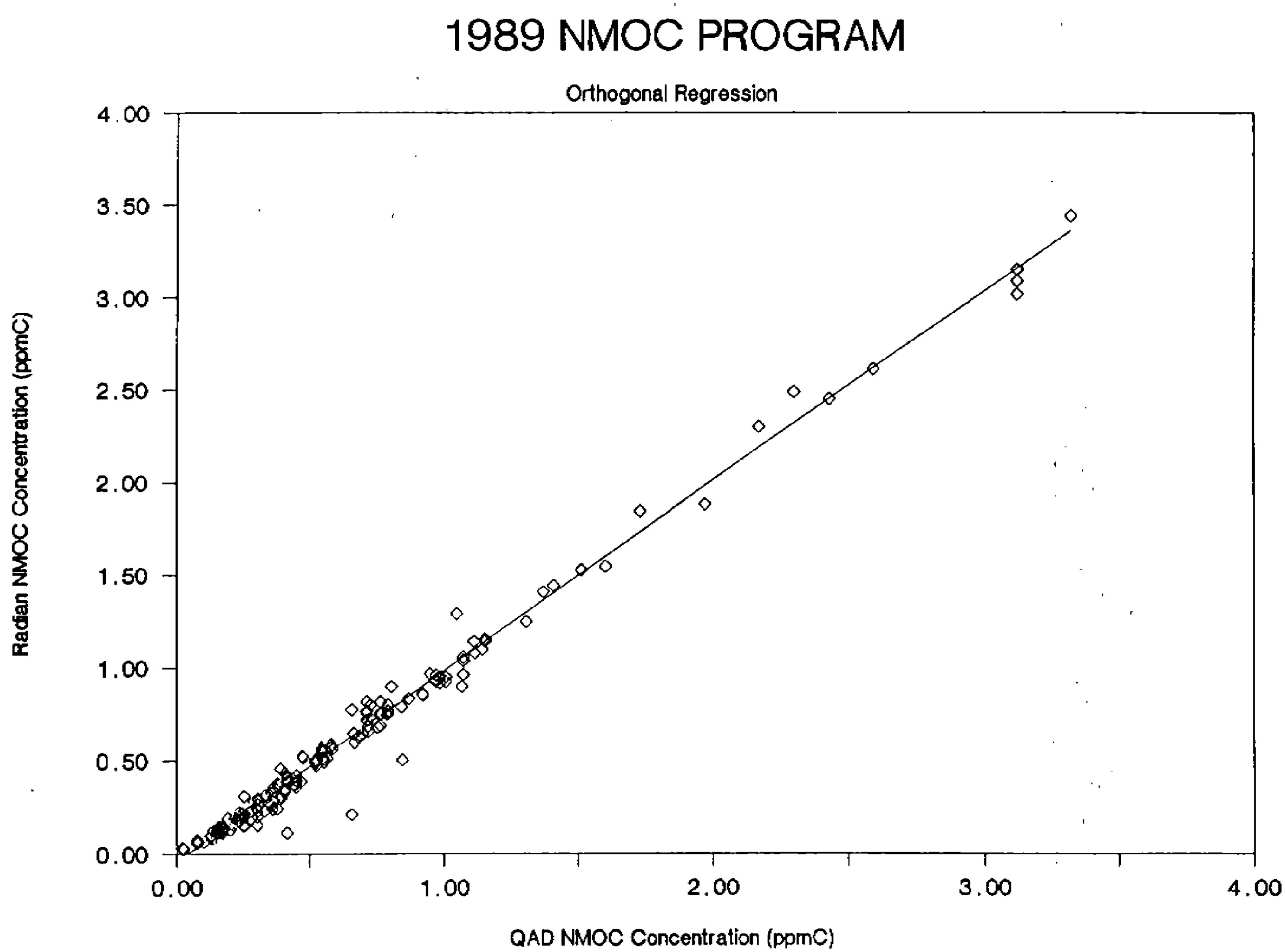


Figure 4-22. Orthogonal regression comparing QAD with Radian NMOC analyses.

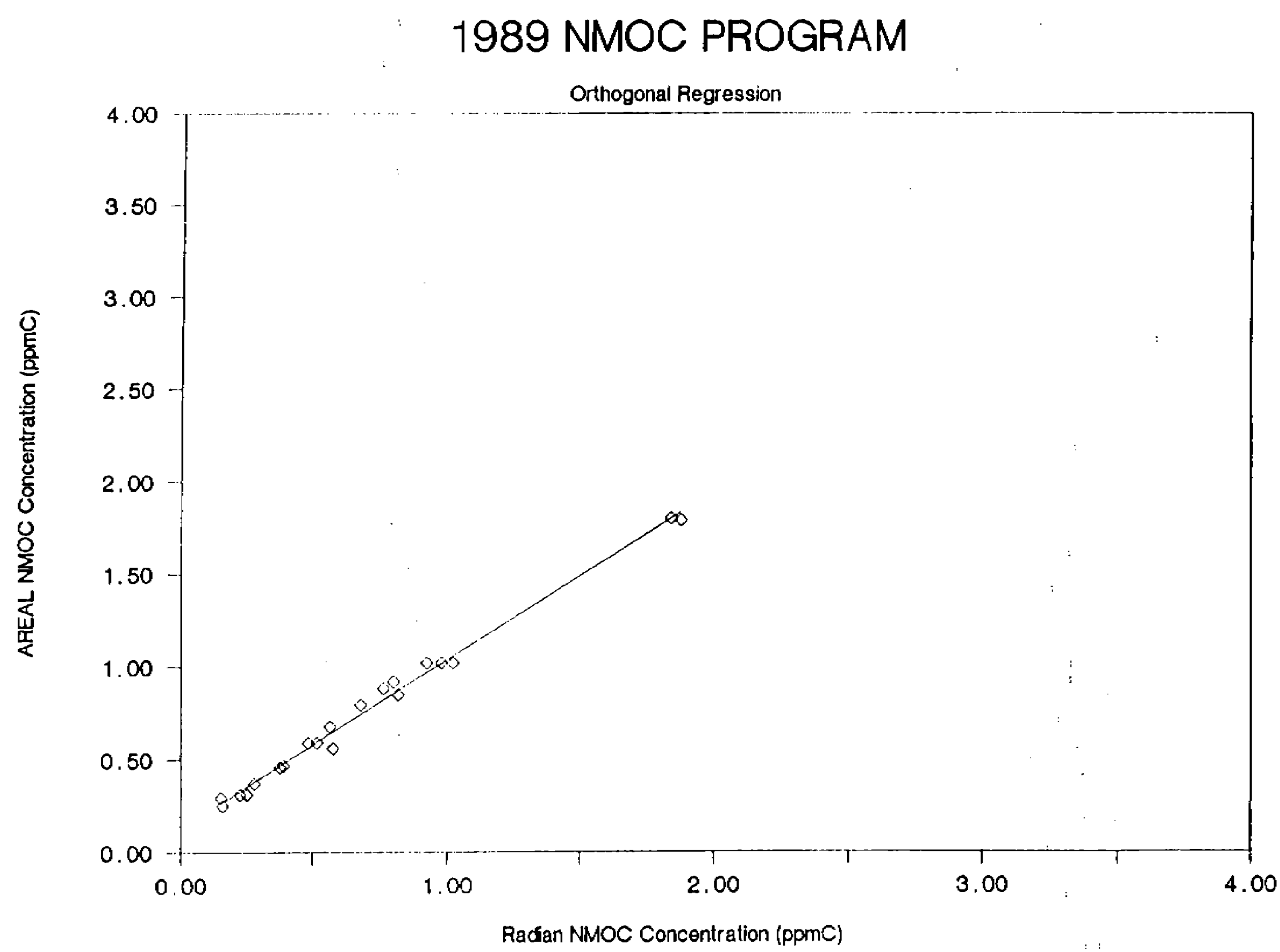


Figure 4-23. Orthogonal regression comparing AREAL with Radian analyses.

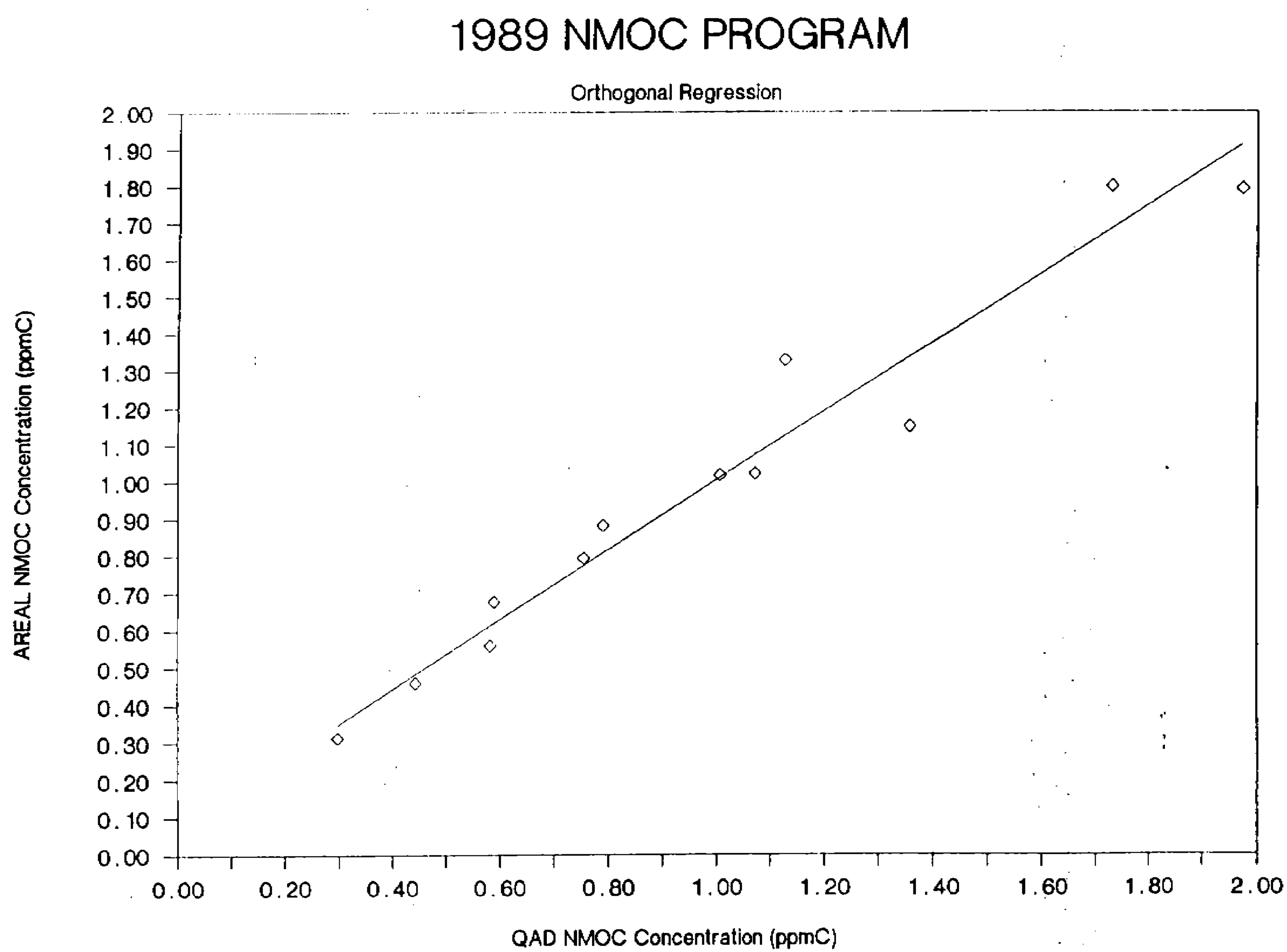


Figure 4-24. Orthogonal regression comparing QAD with AREAL NMOC analyses.

TABLE 4-6. ORTHOGONAL REGRESSION PARAMETERS FOR REPEATED ANALYSES OF SITE SAMPLES

Channel Pair (X-Y)	Cases	Intercept	Slope	Coefficient of Correlation
QAD-Radian	265	-0.041230	1.025452	0.995083
Radian-QAD	265	0.040208	0.975179	0.995083
ASRL-Radian	20	-0.136310	1.098092	0.995908
Radian-ASRL	20	0.124140	0.910670	0.995908
QAD-ASRL	12	0.069707	0.933637	0.9075807
ASRL-QAD	12	-0.074660	1.091079	0.975807

TABLE 4-7. SUMMARY STATISTICS OF COMPARITIVE ANALYSES FOR RADIAN vs. QAD CHANNELS

Statistics	Variables			
	DIFF	ADIFF	PDIFF	APDIFF
Cases	265	265	265	265
Minimum	-0.44600	0.00000	-113.20750	0.00000
Maximum	0.24200	0.44600	48.27590	113.20750
Mean	-0.02736	0.04281	-11.11275	13.92022
Standard Dev.	0.05834	0.04812	16.83605	14.59133
Standard Error	0.00358	0.00296	1.03423	0.89634
Skewness	-1.79171	4.25502	-1.54763	2.65780
Kurtosis	15.79171	26.35624	7.94459	12.16767

DIFF = Radian NMOC concentration - QAD NMOC cocentration, ppmC.
ADIFF = Absolute value of DIFF.
PDIFF = DIFF/((Radian NMOC conc. + QAD NMOC conc.)/2) x 100.
APDIFF = Absolute value of PDIFF.

Summary statistics are given for the same data in Table 4-8 by Radian channel. The data show a mean absolute percent difference ranging from 10.12% for Channel A to 20.29% for Channel B. The mean percent differences range from -18.05% for Channel B to -6.16% for Channel C.

Table 4-9 summarizes statistics for comparative analyses for Radian channels versus AREAL channels. DIFF is the difference between the NMOC values determined by Radian channels and the NMOC values determined by AREAL.

PDIFF averages 12.17%, although DIFF appears to be symmetrical about zero. APDIFF is 0.07%, which is lower than the APDELTA mean of 16.76% for 1988 and 15.88% for 1987. Table 4-10 compares Radian NMOC analyses with AREAL NMOC analyses, by Radian channels. APCDIFF values are 0.08%, 0.07%, 0.06%, and 0.07% comparing the AREAL channel with Radian Channels A, B, C, and D, respectively. PCDIFF averages are 19.06%, 11.46%, 8.17%, and 11.60% for AREAL versus Radian Channels A, B, C, and D, respectively.

Table 4-11 compares repeated analyses of site samples by the EPA-AREAL GC/FID instrument and the EPA-QAD PDFID instrument. The results show that PDELTA averaged 1.97%, while APDIFF averaged 7.85 percent. The table shows that the AREAL concentrations average 1.97% lower than the QAD concentrations. Radian concentrations were 11.11% higher than QAD concentrations. APDIFF between AREAL and QAD concentrations averaged 7.85%, whereas APDIFF for Radian and QAD concentrations averaged 13.92 percent.

Of NMOC concentration measurements, the comparison between Radian and the EPA-QAD channel represents between-laboratory comparisons for the PDFID method. Comparisons between the Radian channels and the EPA-AREAL channel are between-laboratory and between-method comparisons.

Table 4-12 summarizes statistics for repeated analyses on Radian channels. The QAPP[2] specified the channel pair to be involved with the repeated analysis each day. The mean APDIFF was the average percent difference between the second and the first analysis and was 8.24% for the overall data set. Table 4-13 shows the statistics for repeated analyses by Radian channel pairs. Table 4-14 gives the 95% confidence intervals for the mean differences by channel pairs. Figure 4-25 plots the means and 95% confidence intervals listed in Table 4-14. The circles on Figure 4-25 locate the mean difference for each channel pair. The vertical lines span the 95% confidence intervals of the mean differences.

TABLE 4-8. SUMMARY STATISTICS OF COMPARITIVE ANALYSES FOR RADIAN vs. QAD CHANNELS, BY RADIAN CHANNELS

		Variables			
Channel	Statistics	DIFF	ADIFF	PCDIFF	APCDIFF
A	Cases	60	60	60	60
	Minimum	-0.10100	0.00000	-43.98340	0.00000
	Maximum	0.04200	0.10100	33.96230	43.98340
	Mean	-0.02549	0.03033	-8.21561	10.11860
	Std. Dev.	0.02940	0.02429	12.37010	10.84151
	Std. Error	0.00380	0.00314	1.59697	1.39963
	Skewness	-0.21880	0.78384	-0.32503	1.32669
	Kurtosis	-0.09862	-0.00006	2.09816	0.92462
B	Cases	61	61	61	61
	Minimum	-0.44600	0.00100	-113.20750	0.54790
	Maximum	0.18700	0.44600	24.00000	113.20750
	Mean	-0.04782	0.06251	-18.05073	20.28806
	Std. Dev.	0.09045	0.08083	23.91893	22.02065
	Std. Error	0.01158	0.01035	3.06250	2.81946
	Skewness	-1.99550	2.93039	-1.80325	2.26822
	Kurtosis	7.26511	9.40849	4.64537	6.23438
C	Cases	72	72	72	72
	Minimum	-0.10900	0.00200	-45.16130	0.47960
	Maximum	0.24200	0.24200	48.27590	48.27590
	Mean	-0.00757	0.04021	-6.16318	11.64860
	Std. Dev.	0.05563	0.03891	14.86087	11.03469
	Std. Error	0.00656	0.00459	1.75137	1.30045
	Skewness	1.71269	2.40902	0.12394	1.59574
	Kurtosis	4.83983	8.62397	2.25045	2.29043
D	Cases	72	72	72	72
	Minimum	-0.11800	0.00200	-41.69180	0.65250
	Maximum	0.12400	0.12400	24.00000	41.69180
	Mean	-0.03136	0.03914	-12.59858	13.96490
	Std. Dev.	0.03395	0.02443	12.12244	10.49516
	Std. Error	0.00400	0.00288	1.42864	1.23687
	Skewness	1.26306	1.19681	-0.08203	0.66097
	Kurtosis	5.17016	1.99452	0.15337	-0.48202

DIFF = Radian NMOC concentration - QAD concentration, ppmC.
ADIFF = Absolute value of DIFF.
PDIFF = DIFF/((Radian NMOC conc. + QAD NMOC conc.)/2) x 100.
APDIFF = Absolute value of PDIFF.

TABLE 4-9. SUMMARY STATISTICS OF COMPARATIVE ANALYSES FOR RADIAN VS. AREAL CHANNELS

Statistics	Variables			
	DIFF	ADIFF	PDIFF	APDIFF
Cases	29	29	29	29
Minimum	-0.08800	0.00000	-5.55560	0.00000
Maximum	0.14200	0.14200	63.67710	63.67710
Mean	0.05245	0.07114	12.17135	13.95619
Standard Dev.	0.06287	0.03951	15.58129	13.94552
Standard Error	0.01168	0.00734	2.89337	2.58962
Skewness	-0.54910	-0.11230	1.42100	1.90813
Kurtosis	-0.91669	-1.12904	2.49849	4.06895

DIFF = Radian NMOC concentration - AREAL NMOC cocentration, ppmC.
ADIFF = Absolute value of DIFF.
PDIFF = DIFF/((Radian NMOC conc. + AREAL NMOC conc.)/2) x 100.
APDIFF = Absolute value of PDIFF.

TABLE 4-10. SUMMARY STATISTICS OF COMPARATIVE ANALYSES FOR RADIAN vs. AREAL CHANNELS, BY RADIAN CHANNELS

		Variables			
Channel	Statistics	DIFF	ADIFF	PCDIFF	APCDIFF
A	Cases	6	6	6	6
	Minimum	-0.03200	0.01800	-5.55560	1.74760
	Maximum	0.14200	0.14200	63.67710	63.67710
	Mean	0.06000	0.07667	19.06332	21.49772
	Std. Dev.	0.07009	0.04669	25.50778	23.06852
	Std. Error	0.02862	0.01906	10.41351	9.41768
	Skewness	-0.35565	0.05469	0.87667	1.12737
	Kurtosis	-1.40392	-1.21784	-0.42442	-0.11732
B	Cases	6	6	6	6
	Minimum	-0.03500	0.01800	-3.37020	3.16340
	Maximum	0.11800	0.11800	43.90240	43.90240
	Mean	0.05117	0.06883	11.46360	13.64147
	Std. Dev.	0.06679	0.04378	17.64351	15.67428
	Std. Error	0.02727	0.01787	7.20293	6.39900
	Skewness	-0.27044	0.05503	1.08985	1.39529
	Kurtosis	-1.60276	-1.75274	-0.01560	0.46362
C	Cases	8	8	8	8
	Minimum	-0.04400	0.01700	-2.99030	2.41630
	Maximum	0.11200	0.11200	27.25880	27.25880
	Mean	0.04988	0.06513	8.17445	9.52610
	Std. Dev.	0.05614	0.03388	9.88906	8.39349
	Std. Error	0.01985	0.01198	3.49631	2.96755
	Skewness	-0.62645	-0.12212	0.72587	1.24650
	Kurtosis	-1.03630	-1.35774	-0.20380	0.48578
D	Cases	9	9	9	9
	Minimum	-0.08800	0.00000	-4.79300	0.00000
	Maximum	0.13200	0.13200	20.81130	20.81130
	Mean	0.05056	0.07433	11.60134	13.07619
	Std. Dev.	0.07187	0.04271	10.51643	8.34567
	Std. Error	0.02396	0.01424	3.50548	2.78189
	Skewness	-0.77532	-0.53598	-0.69804	-0.69006
	Kurtosis	-0.54871	-0.73919	-1.38054	-1.32778

DIFF = Radian NMOC concentration - AREAL concentration, ppmC.
ADIFF = Absolute value of DIFF.
PDIFF = DIFF/((Radian NMOC conc. + AREAL NMOC conc.)/2) x 100.
APDIFF = Absolute value of PDIFF.

TABLE 4-11. SUMMARY STATISTICS OF COMPARATIVE ANALYSES FOR QAD VS. AREAL CHANNELS

Statistics	Variables			
	DIFF	ADIFF	PDIFF	APDIFF
Cases	12	12	12	12
Minimum	-0.21000	0.00900	-16.74640	0.88890
Maximum	0.19900	0.21000	16.19860	16.74640
Mean	0.00483	0.08250	1.96783	7.84682
Standard Dev.	0.11364	0.07426	9.57992	5.36929
Standard Error	0.03281	0.02144	2.76549	1.54998
Skewness	-0.50045	0.75914	-0.37075	0.55157
Kurtosis	-0.10199	-0.94496	-0.52788	-1.12745

DIFF = QAD NMOC concentration - AREAL NMOC cocentration, ppmC.
ADIFF = Absolute value of DIFF.
PDIFF = DIFF/((QAD NMOC conc. + AREAL NMOC conc.)/2) x 100.
APDIFF = Absolute value of PDIFF.

TABLE 4-12. SUMMARY STATISTICS FOR COMPARATIVE ANALYSES ON RADIAN CHANNELS

Statistics	Variables			
	DIFF	ADIFF	PDIFF	APDIFF
Cases	156	156	156	156
Minimum	-0.18600	0.00000	-76.99115	0.00000
Maximum	0.26800	0.26800	57.09156	76.99115
Mean	0.00174	0.03172	-0.01912	8.24163
Standard Dev.	0.05571	0.04576	14.68051	12.13075
Standard Error	0.00446	0.00366	1.17538	0.97124
Skewness	0.98957	3.01029	-0.40132	3.26699
Kurtosis	8.08381	10.12834	9.41101	11.71517

DIFF = NMOC concentration on Channel Y - NMOC concentration on Channel X, ppmC.
ADIFF = Absolute value of DIFF.
PDIFF = DIFF/((NMOC concentration on Channel Y + NMOC concentration on Channel X)/2) x 100.
APDIFF = Absolute value of PDIFF.

TABLE 4-13. SUMMARY STATISTICS FOR COMPARATIVE ANALYSES ON RADIAN CHANNELS, BY CHANNEL PAIRS

		Variables			
Channel Pair	Statistics	DIFF	ADIFF	PCDIFF	APCDIFF
A-A	Cases	32	32	32	32
	Minimum	-0.03500	0.00100	-18.68512	0.19066
	Maximum	0.20100	0.20100	54.25101	54.25101
	Mean	0.00947	0.02484	1.55887	7.33285
	Std. Dev.	0.04263	0.03567	11.91380	9.43090
	Std. Error	0.00754	0.00631	2.10608	1.66716
	Skewness	2.94114	3.92627	2.62901	4.03023
	Kurtosis	10.83975	16.89304	10.17673	17.52028
B-A	Cases	1	1	1	1
	Minimum	-0.02200	0.02200	-14.37908	14.37908
	Maximum	-0.02200	0.02200	-14.37908	14.37908
	Mean	-0.02200	0.02200	-14.37908	14.37908
	Std. Dev.	-	-	-	-
	Std. Error	-	-	-	-
	Skewness	-	-	-	-
	Kurtosis	-	-	-	-
B-B	Cases	42	42	42	42
	Minimum	-0.18600	0.00100	-76.99115	0.22247
	Maximum	0.26800	0.26800	57.02128	76.99115
	Mean	0.00219	0.04490	-1.00282	12.19596
	Std. Dev.	0.08292	0.06939	22.30106	18.60102
	Std. Error	0.01280	0.01071	3.44113	2.87020
	Skewness	0.73208	2.10357	-1.01309	1.99297
	Kurtosis	4.07878	3.33338	3.67384	3.06927
C-C	Cases	45	45	45	45
	Minimum	-0.12900	0.00100	-24.73118	0.31104
	Maximum	0.07700	0.12900	16.11805	24.73118
	Mean	-0.01024	0.02900	-1.37861	6.48480
	Std. Dev.	0.04070	0.03007	8.68004	5.85478
	Std. Error	0.00607	0.00448	1.29394	0.87278
	Skewness	-0.65008	1.42338	-0.39580	1.10550
	Kurtosis	0.96431	1.69111	0.30422	0.88705

(Continued)

TABLE 4-13. (Continued)

Channel Pair	Statistics	DIFF	ADIFF	PCDIFF	APCDIFF
C-D	Cases	1	1	1	1
	Minimum	-0.01800	0.01800	-2.52809	2.52809
	Maximum	-0.01800	0.01800	-2.52809	2.52809
	Mean	-0.01800	0.01800	-2.52809	2.52809
	Std. Dev.	-	-	-	-
	Std. Error	-	-	-	-
	Skewness	-	-	-	-
	Kurtosis	-	-	-	-
D-B	Cases	1	1	1	1
	Minimum	0.15900	0.15900	57.09156	57.09156
	Maximum	0.15900	0.15900	57.09156	57.09156
	Mean	0.15900	0.15900	57.09156	57.09156
	Std. Dev.	-	-	-	-
	Std. Error	-	-	-	-
	Skewness	-	-	-	-
	Kurtosis	-	-	-	-
D-D	Cases	34	34	34	34
	Minimum	-0.05200	0.00000	-17.87709	0.00000
	Maximum	0.09700	0.09700	19.67621	19.67621
	Mean	0.00641	0.02247	0.32662	5.08818
	Std. Dev.	0.03260	0.02419	7.00108	4.73824
	Std. Error	0.00559	0.00415	1.20068	0.81260
	Skewness	0.98416	1.54196	0.22654	1.43498
	Kurtosis	1.02816	1.74113	1.10642	2.04483

DIFF = NMOC concentration on Channel X - NMOC concentration on Channel Y, ppmC.
ADIFF = Absolute value of DIFF.
PDIFF = DIFF/((NMOC concentration on Channel X + NMOC concentration on Channel Y)/2) x 100.
APDIFF = Absolute value of PDIFF.

TABLE 4-14. 95% CONFIDENCE INTERVALS FOR MEAN DELTA, REPEATED ANALYSES

Channel Pair	Mean Difference (ppmC)	Standard Deviation (ppmC)	Cases	$t_{0.975,n-1}$	95% Confidence Intervals Upper	Lower
A-A	0.00947	0.04263	32	2.040	0.02484	-0.00590
B-B	0.00219	0.08292	42	2.020	0.02804	-0.02366
C-C	-0.01024	0.04070	45	2.017	0.00200	-0.02248
D-D	0.00641	0.03260	34	2.036	0.01779	-0.00497

$t_{0.975,n-1}$ = Student's t-statistic for 95% confidence interval, where n = the number of cases in mean DIFF.

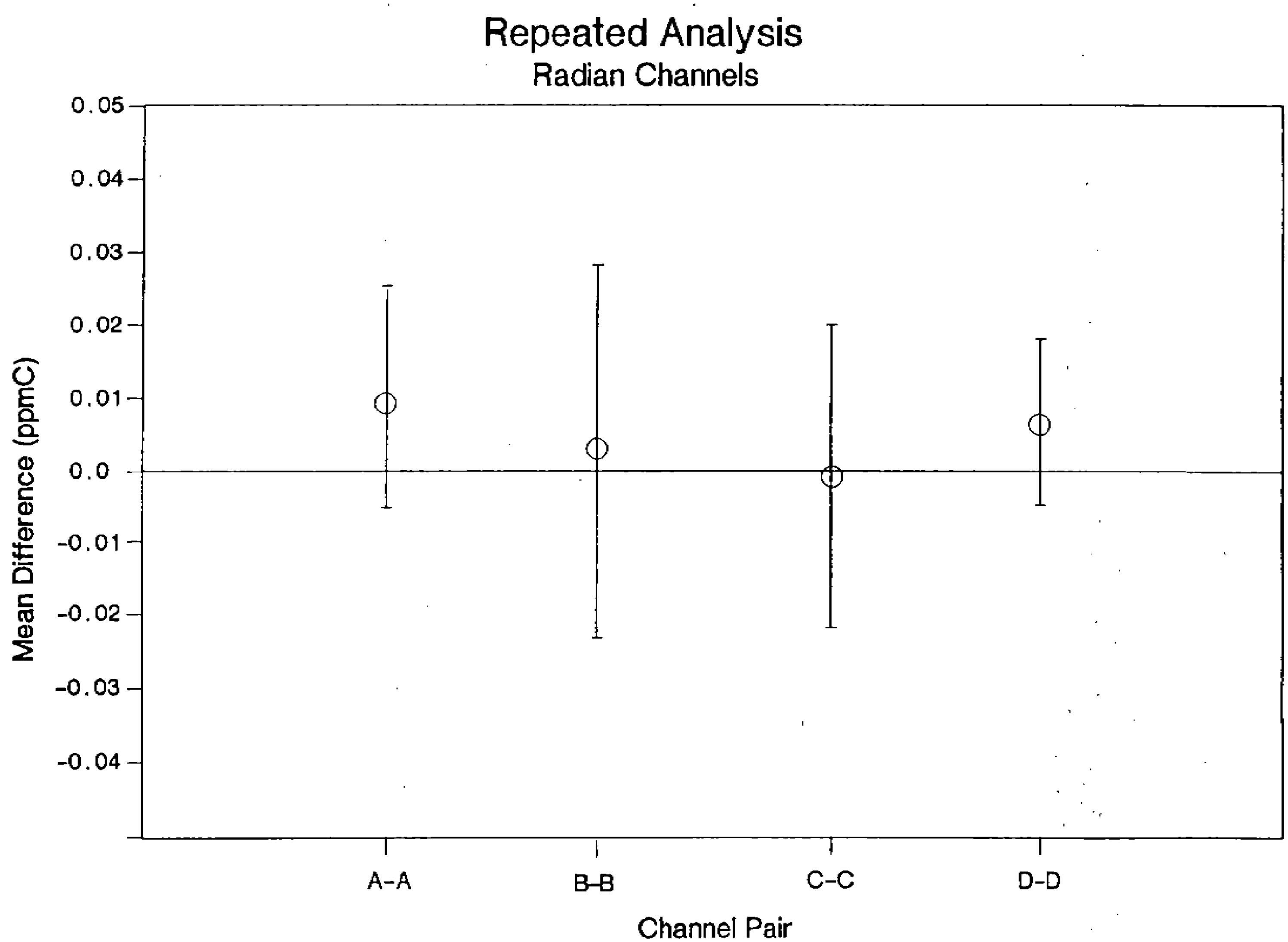


Figure 4-25. 95% Confidence intervals for mean NMOC difference.

4.4.2 <u>Quality Control Chart</u>

A quality control chart was developed for the 1989 replicate analyses and is shown in Figure 4-26. The control chart plots percent difference for the replicate analyses versus Julian date, 1989. The mean line, μ, which is nearly coincident with zero, and two sets of horizontal control lines are shown. Control lines at $\mu \pm 2\sigma$ and $\mu \pm 3\sigma$ are shown on the quality control chart. The percent difference for the control chart is defined as:

% difference = ((NMOC for 2nd analysis - NMOC for 1st analysis) / (Mean NMOC for both analyses)) * 100.

The 2-σ limits, i.e., $\mu \pm 2\sigma$, are termed the warning limits; the 3-σ limits, $\mu \pm 3\sigma$, are called the control limits. The control chart was consulted frequently to see if consecutive replicate determinations were outside the warning or control limits. In only one instance, about 1989 Julian date 270, did consecutive determinations occur outside the warning limits or control limits. More than two consecutive determinations outside the warning limits or the 3-σ limits give some cause for concern and may indicate that something is out of control in the sampling and/or analytical system. As seen in the control chart, in no case was the sampling and/or analytical system out of control. To investigate the nature of the imprecision, or percent difference, the data were examined to determine if percent difference was a function of the average NMOC concentration level. This analysis is given in Section 4.4.3.

4.4.3 <u>Precision Profile</u>

The replicate percent differences were plotted against average NMOC concentration for the replicate pair, and are shown in Figure 4-27. It is clear from the figure that as the NMOC concentration decreases, the imprecision increases. One of the major causes of imprecision at lower concentrations is instrument noise. Since instrument noise is essentially independent of NMOC concentration, the portion of response attributed to noise increases at lower NMOC concentrations. These facts combine to show an increased imprecision at lower NMOC concentrations.

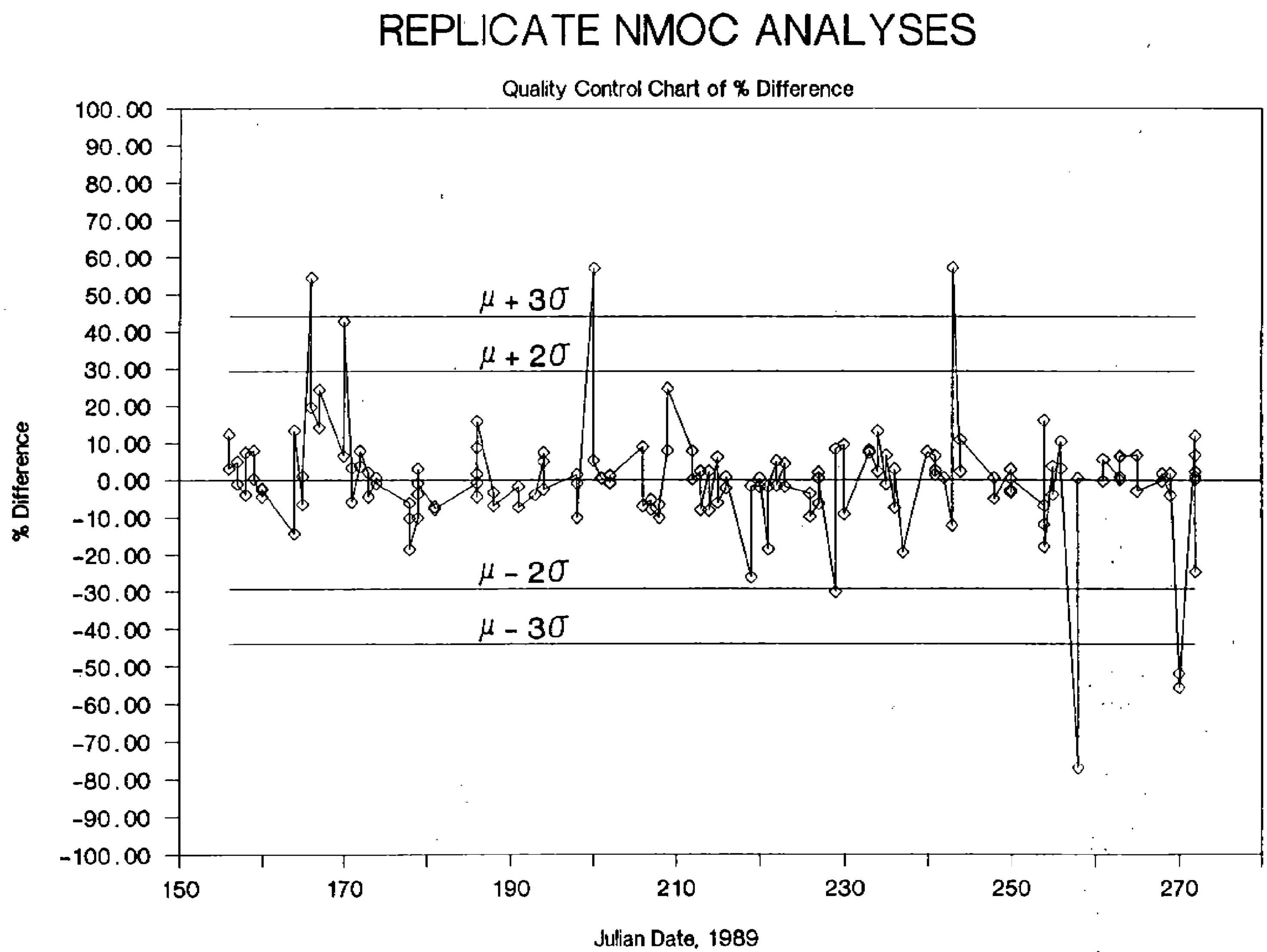


Figure 4-26. Quality control chart of percent difference for replicate NMOC analyses.

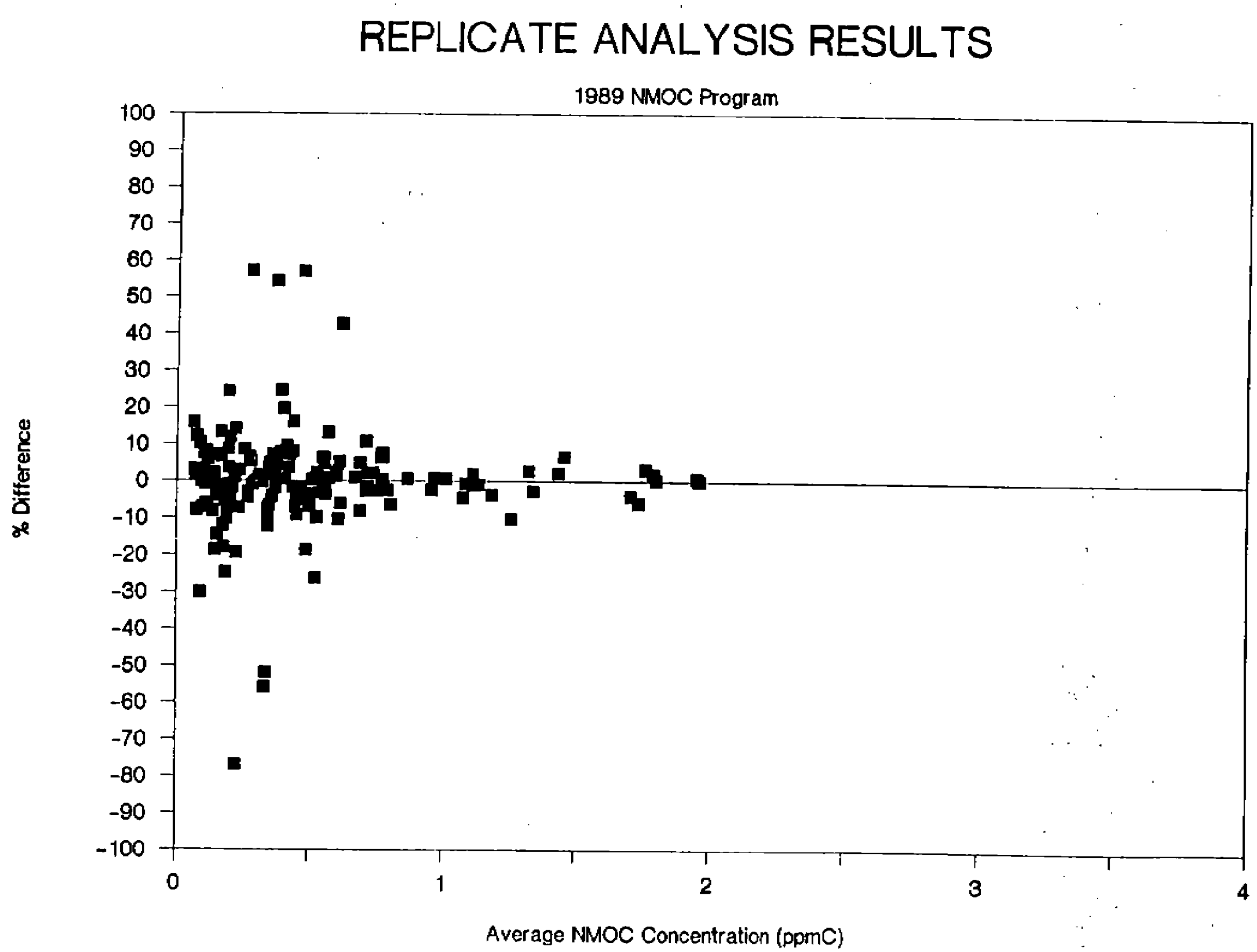


Figure 4-27. Replicate NMOC analysis results comparing average concentration with percent difference.

The NMOC concentration and percent difference for 156 replicate analyses were sorted by NMOC concentration and divided into the eleven NMOC size groups shown in Table 4-15. In the table, below 1.0 ppmC, the size increments are 0.100 ppmC, and show average NMOC concentration (assuming random variable, normally distributed), minimum percent difference, average percent difference, average absolute percent difference, and maximum percent difference for each NMOC size group. The data in the table are plotted in Figures 4-28 and 4-29.

Figure 4-28 shows large fluctuations of average percent difference at the lower NMOC concentrations. At higher NMOC concentrations, the average percent difference is below 2.0 percent. A more striking profile of the replicate precision is seen in Figure 4-29 in which average absolute percent difference is shown to decrease dramatically as the NMOC concentration increases. When the NMOC concentration increases above 0.75 ppmC, the average absolute percent difference levels off at about 3 to 4 percent. Overall average absolute percent difference for all 156 replicates is seen (Figure 4-29) to be about 8.24 percent, which is a very good precision.

This analysis shows that as the NMOC concentration decreases the imprecision of the measurement increases dramatically. Similar results are universally found in analytical instrumentation.

4.4.4 Local Ambient Samples

Table 4-16 presents the overall statistics for local ambient samples. These data include comparisons among Radian channels and EPA channels. The mean differences and the mean percent differences are both relatively small, which indicates that they are random variables. The overall mean absolute percent difference (APDIFF) is 11.05%, which is slightly higher than the precision for repeated analyses (8.24%).

Table 4-17 presents the same information comparing each Radian channel to the QAD results and to other Radian channels. Note from the definition of percent difference, PCDIFF, in this table that the Radian-QAD comparisons are different from a definition of bias, using QAD as the reference. The statistic used to normalize PCDIFF in Table 4-17 is the average of the Radian NMOC and the QAD NMOC, whereas for a bias term, the QAD NMOC is used to normalize the PCDIFF.

TABLE 4-15. 1989 NMOC REPLICATE IMPRECISION

Cases	NMOC Range	Average NMOC ppmC	Minimum % DIFF	Average %DIFF	Absolute %DIFF	Maximum %DIFF
9	0.000-0.099	0.050	-30.168	-0.265	9.788	15.873
31	0.100-0.199	0.150	-24.731	-2.005	7.953	24.289
18	0.200-0.299	0.250	-76.991	-0.564	12.651	57.092
21	0.300-0.399	0.350	-55.689	-1.888	12.446	54.251
17	0.400-0.499	0.450	-18.667	5.284	10.832	57.021
17	0.500-0.599	0.550	-26.170	-0.908	5.120	13.169
8	0.600-0.699	0.650	-10.353	3.951	10.117	42.718
11	0.700-0.799	0.750	-2.667	2.402	4.084	10.837
5	0.800-0.999	0.900	-6.460	-1.397	2.108	0.620
12	1.000-1.499	1.250	-10.267	-0.852	3.191	6.664
7	1.500-1.999	1.750	-5.938	-0.552	2.302	3.126
Overall			-76.991	-0.019	8.242	57.092

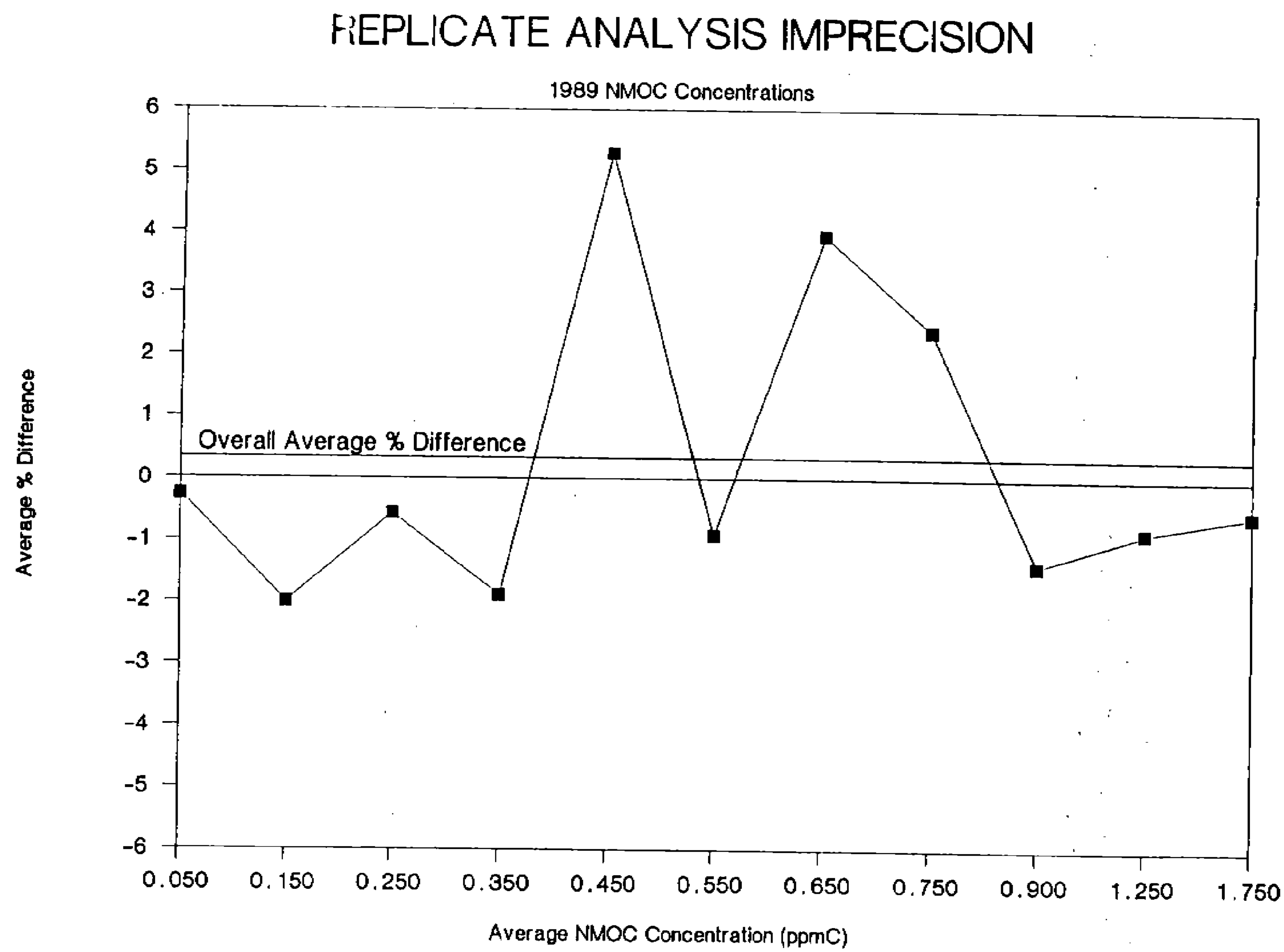


Figure 4-28. Replicate NMOC analysis results comparing average concentration with average percent difference.

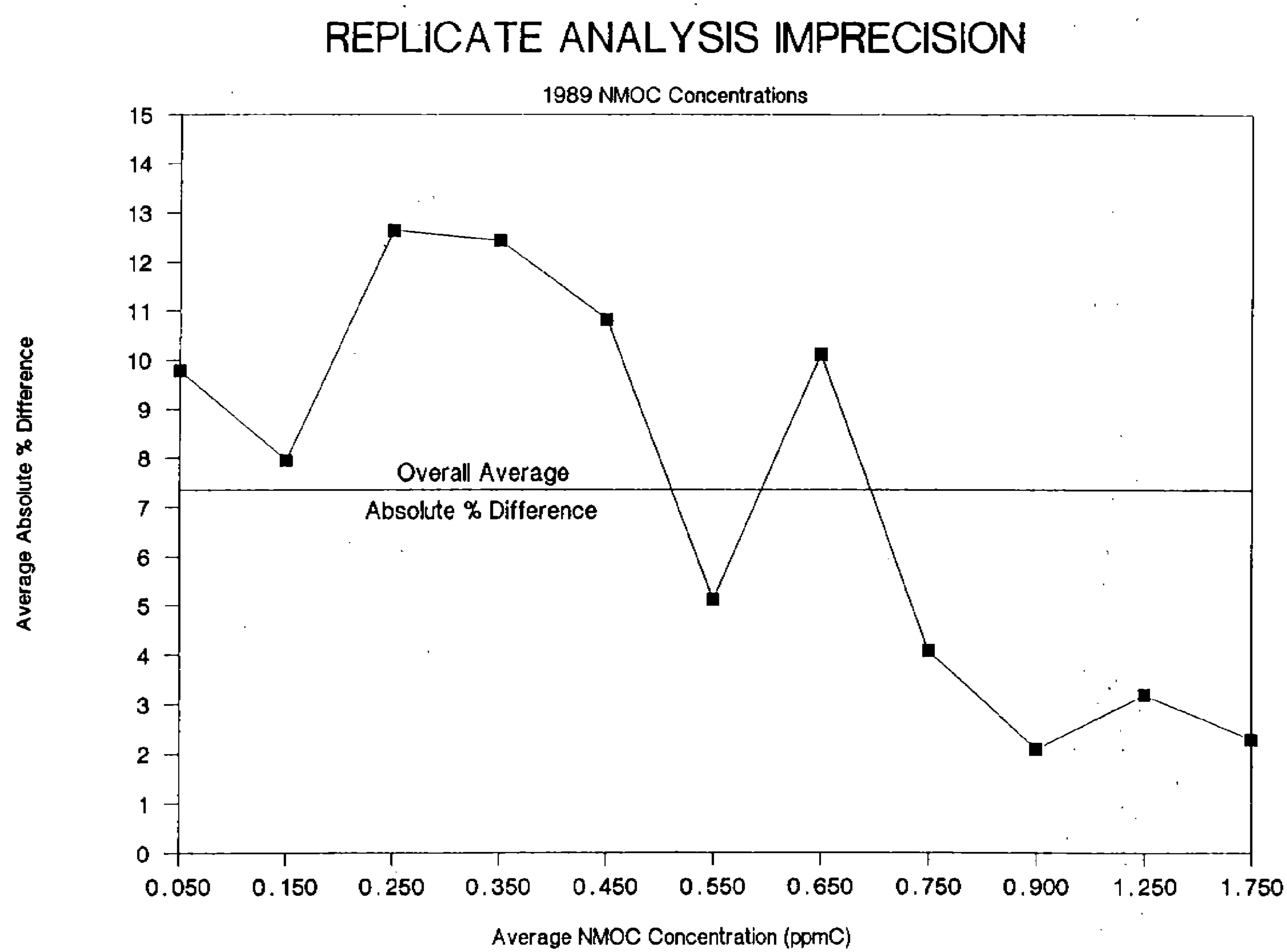


Figure 4-29. Replicate NMOC analysis results comparing average concentration with average absolute percent difference.

TABLE 4-16. OVERALL STATISTICS FOR LOCAL AMBIENT SAMPLES

Statistics	Variables DIFF	ADIFF	PDIFF	APDIFF
Cases	280	280	280	280
Minimum	-0.14600	0.00000	-63.47830	0.00000
Maximum	0.12850	0.14600	53.95350	63.47830
Mean	-0.00495	0.02390	-3.23343	11.05245
Standard Dev.	0.03593	0.02724	15.68687	11.57448
Standard Error	0.00217	0.00164	0.94595	0.69797
Skewness	0.36379	2.11966	0.10861	1.74367
Kurtosis	3.86291	4.82087	2.45216	2.96128

DIFF = NMOC concentration on Channel Y - NMOC concentration on Channel X, ppmC.
ADIFF = Absolute value of DIFF.
PDIFF = DIFF/((NMOC concentration on Channel Y + NMOC concentration on Channel X)/2) x 100.
APDIFF = Absolute value of PDIFF.

TABLE 4-17. STATISTICS FOR LOCAL AMBIENT SAMPLES, BY CHANNEL PAIR

Channel Pair (X-Y)	Statistics	Variables DIFF	ADIFF	PCDIFF	APCDIFF
A-QAD	Cases	28	28	28	28
	Minimum	-0.10100	0.00000	-48.98340	0.00000
	Maximum	0.00900	0.10100	33.96230	43.98340
	Mean	-0.02130	0.02288	-8.83435	11.67844
	Std. Dev.	0.02596	0.02454	15.14308	12.99276
	Std. Error	0.00491	0.00464	2.86177	2.45540
	Skewness	-1.36534	1.57932	-0.12444	1.18721
	Kurtosis	1.65481	2.19975	1.62467	0.14101
B-QAD	Cases	28	28	28	28
	Minimum	-0.14600	0.00100	-63.47830	0.54790
	Maximum	0.05400	0.14600	24.00000	63.47830
	Mean	-0.02886	0.03314	-13.89000	16.12552
	Std. Dev.	0.04050	0.03695	17.58961	15.48576
	Std. Error	0.00765	0.00698	3.32412	2.92653
	Skewness	-1.33754	1.86631	-0.82276	1.41816
	Kurtosis	2.32637	2.73998	1.26396	1.63055
C-QAD	Cases	28	28	28	28
	Minimum	-0.06200	0.00200	-43.35660	0.47960
	Maximum	0.10400	0.10400	48.27590	48.27590
	Mean	-0.01146	0.02482	-7.32042	13.14589
	Std. Dev.	0.03115	0.02162	16.52604	12.22573
	Std. Error	0.00589	0.00409	3.12313	2.31045
	Skewness	2.02745	1.88683	0.95764	1.41498
	Kurtosis	5.33011	4.60223	3.24719	1.47351
D-QAD	Cases	28	28	28	28
	Minimum	-0.06600	0.00200	-30.53440	2.11360
	Maximum	0.04390	0.06600	24.00000	30.53440
	Mean	-0.02561	0.02932	-11.53140	14.18255
	Std. Dev.	0.02186	0.01634	12.02604	8.59821
	Std. Error	0.00413	0.00309	2.27271	1.62491
	Skewness	0.89638	0.38031	0.73319	0.48702
	Kurtosis	2.15813	-0.25904	1.08097	-1.13109

(Continued)

TABLE 4-17. (Continued)

Channel Pair (X-Y)	Statistics	DIFF	ADIFF	PCDIFF	APCDIFF
		Variables			
B-A	Cases	28	28	28	28
	Minimum	-0.13500	0.00100	-46.48190	0.21460
	Maximum	0.06850	0.13500	18.35750	46.48190
	Mean	-0.00859	0.02184	-5.69156	9.11804
	Std. Dev.	0.03882	0.03299	13.97553	11.94535
	Std. Error	0.00734	0.00624	2.64113	2.25746
	Skewness	-1.54903	2.26453	-1.50969	2.05067
	Kurtosis	3.89048	4.42489	2.39299	3.41904
C-A	Cases	28	28	28	28
	Minimum	-0.04100	0.00100	-30.94340	0.20960
	Maximum	0.12850	0.12850	29.89470	30.94340
	Mean	0.01150	0.02217	2.25764	8.96954
	Std. Dev.	0.03638	0.03083	12.18073	8.37355
	Std. Error	0.00700	0.00593	2.34418	1.61149
	Skewness	1.78022	2.27091	-0.43356	1.19267
	Kurtosis	3.19496	4.52118	1.05317	0.86967
C-B	Cases	28	28	28	28
	Minimum	-0.03900	0.00100	-29.65780	0.47060
	Maximum	0.11800	0.11800	53.95350	53.95350
	Mean	0.02070	0.02826	8.17945	12.88185
	Std. Dev.	0.04107	0.03609	18.46039	15.42525
	Std. Error	0.00790	0.00694	3.55270	2.96859
	Skewness	1.28062	1.58497	0.86639	1.46501
	Kurtosis	0.77340	1.22859	0.88956	0.92616
C-D	Cases	28	28	28	28
	Minimum	-0.02500	0.00000	-20.08030	0.00000
	Maximum	0.06900	0.06900	25.00000	25.00000
	Mean	0.01549	0.01911	4.83526	7.74036
	Std. Dev.	0.02152	0.01823	8.54536	5.92323
	Std. Error	0.00414	0.00351	1.64456	1.13993
	Skewness	0.65930	1.19026	-0.72347	1.18709
	Kurtosis	0.32845	0.78246	2.20795	1.34482

(Continued)

TABLE 4-17. (Continued)

Channel Pair (X-Y)	Statistics	DIFF	ADIFF	PCDIFF	APCDIFF
		Variables			
D-A	Cases	28	28	28	28
	Minimum	-0.03600	0.00000	-19.54890	0.00000
	Maximum	0.05950	0.05950	20.09570	20.09570
	Mean	-0.00399	0.01661	-2.58031	7.33664
	Std. Dev.	0.02186	0.01443	8.87573	5.45857
	Std. Error	0.00421	0.00278	1.70813	1.05050
	Skewness	1.19512	1.12369	0.68968	0.81149
	Kurtosis	1.36664	1.02858	0.46638	0.03207
D-B	Cases	28	28	28	28
	Minimum	-0.03200	0.00000	-9.72220	0.00000
	Maximum	0.11000	0.11000	40.60910	40.60910
	Mean	0.00522	0.02907	3.39327	9.01275
	Std. Dev.	0.03534	0.02907	14.87646	12.20297
	Std. Error	0.00680	0.00559	2.86298	2.34846
	Skewness	1.87203	1.96331	1.69810	1.82801
	Kurtosis	2.46241	2.74915	1.46388	1.84601

DIFF = NMOC concentration on Channel Y - NMOC concentration on Channel X, ppmC.
ADIFF = Absolute value of DIFF.
PDIFF = DIFF/((NMOC concentration on Channel X + NMOC concentration on Channel Y)/2) x 100.
APDIFF = Absolute value of PDIFF.

Table 4-18 adds the 95% confidence intervals for the local ambient sample comparisons of the mean values of DIFF (from Table 4-17). Figure 4-30 displays the results of Table 4-18 graphically. Table 4-19 compares the percent differences for the several channel pairs for the site samples and the local ambient samples. For all comparisons, with the exception of C-B, A-QAD, and C-QAD, the percent differences appear to be slightly greater for the site samples than for the local ambient samples.

4.5 DUPLICATE SAMPLE RESULTS

Throughout the 1989 NMOC Monitoring Program, duplicate samples were collected once every two weeks at each site. Each duplicate was analyzed by Radian for its NMOC content.

Table 4-20 summarizes the duplicate sample statistics for NMOC, DIFF, ADIFF, PDIFF, and APDIFF. The mean absolute percent difference between the duplicate samples was 10.62 percent. The absolute percent difference ranged from zero to 80.5 percent. Table 4-21 summarizes the statistics for duplicate analyses by site code. The mean absolute percentage differences between duplicates ranged from 2.88% for LXKY to 29.15% for ELCA.

These results are higher than those found in 1988, but still represent good overall precision. The analytical error in 1988 for repeated analyses was 10.06%, while the precision for duplicates was 8.72 percent. Because the duplicate results include sampling and analysis precision, while the replicate (or repeated analysis) precision relates only to analytical error, the duplicate absolute percent difference is expected to be greater than the replicate absolute percent difference.

4.5.1 Sampling and Analysis Precision

For 75 duplicate ambient air samples, replicate analyses were performed. Each reported analysis was the average of two or three injections of sample into the PDFID instrument. For the determination described below, each injection (rather than the average of two or three injections) was used as a statistic for determining analytical error. The replicate analyses of the duplicate samples were performed on sucessive days. That is, the first analysis, consisting of two or three injections from a duplicate canister, was performed on the day the duplicate canisters were received from a particular

TABLE 4-18. LOCAL AMBIENT SAMPLES CONFIDENCE INTERVALS

Channel Pair (X-Y)	Mean Difference (ppmC)	Standard Deviation (ppmC)	Cases	$t_{0.975,n-1}$	95% Confidence Intervals Upper	Lower
A-QAD	-0.02130	0.02596	28	2.052	-0.01123	-0.03137
B-QAD	-0.02886	0.04050	28	2.052	-0.01315	-0.04457
C-QAD	-0.01146	0.03115	28	2.052	-0.00062	-0.02354
D-QAD	-0.02561	0.02186	28	2.052	-0.01713	-0.03409
B-A	-0.00859	0.03882	28	2.052	0.00643	-0.02361
C-A	0.01150	0.03638	28	2.052	0.02558	-0.00258
C-B	0.02070	0.04107	28	2.052	0.03660	0.00480
C-D	0.01549	0.02152	28	2.052	0.02382	0.00716
D-A	-0.00399	0.02186	28	2.052	0.00447	-0.01245
D-B	0.00522	0.03534	28	2.052	0.01890	-0.00846

$t_{0.975,n-1}$ = Student's t-statistic for 95% confidence interval, where n = the number of cases in mean DIFF.

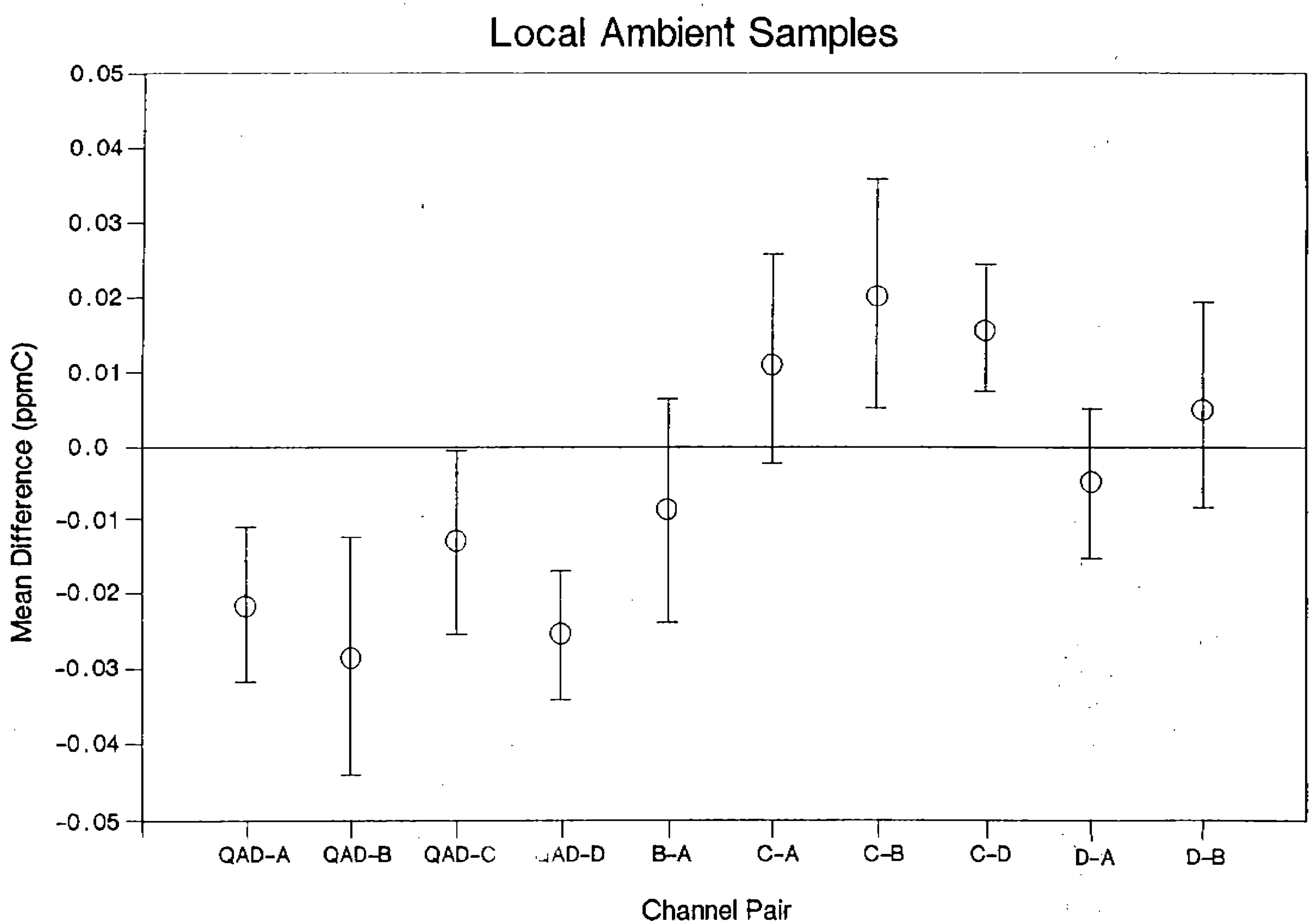


Figure 4-30. 95% Confidence intervals for mean NMOC difference.

TABLE 4-19. COMPARISON OF PERCENT DIFFERENCE IN NMOC CONCENTRATION BETWEEN CHANNEL PAIRS

Channel Pair (X-Y)	Site Samples Percent Difference Mean	Site Samples Percent Difference Standard Deviation	Site Samples Cases	Local Ambient Samples Percent Difference Mean	Local Ambient Samples Percent Difference Standard Deviation	Local Ambient Samples Cases
B-A	-13.25688	23.64949	13	-5.69156	13.97553	28
C-A	4.44166	19.90356	17	2.25764	12.18073	28
C-B	8.08086	14.29609	27	8.17945	18.46039	28
C-D	5.42850	14.18093	21	4.83526	8.54536	28
D-A	2.15075	14.25620	16	-2.58031	8.87573	28
D-B	3.08943	17.41362	23	3.39327	14.87646	28
A-QAD	-8.21561	12.37010	60	-8.83435	15.14308	28
B-QAD	-18.05073	23.91893	61	-13.89000	17.58961	28
C-QAD	-6.16318	14.86087	72	-7.32042	16.52604	28
D-QAD	-12.59858	12.12244	72	-11.53140	12.02604	28

% Difference = (NMOC (X) - NMOC (Y)) / ((NMOC (X) + NMOC (Y)) / 2) * 100

TABLE 4-20. STATISTICS FOR DUPLICATE ANALYSIS

Statistics	Variables NMOC	DIFF	ADIFF	PDIFF	APDIFF
Cases	181	181	181	181	181
Minimum	0.04850	-0.37600	0.00000	-80.51390	0.00000
Maximum	2.81950	0.41300	0.41300	71.54470	80.51390
Mean	0.54618	0.01505	0.04448	4.24458	10.62149
Standard Dev.	0.44515	0.07811	0.06588	17.22531	14.19102
Standard Error	0.03309	0.00581	0.00490	1.28035	1.05481
Skewness	1.83473	0.65604	3.11126	0.65214	2.52250
Kurtosis	4.22508	9.29811	11.36843	5.77036	6.97082

NMOC = Average NMOC concentration of duplicate samples, ppmC.
DIFF = Difference between NMOC concentrations for duplicate samples, ppmC.
ADIFF = Absolute value of DIFF.
PDIFF = DIFF/((NMOC concentration for duplicate 1 + NMOC concentration for duplicate 2)/2) x 100.
APDIFF = Absolute value of PDIFF.

TABLE 4-21. DUPLICATE ANALYSES STATISTICS, BY SITE

Site Code	NMOC, ppmC		ADIFF, ppmC		APDIFF, ppmC		Dup. Pairs
	Mean	SD	Mean	SD	Mean	SD	
ALCA	0.19033	0.23943	0.02111	0.02848	13.96249	13.86315	9
BACA	0.71422	0.37356	0.09733	0.13456	14.82464	17.20990	9
BMTX	0.85522	0.50058	0.05467	0.04629	7.60719	7.88346	9
C3IL	0.22596	0.14825	0.01219	0.00902	7.91159	6.94458	7
C6IL	0.98136	0.54669	0.04786	0.06376	7.00376	10.59426	7
DLTX	0.46469	0.22671	0.06688	0.11841	14.06729	23.79612	8
ELCA	0.59596	0.34278	0.09493	0.14461	17.07223	29.14641	8
ELTX	0.31621	0.16184	0.02471	0.02666	8.72313	8.91677	8
FECA	0.44213	0.19251	0.06800	0.05870	15.28104	14.24468	8
GRMI	0.54258	0.21330	0.03917	0.04976	6.96135	6.14543	6
H1TX	0.81843	0.55971	0.07257	0.09379	13.90359	23.59036	7
LBCA	0.94786	0.63284	0.06286	0.09184	11.85637	20.47535	7
LXKY	0.46431	0.54815	0.01263	0.01004	3.81114	2.88262	8
M1NY	0.47006	0.19207	0.02688	0.02406	6.42121	5.27519	8
MGAL	0.23471	0.10354	0.03886	0.02706	19.76096	17.55192	7
MNY	0.55985	0.22494	0.04890	0.04696	8.88094	7.47697	10
NWNJ	0.47671	0.21336	0.04514	0.02898	11.80123	10.54608	7
PLNJ	0.59845	0.41449	0.03970	0.04496	9.79536	12.82757	10
RLNC	0.17717	0.12827	0.01933	0.01869	13.20125	10.86335	6
RSCA	1.28519	0.74066	0.02913	0.03072	3.43878	5.51916	8
S2MO	0.49364	0.15982	0.03643	0.04311	9.69097	16.22818	7
S3CA	0.24430	0.16460	0.02140	0.02512	7.72415	6.08258	10
S4CA	0.42913	0.46157	0.03375	0.05370	11.83333	19.22213	8

ADIFF = The absolute value of the difference between duplicates, ppmC.
APDIFF = ADIFF/((NMOC duplicate 1 + NMOC duplicate 2)/2)*100

site. After the first replicate analysis, the canister was disconnected from the PDFID instrument and set aside in the laboratory and analyzed for the second replicate analysis on the next day, or within 72 hours if the first analysis occurred on Friday.

Duplicate samples were taken simultaneously in 6-L stainless steel canisters connected to a tee, the stem of which was connected to the NMOC sampler manifold. All of the duplicate samples for which there were replicated analyses are listed in Table 4-22.

The number of injections per analysis was governed by the standard deviation of the NMOC results of the first two injections during each analysis. If the standard deviation was 0.02 ppmC or greater, a third injection was performed, otherwise only two injections were performed for each analysis.

The analyses of variance (ANOVAs) discussed in Tables 4-23 and 4-24 were designed to differentiate between the analytical error of the PDFID NMOC measurement, the effect of the replicate analyses, and the duplicate sample effect. The model for the ANOVA is given below:

$$Y_{ijkl} = \mu + S_i + D_{j(i)} + R_{k(ij)} + e_{l(ijk)},$$

Where:

- Y_{ijkl} = NMOC concentration by PDFID analysis, ppmC;
- μ = overall average NMOC concentration, ppmC;
- S_i = ambient air sample effect, i=1,2...75 samples;
- $D_{j(i)}$ = duplicate sample number for each ambient air sample, i, j = duplicate number = 1 or 2;
- $R_{k(ij)}$ = replicate sample number, k, for each duplicate j and each ambient air sample i, r = replicate number = 1, 2; and
- $e_{l(ijk)}$ = residual error, or analytical error, where l is the number of injections.

Variable effects $D_{j(i)}$, $R_{k(ij)}$, and $e_{l(ijk)}$ are all nested effects, and in this experiemental design there are no interaction terms. The residual mean-square error term is equal to the analytical error variance. The replicate

TABLE 4-22. REPLICATE ANALYSIS OF DUPLICATE SAMPLES FOR 1989

Sample No.	Site Code	Julian Date Sampled	Sample I.D. Number	Mean NMOC ppmC	Mean NMOC ppmC	Overall Mean	% Diff	Absolute % Diff	Sample Overall Mean	Duplicate % Diff.	Duplicate Abs. % Diff.
1	ALCA	156	1016	0.069	0.078	0.0735	12.24490	12.24490			
	ALCA	156	1017	0.065	0.067	0.0660	3.03030	3.03030	0.06975	-10.75269	10.75269
2	C6IL	157	1041	0.542	0.569	0.5555	4.86049	4.86049			
	C6IL	157	1042	0.553	0.547	0.5500	-1.09091	1.09091	0.55275	-0.99502	0.99502
3	ELCA	158	1066	0.152	0.146	0.1490	-4.02685	4.02685			
	ELCA	158	1067	0.148	0.159	0.1535	7.16612	7.16612	0.15125	2.97521	2.97521
4	PLNJ	159	1076	0.377	0.408	0.3925	7.89809	7.89809			
	PLNJ	159	1077	0.370	0.371	0.3705	0.26991	0.26991	0.38150	-5.76671	5.76671
5	MGAL	160	1113	0.207	0.198	0.2025	-4.44444	4.44444			
	MGAL	160	1114	0.184	0.180	0.1820	-2.19780	2.19780	0.19225	-10.66320	10.66320
6	DLTX	160	1131	0.802	0.782	0.7920	-2.52525	2.52525			
	DLTX	160	1132	0.760	0.740	0.7500	-2.66667	2.66667	0.77100	-5.44747	5.44747
7	S3CA	164	1159	0.164	0.142	0.1530	-14.37908	14.37908			
	S3CA	164	1160	0.155	0.177	0.1660	13.25301	13.25301	0.15950	8.15047	8.15047
8	S4CA	165	1191	0.205	0.192	0.1985	-6.54912	6.54912			
	S4CA	165	1192	0.217	0.219	0.2180	0.91743	0.91743	0.20825	9.36375	9.36375
9	C6IL	166	1207	0.270	0.471	0.3705	54.25101	54.25101			
	C6IL	166	1208	0.362	0.441	0.4015	19.67621	19.67621	0.38600	8.03109	8.03109
10	BACA	167	1242	0.204	0.235	0.2195	14.12301	14.12301			
	BACA	167	1243	0.170	0.217	0.1935	24.28941	24.28941	0.20650	-12.59080	12.59080
11	ELCA	170	1258	0.738	0.787	0.7625	6.42623	6.42623			
	ELCA	170	1259	0.486	0.750	0.6180	42.71845	42.71845	0.69025	-20.93444	20.93444
12	LBCA	171	1275	1.732	1.787	1.7595	3.12589	3.12589			
	LBCA	171	1276	1.786	1.683	1.7345	-5.93831	5.93831	1.74700	-1.43102	1.43102
13	ELTX	172	1303	0.416	0.431	0.4235	3.54191	3.54191			
	ELTX	172	1304	0.389	0.420	0.4045	7.66378	7.66378	0.41400	-4.58937	4.58937
14	RSCA	173	1335	1.102	1.123	1.1125	1.88764	1.88764			
	RSCA	173	1336	1.102	1.053	1.0775	-4.54756	4.54756	1.09500	-3.19635	3.19635
15	MNY	174	1357	1.010	1.016	1.0130	0.59230	0.59230			
	MNY	174	1358	1.140	1.129	1.1345	-0.96959	0.96959	1.07375	11.31548	11.31548
16	NWNJ	178	1376	0.636	0.598	0.6170	-6.15883	6.15883			
	NWNJ	178	1377	0.640	0.577	0.6085	-10.35333	10.35333	0.61275	-1.38719	1.38719
17	ELCA	179	1423	1.321	1.192	1.2565	-10.26661	10.26661			
	ELCA	179	1424	1.205	1.160	1.1825	-3.80550	3.80550	1.21950	-6.06806	6.06806
18	PLNJ	179	1450	0.235	0.242	0.2385	2.93501	2.93501			
	PLNJ	179	1451	0.287	0.284	0.2855	-1.05079	1.05079	0.26200	17.93893	17.93893
19	ALCA	181	1478	0.101	0.094	0.0975	-7.17949	7.17949			
	ALCA	181	1479	0.079	0.073	0.0760	-7.89474	7.89474	0.08675	-24.78386	24.78386
20	RLNC	186	1506	0.110	0.109	0.1095	-0.91324	0.91324			
	RLNC	186	1547	0.116	0.118	0.1170	1.70940	1.70940	0.11325	6.62252	6.62252
21	S4CA	186	1531	0.244	0.266	0.2550	8.62745	8.62745			
	S4CA	186	1532	0.273	0.261	0.2670	-4.49438	4.49438	0.26100	4.59770	4.59770

TABLE 4-22. (CONTINUED)

Sample No.	Site Code	Julian Date Sampled	Sample I.D. Number	Mean NMOC ppmC	Mean NMOC ppmC	Overall Mean	% Diff	Absolute % Diff	Sample Overall Mean	Duplicate % Diff.	Duplicate Abs. % Diff.
22	C3IL	186	1554	0.070	0.071	0.0705	1.41844	1.41844			
	C3IL	186	1555	0.058	0.068	0.0630	15.87302	15.87302	0.06675	-11.23596	11.23596
23	LXKY	188	1585	0.502	0.485	0.4935	-3.44478	3.44478			
	LXKY	188	1586	0.518	0.483	0.5005	-6.99301	6.99301	0.49700	1.40845	1.40845
24	GRMI	191	1603	0.213	0.209	0.2110	-1.89573	1.89573			
	GRMI	191	1604	0.243	0.226	0.2345	-7.24947	7.24947	0.22275	10.54994	10.54994
25	ELTX	194	1702	0.340	0.357	0.3485	4.87805	4.87805			
	ELTX	194	1703	0.348	0.374	0.3610	7.20222	7.20222	0.35475	3.52361	3.52361
26	ELCA	198	1750	0.219	0.222	0.2205	1.36504	7.20222			
	ELCA	198	1751	0.197	0.195	0.1960	-1.02041	1.02041	0.20825	-11.76471	11.76471
27	LBCA	200	1800	0.336	0.604	0.4700	57.02128	57.02128			
	LBCA	200	1801	0.597	0.629	0.6130	5.22023	5.22023	0.54150	26.40813	26.40813
28	ALCA	201	1817	0.771	0.773	0.7720	0.25907	0.25907			
	ALCA	201	1818	0.862	0.867	0.8645	0.57837	0.57837	0.81825	11.30461	11.30461
29	BACA	202	1851	1.090	1.081	1.0855	-0.82911	0.82911			
	BACA	202	1852	1.121	1.109	1.1150	-1.07623	1.07623	1.10025	2.68121	2.68121
30	DLTX	202	1887	0.316	0.320	0.3180	1.25786	1.25786			
	DLTX	202	1888	0.668	0.674	0.6710	0.89419	0.89419	0.49450	71.38524	71.38524
31	S3CA	206	1909	0.186	0.203	0.1945	8.74036	8.74036			
	S3CA	206	1910	0.206	0.192	0.1990	-7.03518	7.03518	0.19675	2.28717	2.28717
32	S4CA	207	1929	0.190	0.180	0.1850	-5.40541	5.40541			
	S4CA	207	1930	0.195	0.180	0.1875	-8.00000	8.00000	0.18625	1.34228	1.34228
33	LXKY	208	1956	0.362	0.327	0.3445	-10.15965	10.15965			
	LXKY	208	1957	0.361	0.338	0.3495	-6.58083	6.58083	0.34700	1.44092	1.44092
34	FECA	209	1985	0.396	0.428	0.4120	7.76699	7.76699			
	FECA	209	1986	0.343	0.439	0.3910	24.55243	24.55243	0.40150	-5.23039	5.23039
35	S4CA	212	1989	0.101	0.109	0.1050	7.61905	7.61905			
	S4CA	212	1990	0.092	0.092	0.0920	0.00000	0.00000	0.09850	-13.19797	13.19797
36	C3IL	213	2018	0.138	0.141	0.1395	2.15054	2.15054			
	C3IL	213	2019	0.142	0.131	0.1365	-8.05861	8.05861	0.13800	-2.17391	2.17391
37	MNY	214	2062	0.710	0.725	0.7175	2.09059	2.09059			
	MNY	214	2063	0.715	0.659	0.6870	-8.15138	8.15138	0.70225	-4.34318	4.34318
38	DLTX	215	2115	0.114	0.121	0.1175	5.95745	5.95745			
	DLTX	215	2116	0.116	0.109	0.1125	-6.22222	6.22222	0.11500	-4.34783	4.34783
39	BMTX	216	2089	0.966	0.944	0.9550	-2.30366	2.30366			
	BMTX	216	2090	0.965	0.971	0.9680	0.61983	0.61983	0.96150	1.35205	1.35205
40	FECA	219	2128	0.592	0.455	0.5235	-26.17001	26.17001			
	FECA	219	2129	0.441	0.433	0.4370	-1.83066	1.83066	0.48025	-18.01145	18.01145
41	S2MO	220	2149	0.470	0.461	0.4655	-1.93340	1.93340			
	S2MO	220	2150	0.508	0.510	0.5090	0.39293	0.39293	0.48725	8.92766	8.92766
42	ALCA	221	2177	0.158	0.131	0.1445	-18.68512	18.68512			
	ALCA	221	2178	0.155	0.152	0.1535	-1.95440	1.95440	0.14900	6.04027	6.04027

TABLE 4-22. (CONTINUED)

Sample No.	Site Code	Julian Date Sampled	Sample I.D. Number	Mean NMOC ppmC	Mean NMOC ppmC	Overall Mean	% Diff	Absolute % Diff	Sample Overall Mean	Duplicate % Diff.	Duplicate Abs. % Diff.
43	BACA	222	2194	0.670	0.704	0.6870	4.94905	4.94905			
	BACA	222	2195	0.723	0.712	0.7175	-1.53310	1.53310	0.70225	4.34318	4.34318
44	ELCA	223	2225	0.370	0.386	0.3780	4.23280	4.23280			
	ELCA	223	2226	0.376	0.369	0.3725	-1.87919	1.87919	0.37525	-1.46569	1.46569
45	S4CA	226	2261	0.571	0.550	0.5605	-3.74665	3.74665			
	S4CA	226	2262	0.552	0.500	0.5260	-9.88593	9.88593	0.54325	-6.35067	6.35067
46	BMTX	227	2280	0.831	0.779	0.8050	-6.45963	6.45963			
	BMTX	227	2281	0.863	0.868	0.8655	0.57770	0.57770	0.83525	7.24334	7.24334
47	LXKY	227	2312	1.771	1.806	1.7885	1.95695	1.95695			
	LXKY	227	2313	1.796	1.800	1.7980	0.22247	0.22247	1.79325	0.52976	0.52976
48	S3CA	229	2346	0.103	0.076	0.0895	-30.16760	30.16760			
	S3CA	229	2347	0.105	0.114	0.1095	8.21918	8.21918	0.09950	20.10050	20.10050
49	LBCA	230	2360	0.394	0.433	0.4135	9.43168	9.43168			
	LBCA	230	2361	0.475	0.433	0.4540	-9.25110	9.25110	0.43375	9.33718	9.33718
50	S2MO	233	2372	0.412	0.443	0.4275	7.25146	7.25146			
	S2MO	233	2373	0.419	0.454	0.4365	8.01833	8.01833	0.43200	2.08333	2.08333
51	GRMI	234	2397	0.520	0.531	0.5255	2.09324	2.09324			
	GRMI	234	2398	0.532	0.607	0.5695	13.16945	13.16945	0.54750	8.03653	8.03653
52	S3CA	235	2438	0.163	0.161	0.1620	-1.23457	1.23457			
	S3CA	235	2439	0.163	0.174	0.1685	6.52819	6.52819	0.16525	3.93343	3.93343
53	ELTX	236	2444	0.357	0.331	0.3440	-7.55814	7.55814			
	ELTX	236	2445	0.358	0.368	0.3630	2.75482	2.75482	0.35350	5.37482	5.37482
54	LBCA	240	2482	0.741	0.799	0.7700	7.53247	7.53247			
	LBCA	241	2483	0.747	0.796	0.7715	6.35126	6.35126	0.77075	0.19462	0.19462
55	ELCA	241	2515	0.595	0.603	0.5990	1.33556	1.33556			
	ELCA	241	2516	0.595	0.610	0.6025	2.48963	2.48963	0.60075	0.58261	0.58261
56	S4CA	243	2577	0.364	0.322	0.3430	-12.24490	12.24490			
	S4CA	243	2578	0.199	0.358	0.2785	57.09156	57.09156	0.31075	-20.75623	20.75623
57	FECA	244	2617	0.727	0.743	0.7350	2.17687	2.17687			
	FECA	244	2618	0.672	0.749	0.7105	10.83744	10.83744	0.72275	-3.38983	3.38983
58	ELTX	248	2642	0.403	0.405	0.4040	0.49505	0.49505			
	ELTX	248	2643	0.464	0.441	0.4525	-5.08287	5.08287	0.42825	11.32516	11.32516
59	H1TX	250	2646	1.303	1.340	1.3215	2.79985	2.79985			
	H1TX	250	2647	1.357	1.320	1.3385	-2.76429	2.76429	1.33000	1.27820	1.27820
60	S2MO	250	2682	0.546	0.528	0.5370	-3.35196	3.35196			
	S2MO	250	2683	0.524	0.525	0.5245	0.19066	0.19066	0.53075	-2.35516	2.35516
61	GRMI	254	2707	0.462	0.431	0.4465	-6.94289	6.94289			
	GRMI	254	2708	0.405	0.476	0.4405	16.11805	16.11805	0.44350	-1.35287	1.35287
62	MGAL	254	2736	0.185	0.164	0.1745	-12.03438	12.03438			
	MGAL	254	2737	0.195	0.163	0.1790	-17.87709	17.87709	0.17675	2.54597	2.54597
63	LXKY	255	2783	0.194	0.201	0.1975	3.54430	3.54430			
	LXKY	255	2784	0.184	0.177	0.1805	-3.87812	3.87812	0.18900	-8.99471	8.99471

TABLE 4-22. (CONTINUED)

Sample No.	Site Code	Julian Date Sampled	Sample I.D. Number	Mean NMOC ppmC	Mean NMOC ppmC	Overall Mean	% Diff	Absolute % Diff	Sample Overall Mean	Duplicate % Diff.	Duplicate Abs. % Diff.
64	RLNC	256	2758	0.083	0.092	0.0875	10.28571	10.28571			
	RLNC	256	2759	0.098	0.101	0.0995	3.01508	3.01508	0.09350	12.83422	12.83422
65	S4CA	258	2838	0.313	0.139	0.2260	-76.99115	76.99115			
	S4CA	258	2839	0.306	0.307	0.3065	0.32626	0.32626	0.26625	30.23474	30.23474
66	MNY	261	2863	0.322	0.321	0.3215	-0.31104	0.31104			
	MNY	261	2864	0.273	0.288	0.2805	5.34759	5.34759	0.30100	-13.62126	13.62126
67	LBCA	263	2879	1.945	1.961	1.9530	0.81925	0.81925			
	LBCA	263	2880	1.961	1.961	1.9610	0.00000	0.00000	1.95700	0.40879	0.40879
68	ELCA	263	2938	0.538	0.572	0.5550	6.12613	6.12613			
	ELCA	263	2939	0.531	0.566	0.5485	6.38104	6.38104	0.55175	-1.17807	1.17807
69	MGAL	265	2953	0.268	0.286	0.2770	6.49819	6.49819			
	MGAL	265	2954	0.271	0.263	0.2670	-2.99625	2.99625	0.27200	-3.67647	3.67647
70	LXKY	268	2977	0.298	0.297	0.2975	-0.33613	0.33613			
	LXKY	268	2978	0.308	0.313	0.3105	1.61031	1.61031	0.30400	4.27632	4.27632
71	S2MO	269	3003	0.367	0.352	0.3595	-4.17246	4.17246			
	S2MO	269	3004	0.367	0.373	0.3700	1.62162	1.62162	0.36475	2.87868	2.87868
72	ELCA	270	3024	0.427	0.251	0.3390	-51.91740	51.91740			
	ELCA	270	3025	0.427	0.241	0.3340	-55.68862	55.68862	0.33650	-1.48588	1.48588
73	C3IL	272	3048	0.190	0.214	0.2020	11.88119	11.88119			
	C3IL	272	3049	0.209	0.163	0.1860	-24.73118	24.73118	0.19400	-8.24742	8.24742
74	RSCA	272	3089	1.420	1.450	1.4350	2.09059	2.09059			
	RSCA	272	3090	1.407	1.504	1.4555	6.66438	6.66438	1.44525	1.41844	1.41844
75	PLNJ	272	3110	0.542	0.546	0.5440	0.73529	0.73529			
	PLNJ	272	3111	0.557	0.557	0.5570	0.00000	0.00000	0.55050	2.36149	2.36149
			Overall Average			0.5019	0.34232	8.24108	0.50189	1.29576	8.01005

TABLE 4-23. ANOVA FOR DUPLICATE - REPLICATE SETS.

Source	Sum-of-Squares	DF	Mean-Square	F-Ratio	P
Replicate Set No. 1					
S_i	0.678345E+02	49	1.384377820	0.505878E+03	0.000000000
$D_{j(i)}$	0.012204354	1	0.012204354	4.459702798	0.035362692
$R_{k(i)}$	0.002064966	1	0.002064966	0.754577701	0.385584881
$e_{l(ijk)}$	1.028955822	376	0.002736585		
Replicate Set No. 2					
S_i	0.710466E+02	50	1.420932589	0.655102E+03	0.000000000
$D_{j(i)}$	0.026215439	1	0.026215439	0.120863E+02	0.000566336
$R_{k(i)}$	0.002803749	1	0.002803749	1.292630981	0.256276338
$e_{l(ijk)}$	0.828567488	382	0.02169025		

TABLE 4-24. EXPECTED MEAN SQUARES FOR NESTED EXPERIMENT

Model	EMS
S_i	$\sigma_e^2 + 2.147\ \sigma_R^2 + 4.293\ \sigma_D^2 + 107.35\ \sigma_S^2$
$D_{j(i)}$	$\sigma_e^2 + 2.147\ \sigma_R^2 + 4.293\ \sigma_D^2$
$R_{k(ij)}$	$\sigma_e^2 + 2.147\ \sigma_R^2$
$e_{l(ijk)}$	σ_e^2

mean-square is the between-replicate term and contains both analyical error and the error associated with removing the sample from the canister. The duplicate mean-square contains both analytical error, the error in removing the sample from the canister, and the error between duplicate samples. The ambient sample mean-square term contains all the previous errors and the effect of different sites and sampling days from sample to sample.

The data set was divided into two overlapping sets of 50 (50 in Replicate Set No. 1 and 51 in Replicate Set No. 2) each. This was done because running the entire data set resulted in a matrix that was not solvable in SYSTAT®. The ANOVA tables for the two sets are given in Tables 4-23 and 4-24. Probabilities less than 0.05 are taken to be significant. Therefore, in both data sets, $D_{j(i)}$ and S_i are significant. The latter, or the ambient sample term, was expected to be significant. The duplicate term was significant, which implies that the sample within the canister on the average has a significantly different concentration upon analysis.

On the other hand, the replicate effect, $R_{k(ij)}$, was not significant in either data set. Table 4-24 reflects the fact that there were, on the average, two replicates, two duplicates, and 75 ambient air samples. There were a total of 644 injections, or 2.147 injections per ambient air sampler per duplicate per replicate. From the ANOVA tables it was concluded that the replicate mean-square was not significantly different from zero.

The variance of the analytical precision is σ_e^2, which may be pooled between replicate sets in Table 4-23 to give 0.002450558. The duplicate variance is calculated from a pooled value of mean-square for duplicates equal to 0.019209897.

$$0.019209897 = \sigma_e^2 + 4.293\ \sigma_D^2$$

$$\sigma_D^2 = (0.019209897 - 0.002450558) / 4.293$$

$$\sigma_D^2 = 0.003903876$$

Therefore, a standard deviation for analysis is equal to:

$$s_e = \sqrt{\sigma^2} = \sqrt{0.002450558} = 0.0495.$$

The standard deviation for duplicates is equal to:

$$s_D = \sqrt{\sigma_D^2} = \sqrt{0.003903876} = 0.0625,$$

or about 25% higher.

The fact that the duplicate effect is significant means that, on the average, there is a difference in the concentration between duplicates that is greater than can be attributed to analytical error. This means that on the average there is a significant difference between the concentration of the samples in the duplicate canisters when they are analyzed.

A possible explanation for this phenomenon is that carryover of adsorbed organic material is different between duplicate canisters. In order to test this hypothesis further, it is recommended that: (1) during the 1990 NMOC Monitoring Program a record be kept of the NMOC concentration in a duplicate canister before cleanup, and the zero-air NMOC concentration at the time of the third pressurization with clean humidified air during cleanup; and (2) the duplicate sample schedule be so arranged that the same amount of time elapses between sampling and analysis for all duplicate samples. The latter specification may require that duplicate samples, for which replicate analyses are performed, will be taken only on Mondays and Tuesdays so that the time between the first and second replicate analyses is 24 hours.

4.5.2 Quality Control Chart

The duplicate quality control chart showing the 2-σ warning limits and the 3-σ control limits is shown in Figure 4-31. The chart was updated daily in order to monitor whether the NMOC program sampling and analytical systems were in control. From 1989 Julian date 240 through about 265 the control chart shows a number of excursions outside either the warning limits ($\mu \pm 2\sigma$) or the control limits ($\mu \pm 3\sigma$). There was, however, no indication (more than two successive points outside either the warning limits or the control limits) of loss of control. It is necessary to keep in mind that although the analytical systems were centrally located, the sampling systems, which contributed significantly to the overall system variability, were located at 45 sites across the country.

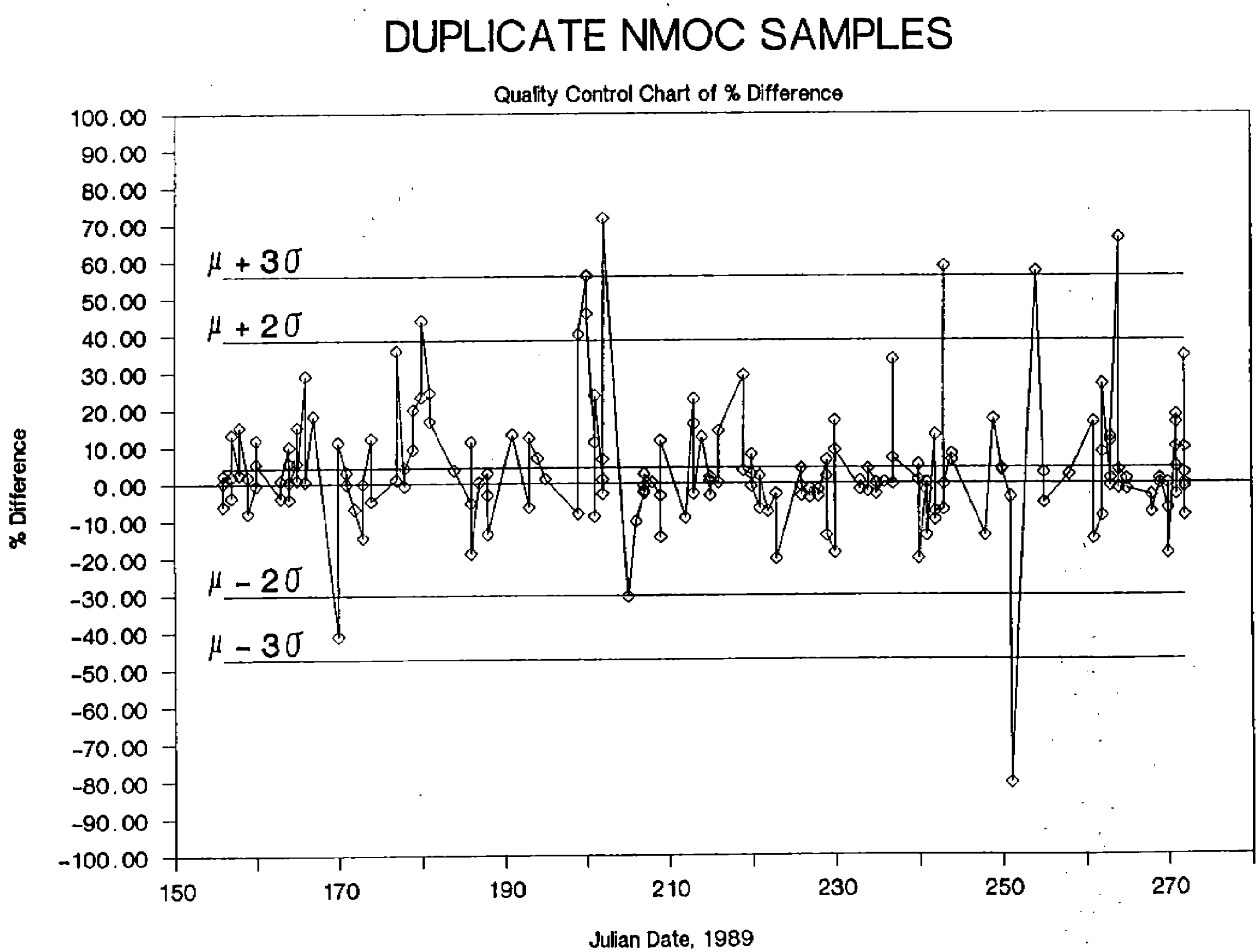


Figure 4-31. Quality control chart of percent difference for duplicate NMOC analyses.

4.5.3 Precision Profile

As in the case of replicate analyses, the data show that at lower NMOC concentrations, percent difference between duplicate analyses increases. Figure 4-32 shows percent difference plotted against average NMOC concentration. Table 4-25 summarizes the duplicate imprecision into eleven data sets summarized by average NMOC concentrations ranging from 0.050 to 2.25. Average percent difference and average absolute percent difference from Table 4-25 are plotted in Figures 4-33 and 4-34, respectively. The trend of increasing imprecision at NMOC concentration levels below 1.0 ppmC is clear.

4.6 CANISTER PRESSURE RESULTS

Canister pressure results for the NMOC Monitoring Program are important to be sure that the ambient air samples obtained are representative. The NMOC sampling systems are designed to obtain an integrated ambient air sample between 6:00 a.m. and 9:00 a.m., or at other programmed intervals. The flow rate of the sample into the 6-L canister is controlled by a critical orifice, which requires a pressure drop across the orifice sufficiently high to maintain sonic velocity in the orifice. If sonic velocity can be maintained in the orifice for the entire sampling period, then the flow rate into the canister is constant and the sample is properly integrated. The temperature must also be assumed to remain constant over the sampling period.

As the final canister pressure increases, there is a pressure downstream of the sonic orifice at which the sonic velocity can no longer be maintained. Canister pressures are being measured to obtain a better understanding of the range and magnitude of pressures being generated by the NMOC sampling systems. Canister pressure data are given in Tables 4-26 and 4-27 for both single canister samples and duplicate samples. The pressures reported in Tables 4-26 and 4-27 are the canister sampling pressures measured immediately before analysis in the laboratory. A significant decrease between the field sampling pressure and the laboratory value might indicate a leak. The canister was leak tested when this occurred.

Table 4-26 gives statistics for single and duplicate samples. All sample canisters averaged 14.9 psig, while duplicate samples averaged

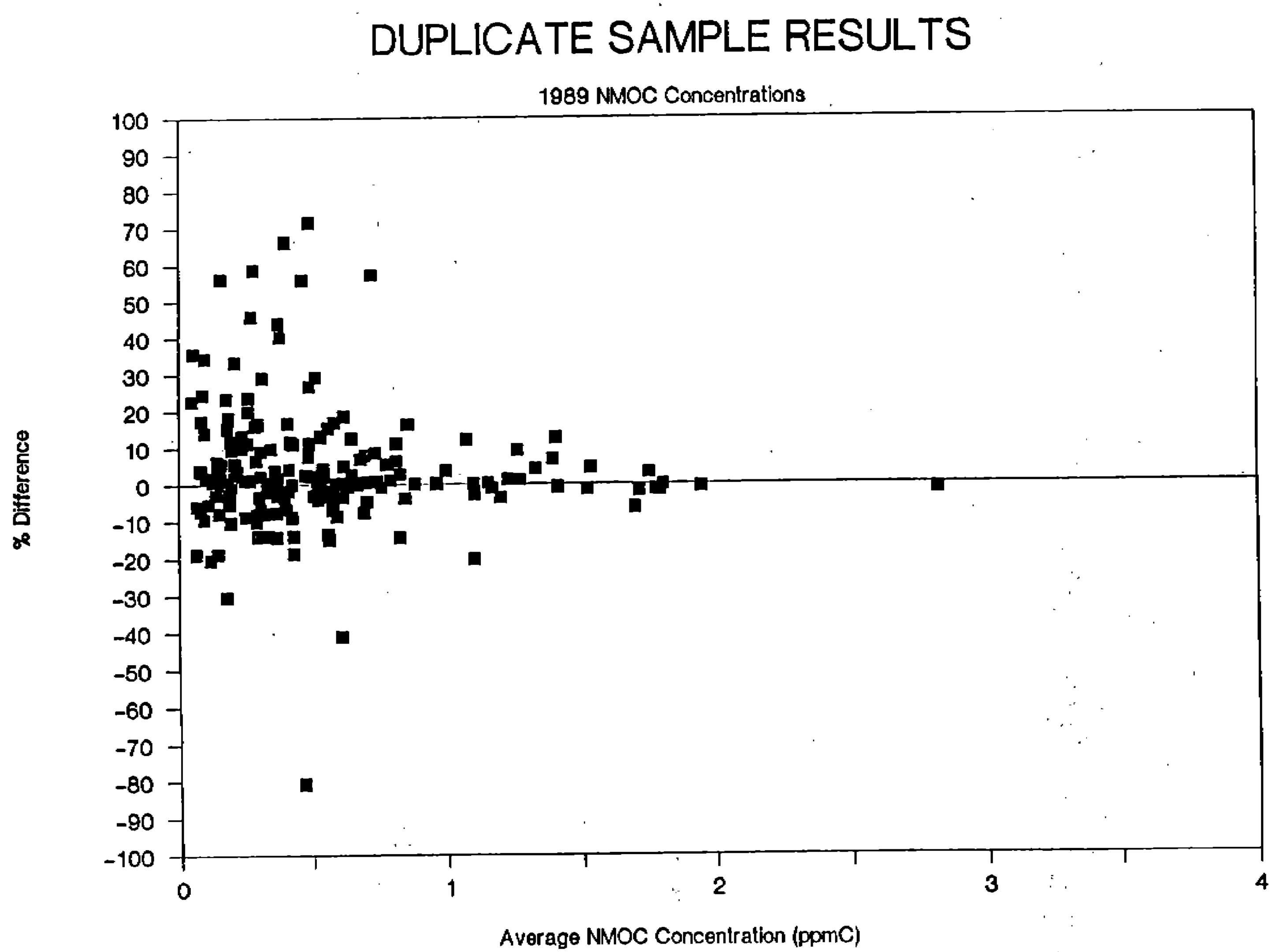


Figure 4-32. Duplicate NMOC sample results comparing average concentrations with percent difference.

TABLE 4-25. 1989 NMOC DUPLICATE IMPRECISION

Cases	NMOC Range	NMOC ppmC	Minimum % Diff.	Average % Diff.	Absolute % Diff.	Maximum %Diff.
12	0.000-0.099	0.050	-18.750	9.553	16.432	35.714
25	0.100-0.199	0.150	-30.471	1.521	10.167	56.151
22	0.200-0.299	0.250	-9.881	12.611	15.042	58.615
25	0.300-0.399	0.350	-14.344	2.512	8.765	43.968
19	0.400-0.499	0.450	-80.514	8.281	22.018	71.545
24	0.500-0.599	0.550	-14.925	0.714	6.662	29.235
12	0.600-0.699	0.650	-41.176	-0.579	8.274	18.474
9	0.700-0.799	0.750	-4.664	8.430	9.641	57.163
8	0.800-0.999	0.900	-14.475	2.281	6.844	16.336
15	1.000-0.499	1.250	-20.271	1.445	5.281	12.442
10	1.500-3.000	2.250	-6.459	-0.796	2.282	4.361
Overall			-80.514	4.179	10.128	71.545

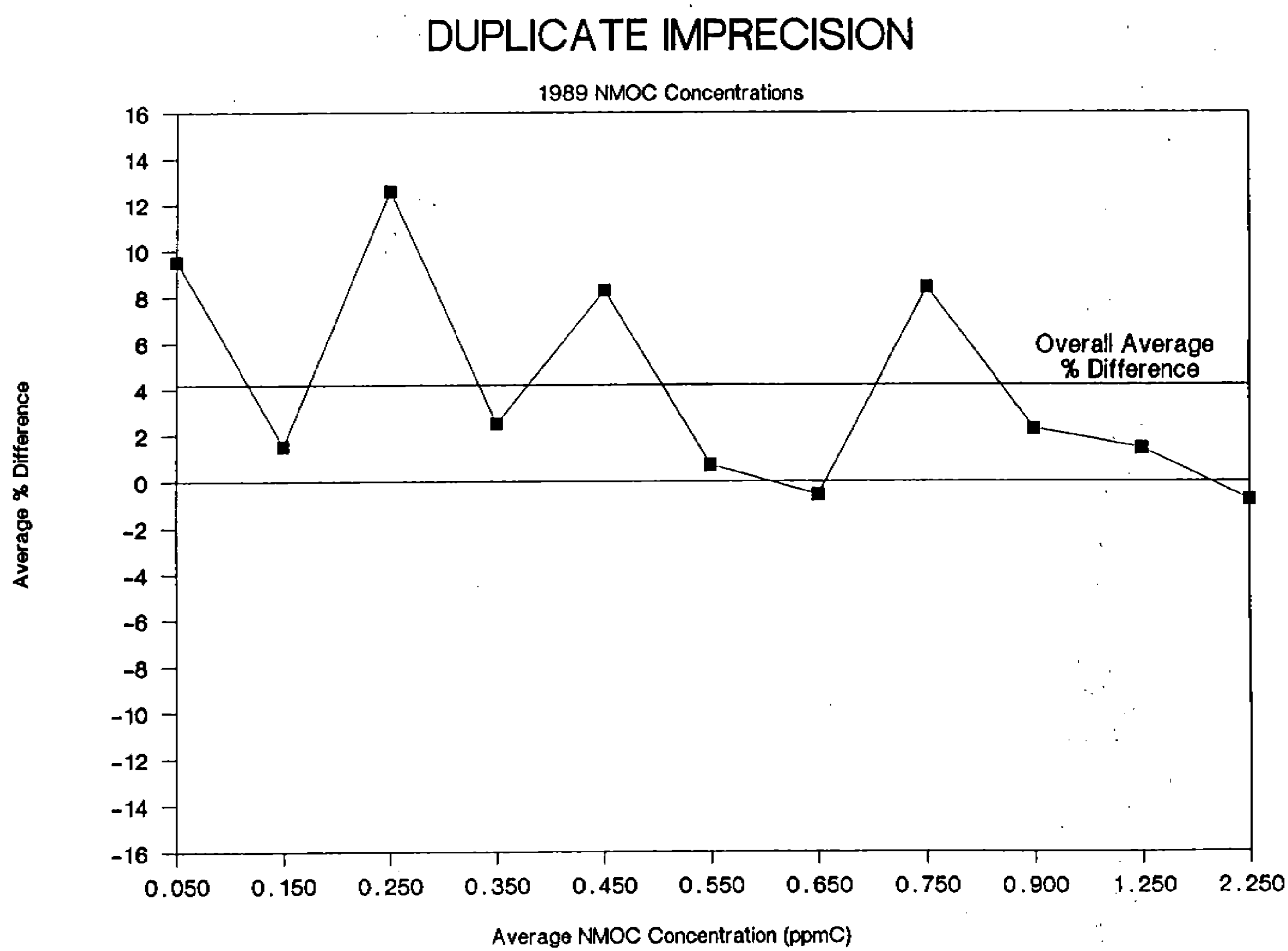


Figure 4-33. Duplicate NMOC sample results comparing average concentration with average percent difference.

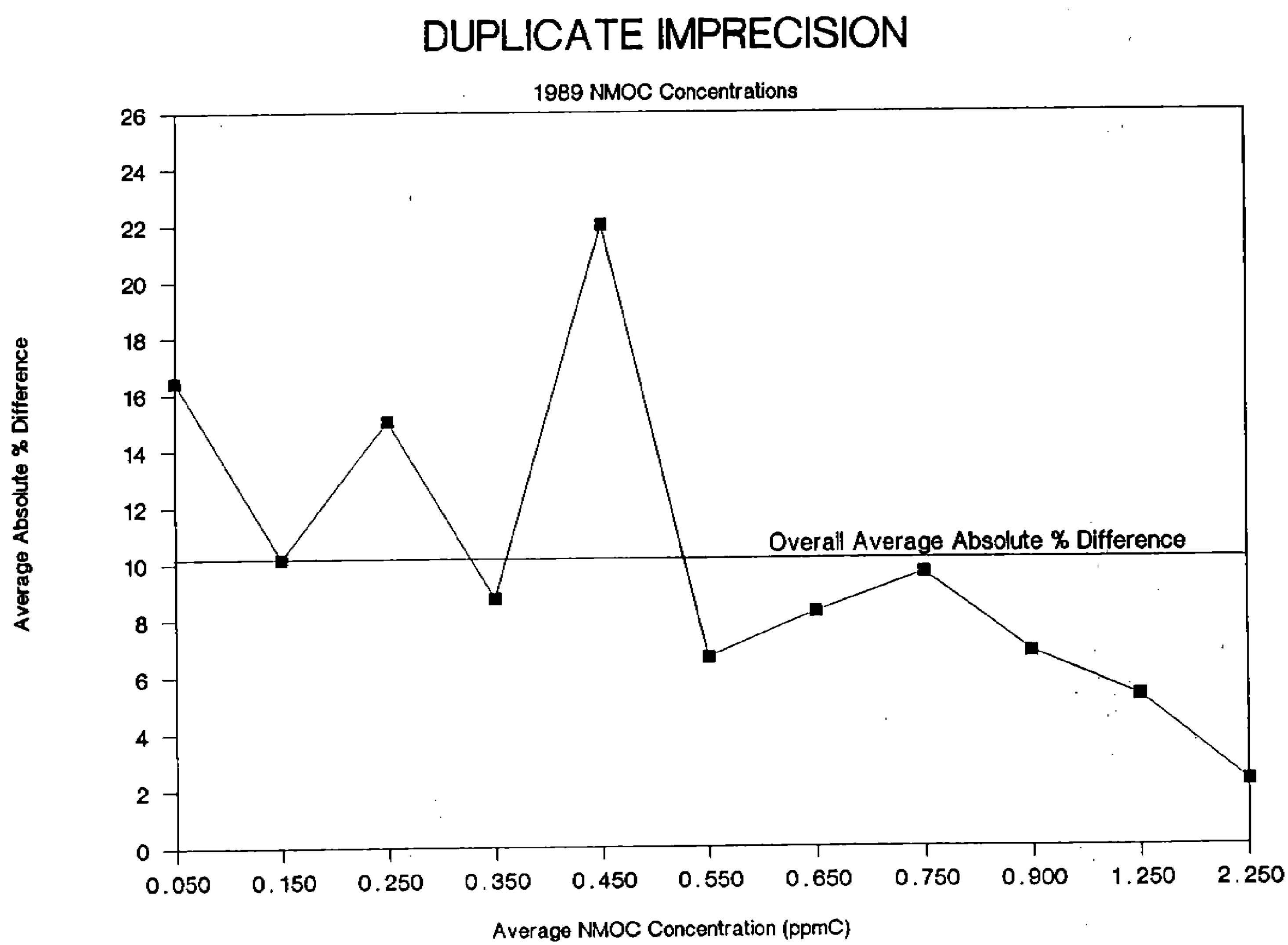


Figure 4-34. Duplicate NMOC sample results comparing average concentration with average absolute percent difference.

TABLE 4-26. NMOC PRESSURE STATISTICS

Statistics	All Samples	Duplicate Sample Canisters
Number of Cases	1956	388
Minimum Pressure, psig	5.0	6.0
Maximum Pressure, psig	29.0	29.0
Mean Pressure, psig	14.867	16.846
Median Pressure, psig	15.0	16.0
Standard Deviation, psig	3.031	3.450
Skewness	0.398	0.749
Kurtosis	1.714	2.020

TABLE 4-27. PRESSURE DISTRIBUTION OF NMOC AMBIENT AIR SAMPLES

Pressure Range, psig	Single Sample Cases	Duplicate Sample Canister Cases
Blank[a]	1	1
4.0 to 4.9	0	0
5.0 to 5.9	1	0
6.0 to 6.9	7	1
7.0 to 7.9	2	0
8.0 to 8.9	20	4
9.0 to 9.9	22	1
10.0 to 10.9	116	4
11.0 to 11.9	73	2
12.0 to 12.9	158	13
13.0 to 13.9	148	21
14.0 to 14.9	338	36
15.0 to 15.9	235	40
16.0 to 16.9	340	72
17.0 to 17.9	170	45
18.0 to 18.9	165	64
19.0 to 19.9	55	26
20.0 to 20.9	50	19
21.0 to 21.9	8	4
22.0 to 22.9	21	11
23.0 to 23.9	2	2
24.0 to 24.9	12	10
25.0 to 25.9	0	0
26.0 to 26.9	2	2
27.0 to 27.9	2	2
28.0 to 28.9	7	7
29.0 to 29.9	1	1
TOTAL	1956	388[b]

[a]Blank indicates no pressure reading given for sample.
[b]Equals 194 duplicate samples.

16.8 psig. The column entitled "All Samples" includes pressures from both single samples and duplicate samples. Standard deviations were 3.031 and 3.450 psig, respectively. The data show little skewness, so the distribution is approximately symetrical.

4.7 CANISTER CLEANUP RESULTS

Prior to the start of the 1989 NMOC Sampling and Analysis Program all of the canisters were cleaned and analyzed for their NMOC content to establish canister initial conditions. The resulting analysis with cleaned, dried air that had been humidified averaged 5.5 area counts (0.0017 ppmC), ranging from zero to 66.69 area counts (0.021 ppmC). Any canisters that produced more than 0.025 ppmC were recleaned.

Continual monitoring of the cleanup was important to ensure that there was negligible carryover from one site sample to the next. The daily canister cleanup procedure is described in detail in Section 3.4. The NMOC content was below 0.030 ppmC and cleanup was considered to be satisfactory.

Percent recoveries, or percent cleanup, in 1989 averaged 99.742%, (99.689% in 1988, 99.374% in 1987, 99.891% in 1986, and 99.898% in 1985), ranging from 92.12% to 100 percent. The reported percent cleanup figures should be considered minimum values. The actual percent cleanup was greater than the reported values because, after the percent cleanup was measured, the canister was evacuated a third time before being shipped to the site.

4.8 EXTERNAL AUDIT RESULTS

Primary measures of accuracy were calculated from the results of the analysis of audit samples provided by EPA-QAD. Results are reported in terms of percent bias, relative to the EPA standards.

Audit samples of propane provided by EPA-QAD were referenced to NBS SRM propane No. 1668B. Each Radian channel and the EPA-AREAL channel analyzed each audit sample. The results of these analyses are given in Table 4-28. Audit sample bias, percent bias, and absolute percent bias are shown in Table 4-29. In Table 4-29, all bias measurements are relative to the QAD results. Overall Radian average bias was 0.84%, indicating Radian channels averaged 0.84% lower than the EPA-QAD reference values. Radian mean bias ranged from 0.38% for Channel B to 1.29% for Channel C. The overall average

TABLE 4-28. 1989 NMOC AUDIT SAMPLE RESULTS

Analyzed		Radian	Channel				QAD	AREAL
Date	Julian Date	ID Number	A NMOC ppmC	B NMOC ppmC	C NMOC ppmC	D NMOC ppmC	NMOC ppmC	NMOC ppmC
06/05/89	156	1005	1.154	1.141	1.142	1.142	1.154	--
06/05/89	156	1006	3.090	3.019	3.153	3.151	3.120	--
07/13/89	194	1647	0.563	0.575	0.566	0.560	0.545	--
07/13/89	194	1648	1.525	1.531	1.526	1.531	1.512	--
07/31/89	212	1969	0.740	0.758	0.727	0.719	0.724	--
08/17/89	229	2290	0.772	0.764	0.799	0.750	0.791	0.882
09/28/89	271	3020	0.592	0.578	0.577	0.560	0.582	0.560
09/28/89	271	3021	1.039	1.056	0.965	1.040	1.074	1.021

TABLE 4-29. AUDIT SAMPLES, RELATIVE TO EPA-QUALITY ASSURANCE DIVISION (QAD) RESULTS

	DELTAA ppmC	DELTAB ppmC	DELTAC ppmC	DELTAD ppmC	DELTAE ppmC	Chan. A Percent Bias	Chan. B Percent Bias	Chan. C Percent Bias	Chan. D Percent Bias	Chan. E Percent Bias	
	0.00000	-0.01300	-0.01200	-0.01200	-	0.00000	-1.12652	-1.03986	-1.03986	-	
	-0.03000	-0.10100	0.03300	0.03100	-	-0.96154	-3.23718	1.05769	0.99359	-	
	0.01800	0.03000	0.02100	0.01500	-	3.30275	5.50459	3.85321	2.75229	-	
	0.01300	0.01900	0.01400	0.01900	-	0.85979	1.25661	0.92593	1.25661	-	
	0.01600	0.03400	0.00300	-0.00500	-	2.20994	4.69613	0.41436	-0.69061	-	
	-0.01900	-0.02700	0.00800	-0.04100	-0.09050	-2.40202	-3.41340	1.01138	-5.18331	-11.44121	Radian
	0.01000	-0.00400	-0.00500	-0.02200	0.02250	1.71821	-0.68729	-0.85911	-3.78007	3.86598	Percent
	-0.03500	-0.01800	-0.10900	-0.03400	0.05300	-3.25885	-1.67598	-10.14898	-3.16574	4.93482	Bias
Average	-0.00338	-0.01000	-0.00588	-0.00613	-0.00500	0.18354	0.16462	-0.59817	-1.10714	-0.88014	-0.33929
Std. Dev.	0.02153	0.04319	0.04403	0.02601	0.07560	2.28437	3.38900	4.13999	2.75347	9.16176	3.21810

For Channel A:
DELTAA ppmC = NMOCA - QAD
Percent Bias = (DELTAA ppmC)/Q*100

Channel E is EPA-ASRL Channel

Absolute Values of Percent Bias

	0.00000	1.12652	1.03986	1.03986	-	
	0.96154	3.23718	1.05769	0.99359	-	
	3.30275	5.50459	3.85321	2.75229	-	
	0.85979	1.25661	0.92593	1.25661	-	
	2.20994	4.69613	0.41436	0.69061	-	Radian
	2.40202	3.41340	1.01138	5.18331	11.44121	Absolute
	1.71821	0.68729	0.85911	3.78007	3.86598	Percent
	3.25885	1.67598	10.14898	3.16574	4.93482	Bias
Average	1.83914	2.69971	2.41381	2.35776	6.74734	2.32761
Std. Dev.	1.17949	1.78512	3.29993	1.62150	4.09999	2.12701

absolute percent bias for the Radian channels was 2.33 percent. These accuracy measurements show excellent agreement with the reference values, and lend confidence to the 1989 NMOC concentration results determined on all the Radian channels.

The EPA-AREAL channel averaged -0.9% bias, relative to EPA-QAD. Figures 4-35, 4-36, 4-37, and 4-38 show the audit bias results for the Radian channels versus the reference values provided by EPA-QAD. Figure 4-39 shows the audit bias results for EPA-AREAL versus EPA-QAD.

4.9 DATA VALIDATION

The secondary backup disks were updated daily on 20 megabyte hard disks. At the completion of the sampling and analysis phase 26.4% of the data base was checked to verify its validity. Items checked included original data sheets, checks of all the calculations, and data transfers. In making the calculations for the final report and other reports, corrections were made to the data base as errors or omissions were encountered.

A total of 2,576 NMOC concentration measurements were performed by Radian in June through September 1989. For the regular 1989 NMOC Monitoring Program, there were 2,495 NMOC concentration measurements which included 1,965 sample analyses, 150 repeated analyses, 38 local ambient samples (x 4 analyses each), and 8 audit samples (x 4 analyses each). The remaining 81 analyses included analyses from the 1989 Raleigh diurnal study, the Maryland NMOC Monitoring Program, and the Portland Monitoring Program.

A percentage of the data base (14.6%, 373 cases out of 2,560 data points) was selected at random and validated according to the procedure outlined below.

A. Calibration factors were checked.

1. The area count from the strip chart that was used to determine the calibration factor was examined to verify that the data had been properly transferred to the calibration form.

2. The calibration form was examined to verify that the calculations had been correctly made.

3. Each datum on the disk was compared to the corresponding datum on the calibration sheet for accuracy.

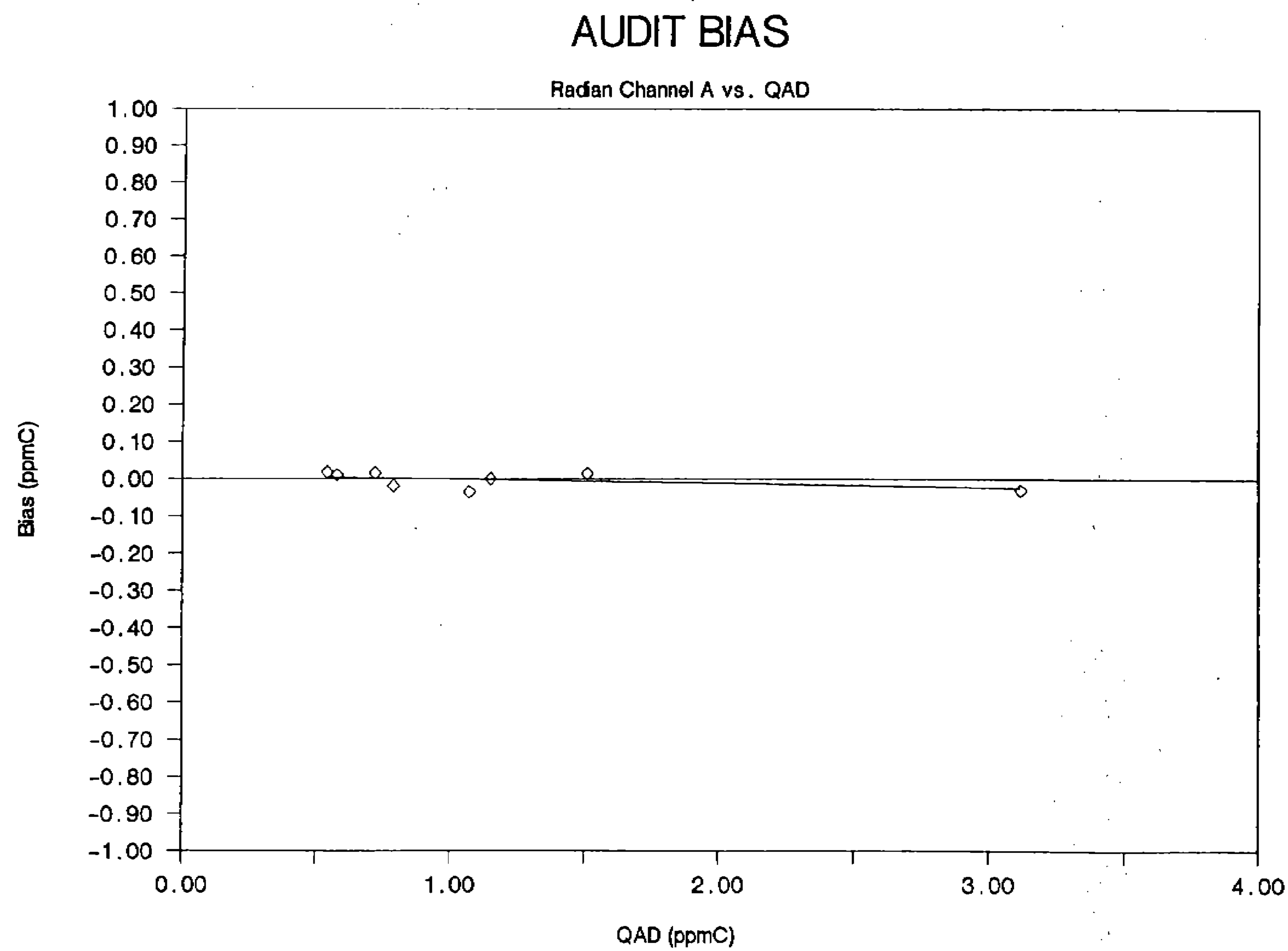


Figure 4-35. Audit Bias, Radian Channel A vs. EPA-QAD.

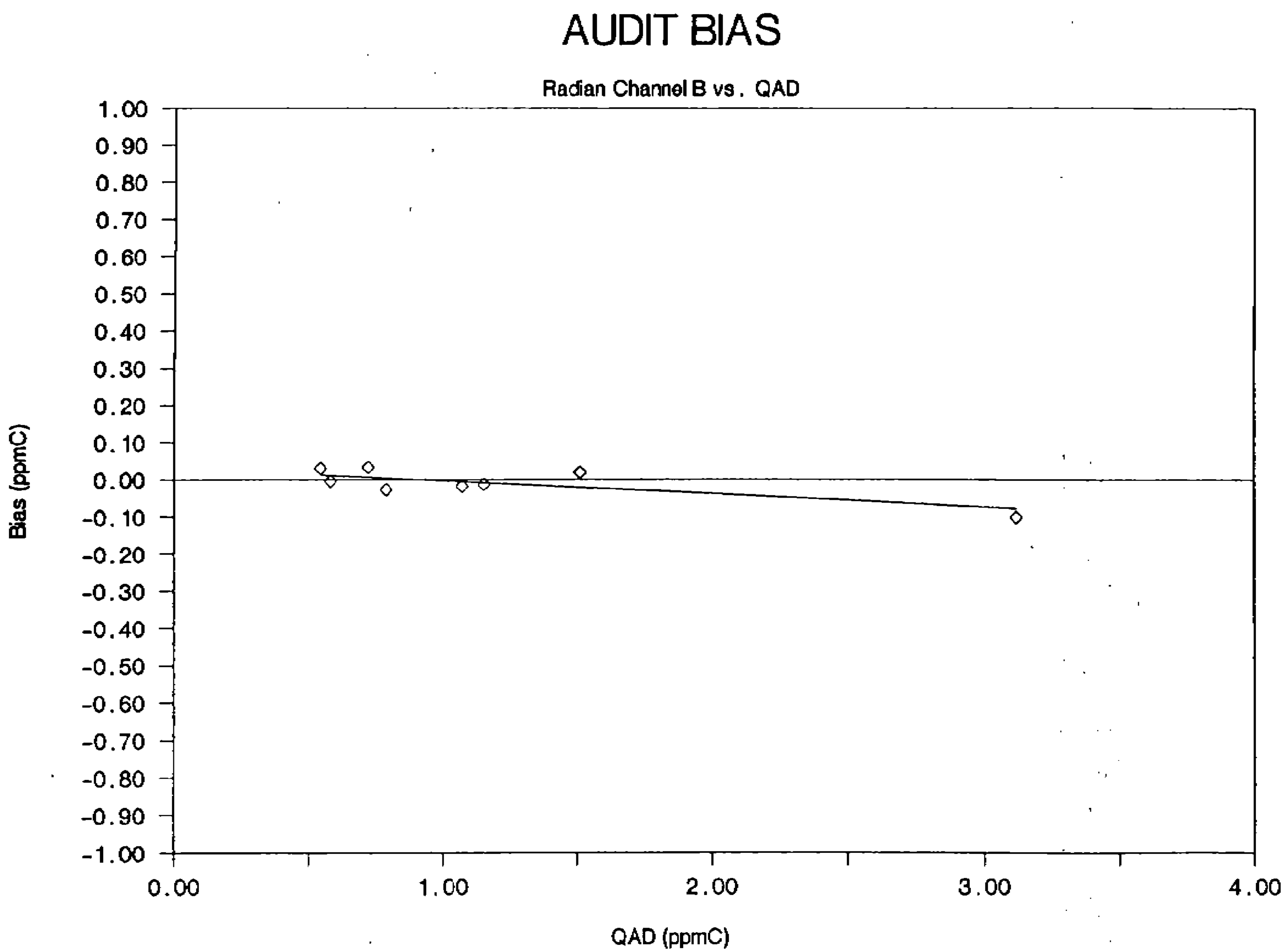


Figure 4-36. Audit Bias, Radian Channel B vs. EPA-QAD.

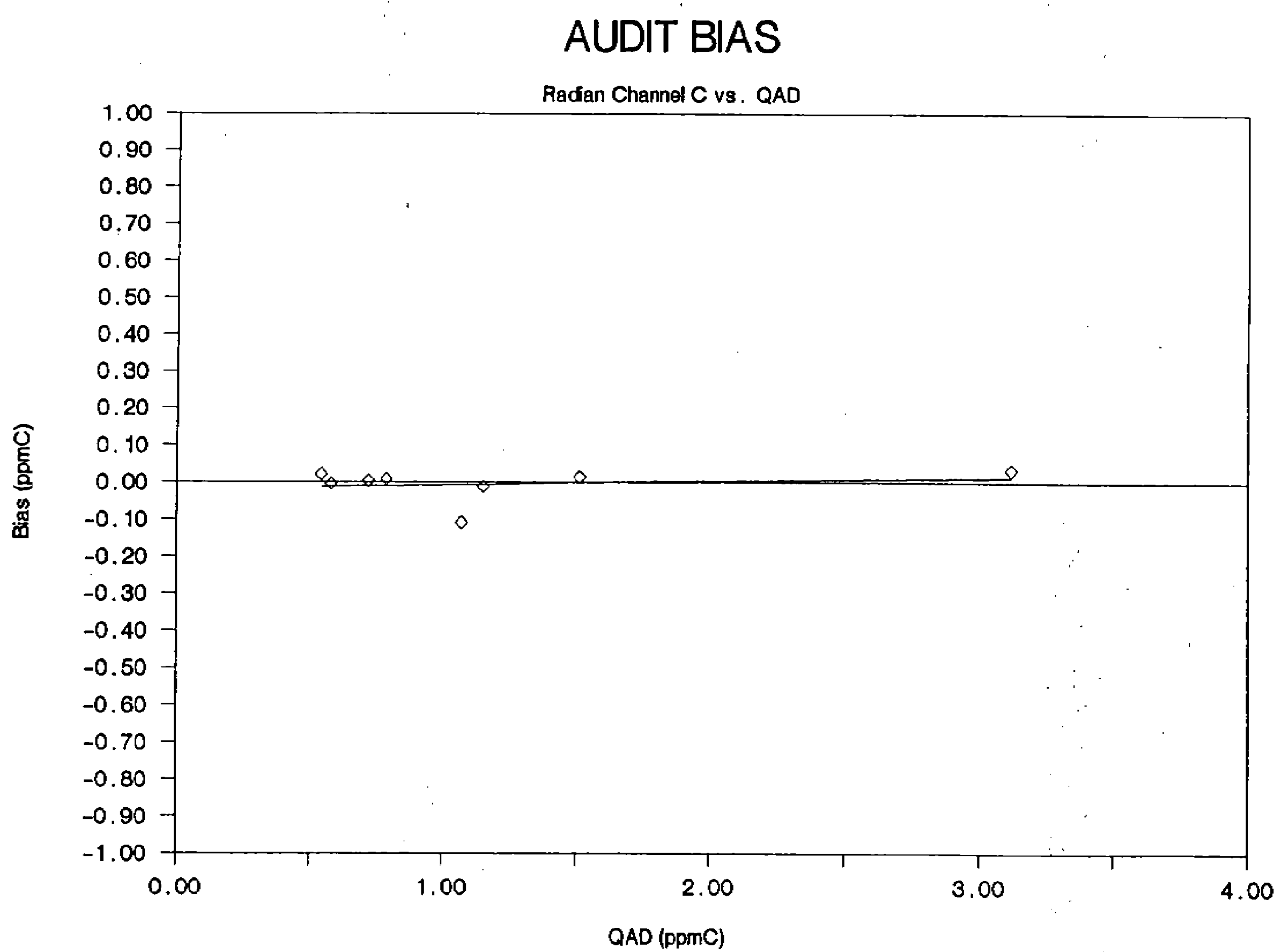


Figure 4-37. Audit Bias, Radian Channel C vs. EPA-QAD.

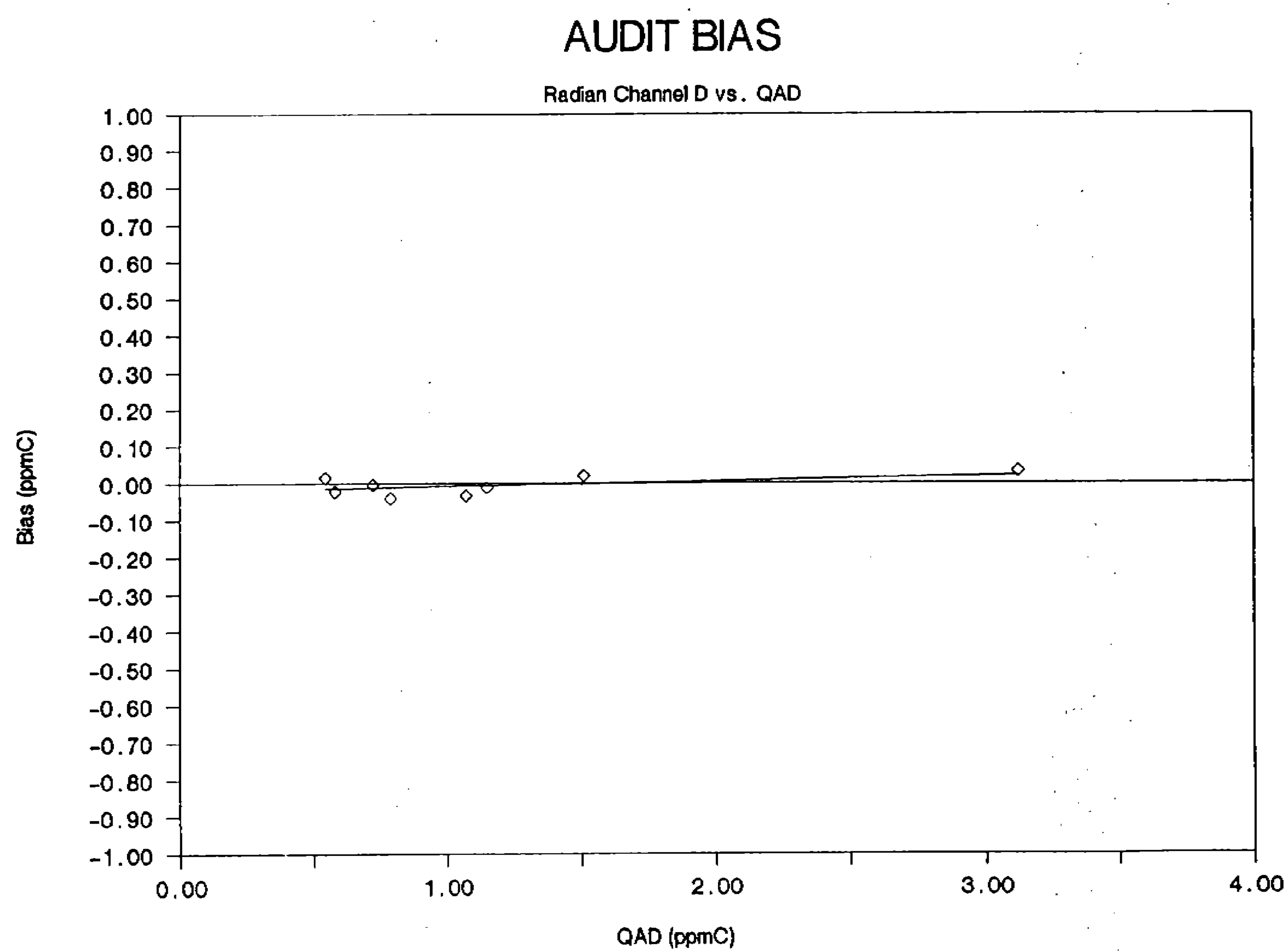


Figure 4-38. Audit Bias, Radian Channel D vs. EPA-QAD.

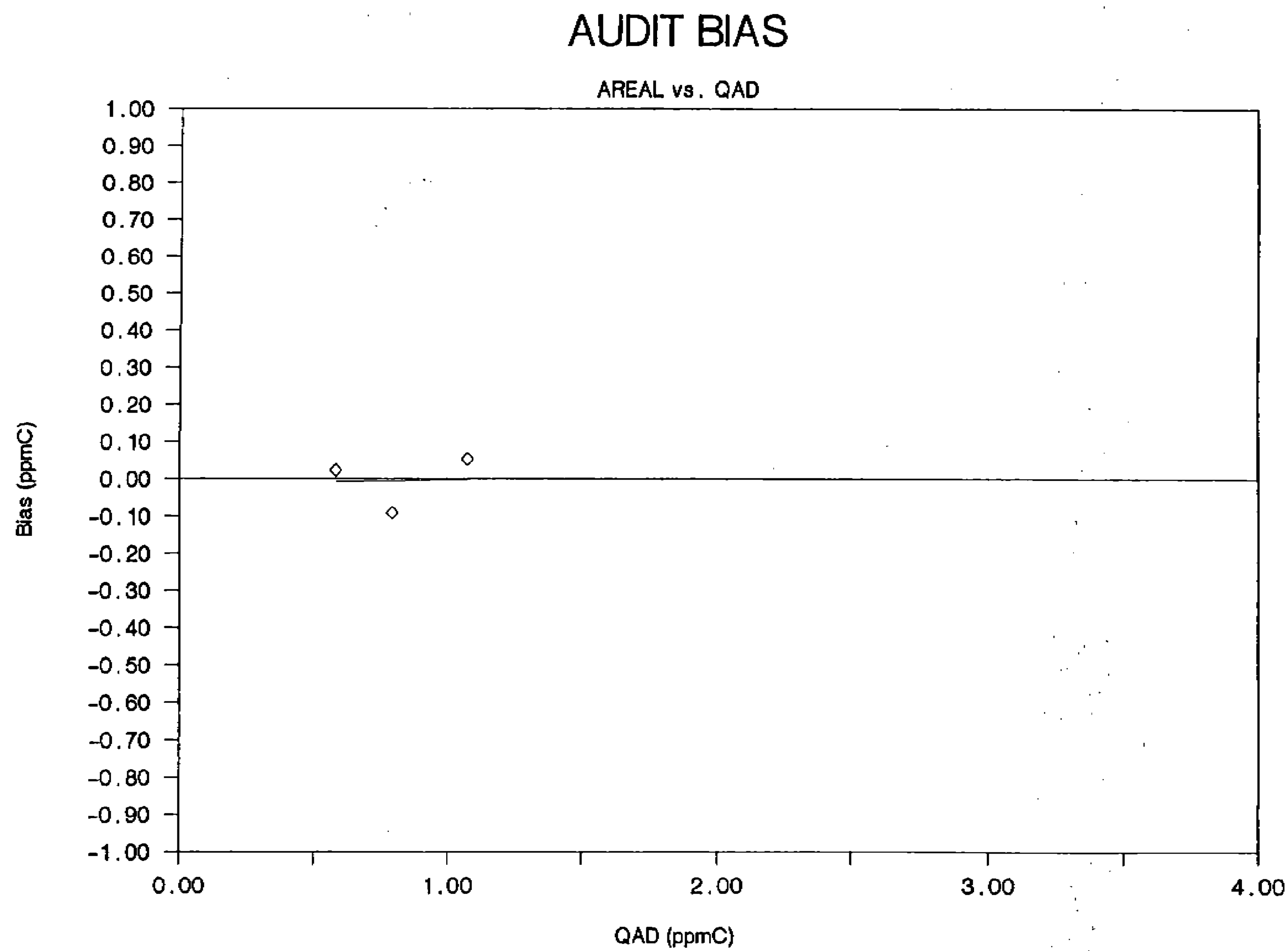


Figure 4-39. Audit Bias, EPA-AREAL vs. EPA-QAD.

B. Analysis data were checked.

1. Area counts were verified from the appropriate strip chart.

2. Calculations were reverified on the analysis forms.

3. Each datum on the disk was compared to the corresponding item on the analysis form.

C. Field data sheet was checked.

1. Each datum on the disk was compared to the corresponding datum on the field data sheet.

The error rate was calculated in terms of the number of items transferred from the original data sources. For each NMOC value in the 1989 data set, 36 items were transferred from original sources to the magnetic disks. In the data validation study each item on the disk was compared with the corresponding value on the original source of data. Seventy-nine errors were found (and corrected) for an expected error percentage of 0.369.

Each time the data file was opened and a suspected error found, the error was checked against the original archived documents, and corrected where appropriate.

4.10 NMOC MONITORING PROGRAM RECORDS

The quality assurance records developed by Radian for this project are extensive and will be preserved as archives. One of the most important objectives of the study was to develop a data base that is well planned and documented and contains NMOC data of known and verifiable quality. Achieving that objective has involved keeping and preserving a number of records that trace the project from planning through reporting.

4.10.1 Archives

In order to keep detailed records that document the quality of the measurements made, Radian developed the following original material:

- Quality Assurance Project Plan (QAPP);
- Notebooks;
- Field Data Sheets;
- Laboratory Calibration Sheets;
- Laboratory Analysis Sheets;

- Chromatographic Strip Charts;
- EPA-AREAL and EPA-QAD NMOC Results;
- Bi-weekly, Monthly Reports to EPA;
- Memoranda and Correspondence; and
- Final Report.

In addition to the above items, several papers to be presented at technical meetings and symposia and published in technical journals will be added to the archives.

The QAPP[2] was the Quality Assurance Project Plan and the workplan. The QAPP was designed according to the EPA Quality Assurance Guidelines, and set the pattern of steps necessary to document and control the quality of the data obtained throughout the study.

Several notebooks were necessary to maintain day-to-day records of the project. Field and laboratory data sheets were designed in advance, so that the data recorded appeared in a logical sequence and filled in blanks on the sheet. Additional space was provided for other comments. Each NMOC analysis was assigned a unique Radian Identification Number. Field data sheets and shipping records accompanied the canisters in transit.

4.10.2 Magnetic Disks

In order to manage the data base for report generation and data analysis, pertinent data from the various data sheets and notebooks were transferred to 20 megabyte magnetic disks. The following software was used in the construction of the data base: Paradox 3®, Lotus 1-2-3®, and PC File+®. Statistical calculations were done using SYSTAT® software. The data access is rapid and in a convenient form. The primary 20 megabyte magnetic disk has three backup disks.

5.0 NMOC DATA ANALYSIS AND CHARACTERIZATION

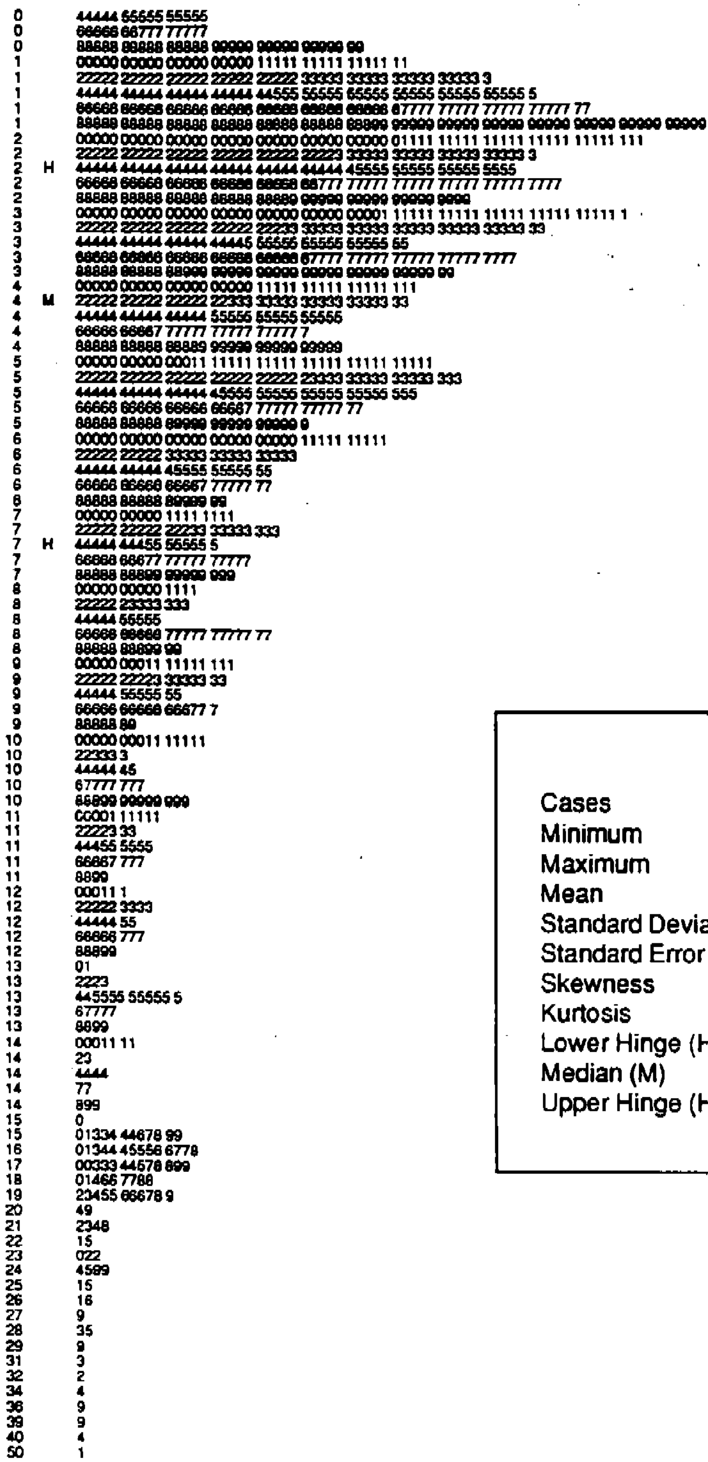
The purpose of this section is to characterize the NMOC data qualitatively as well as quantitatively. The NMOC data are shown to fit a two-parameter lognormal distribution better than a normal Gaussian distribution. The summary NMOC data for the sites of the 1989 study are given in Appendix E.

5.1 OVERALL CHARACTERIZATION

Figure 5-1 gives a stem-and-leaf plot of the 1989 Morning Site NMOC data along with statistics for NMOC. The stem-and-leaf plots show the actual NMOC concentrations truncated to two or three decimal points. The digits to the left of the vertical open space are called stems and the digits to the right of the open space are the leaves. The data are sorted from the smallest at the top of the graph to the largest at the bottom of the graph. The minimum NMOC value measured was 0.043 ppmC and is shown as "0   4" on the first row at the top of the plot. The maximum NMOC concentration measured was 5.013, shown as "50   1" in the bottom row of the chart. The plot shows 1,784 leaves, one for each NMOC Morning Site datum in the 1989 program. The H's in the open vertical space locate the stem and leaf for the upper and lower hinges, and the M locates the stem and leaf for the median. The median separates the sorted NMOC concentrations into two equal halves; the hinges (or quartiles) separate each half into quarters. The "H spread" or inter-quartile range is the difference between the NMOC values of the two hinges.

Statistics shown for NMOC are number of cases, minimum, maximum, mean, median, standard deviation, standard error, skewness, kurtosis, and the two hinges. Each NMOC determination is the average of two or three injections of the site sample.

The standard error is the standard deviation divided by the square root of the number of cases. Positive skewness is a third moment about the mean value, and characterizes a tail to the right of the mean value. A normal Gaussian distribution has a skewness of zero. The skewness of 2.46 for the 1989 NMOC data suggests a lognormal frequency distribution; that is supported



NMOC, ppmC	
Cases	1784
Minimum	0.043
Maximum	5.013
Mean	0.577
Standard Deviation	0.493
Standard Error	0.012
Skewness	2.460
Kurtosis	10.327
Lower Hinge (H)	0.242
Median (M)	0.434
Upper Hinge (H)	0.747

Figure 5-1. Stem-and-leaf plot of the 1989 morning NMOC data.

2793524R

by the fact that for the logarithm of the NMOC value (ln(NMOC)) (see Figure 5-2), skewness equals -0.087, which is close to zero. Kurtosis is the fourth moment about the mean and relates to the pointedness of the distribution. A distribution more pointed than a normal distribution, having the same standard deviation, has a kurtosis greater than 3.0.

Figure 5-2 is a stem-and-leaf plot of the 1989 ln(NMOC) data. The plot shows an approximately symmetrical distribution (skewness = -0.087). The kurtosis equal to -0.274 indicates the ln(NMOC) distribution to be less pointed than a normal distribution.

The shape of the stem-and-leaf plots suggests a lognormal distribution. Figures 5-3 and 5-4 support the lognormal distribution hypothesis for NMOC. The vertical scales in Figures 5-3 and 5-4 are arranged so that if the cumulative frequency of occurrence of NMOC were normally distributed, the numbers would plot into a straight line. The line in Figure 5-3 has a noticeable concave downward trend, indicating that the data do not fit a normal distribution well. Figure 5-4 plots the logarithm of NMOC on the same vertical scale. The fact that the digits on the graph plot into approximately a straight line supports the hypothesis that the NMOC data are approximately lognormally distributed. An asterisk on the graph indicates the location of a single datum. Integers, such as 2, 6, or 9, show the location of the corresponding number of data points. The number 999 shows the approximate location of either 27 data points or 99 + 9 data points. The results, although qualitative, show a dramatic difference between the normal and lognormal hypotheses, and suggest that the latter more nearly describes the NMOC data. Figure 5-4 is labeled a "Normal Probability Plot," but since the independent variable is the logarithm (to the base e) of NMOC, if the relation between the EXPECTED VALUE and ln(NMOC) is linear, a lognormal distribution is obtained.

5.2 MONTHLY VARIATIONS, 1984 - 1989

Table 5-1 partitions the NMOC data for the summer of 1989 into groups which correspond to monthly intervals.

The median, mean, and maximum NMOC concentration for September appear higher than for June, July, or August, but no clear trend is seen for the summer of 1989. Arithmetic means are used in Table 5-1 in spite of the

```
-31      4
-30      7610
-29      66322 0
-28      9883
-27      94332 1
-26      83220
-25      97431 10
-24      98865 44433 11
-23      99888 88766
-22      99987 76655 55444 42111
-21      99888 87776 65554 22110 00
-20      99888 88877 77766 55554 43221 11000 0
-19      98888 77766 55554 44433 32221 11110 00
-18      99998 88888 87777 66666 55544 44443 32222 22211 11100 00000
-17      99999 99988 77777 77776 55544 43333 22222 11100 0
-16      99999 99999 99888 88877 77666 66666 66555 55555 44333 33333 32222 22221 11111 00000 0
-15      99999 99999 88888 87777 77777 76666 65555 44444 44333 33333 22221 11111 11000 00000 00
-14  H   99998 88888 77776 66666 66655 44444 33332 22222 22222 11111 11110 0000
-13      99999 99888 77777 76666 65555 44333 33333 33222 22222 11111 11100 00000 00000 0
-12      99999 88887 77777 76666 66666 66555 55444 44433 33322 22211 11111 00000 0
 11      99999 99998 88888 88888 87777 77777 77766 66666 65555 55555 55544 44433 33333 32222 21111 11111 10000 00000
-10      99999 99999 98888 88887 77777 77776 66655 55554 44443 33333 33222 22222 22111 11111 11110 00000
 -9      99999 99998 88887 77777 77777 77666 65555 44444 33333 33333 33333 32222 22222 22221 11110 00000 000
 -8  M   99999 99988 88888 77777 77766 66665 55555 55555 44443 33333 33333 33222 22111 10000 00000 0
 -7      99999 99888 88887 77777 77665 55554 44444 44433 33332 22222 22211 11100 000
 -6      99999 99999 99888 88777 77766 66666 66666 66666 55555 55555 55554 44444 44444 44333 33333 333333 33222 22221 11111 11100 00000 0
 -5      99999 99999 99999 88888 88887 77777 76666 66666 66666 66655 55544 44433 33333 32222 22221 11111 11100 00000 00000 00000 00
 -4      99999 99998 88888 77777 77666 66666 55555 55544 44444 33333 33222 22211 11111 11110 00000 00000
 -3      99999 88888 87777 77776 66555 55554 44444 33333 33222 22211 11111 11111 10000 0
 -2  H   99999 99888 87777 77666 66666 55555 55555 44444 33333 33322 22222 21111 11100 0
 -1      99999 88888 87777 66666 66554 44444 44443 33333 33333 22222 21111 00000 000
 -0      99999 99998 88877 77777 77777 66666 55555 55444 44443 33333 33333 22211 11110
  0      00000 00001 11111 22233 34444 44566 67777 77888 88889 99999 99
  1      00000 00112 22223 33444 44445 55666 66778 88899 99
  2      00001 11111 22222 33333 44445 55567 77889 99
  3      00000 00000 11112 23344 44444 55666 6899
  4      00011 23333 55566 67789 99
  5      00011 11233 44555 67778 899
  6      12223 33556 67777 789
  7      13556 79
  8      13449 9
  9      11236 7
 10      2449
 11      46
 12      3
 13      089
 16      1
```

	ln(NMOC)
Cases	1784
Minimum	-3.147
Maximum	1.612
Mean	-0.853
Standard Deviation	0.792
Standard Error	0.019
Skewness	-0.087
Kurtosis	-0.274
Lower Hinge (H)	-1.420
Median (M)	-0.836
Upper Hinge (H)	-0.292

2793525R

Figure 5-2. Stem-and-leaf plot for the morning ln(NMOC) data.

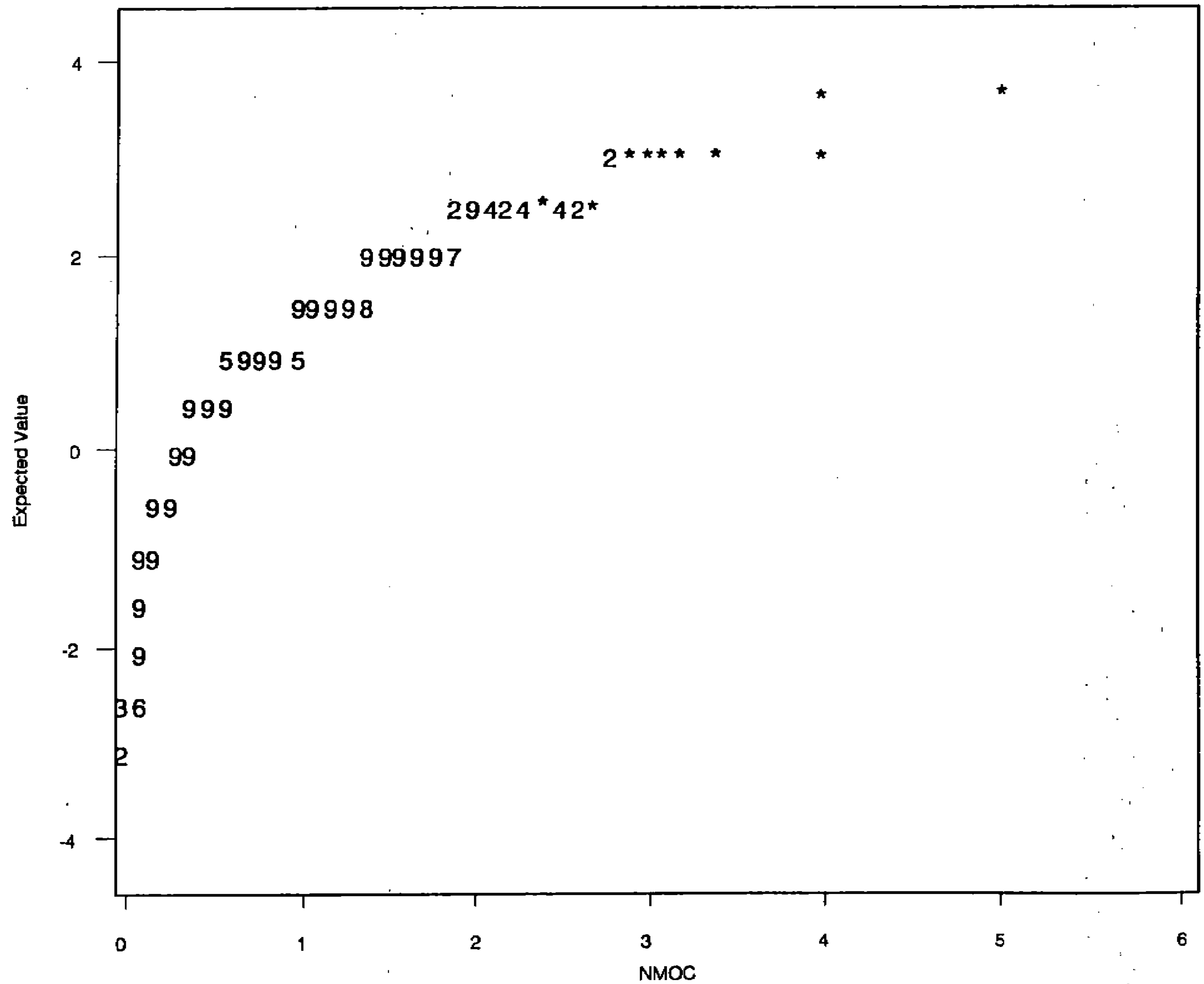


Figure 5-3. Cumulative frequency distribution for 1989 NMOC data.

2793530R

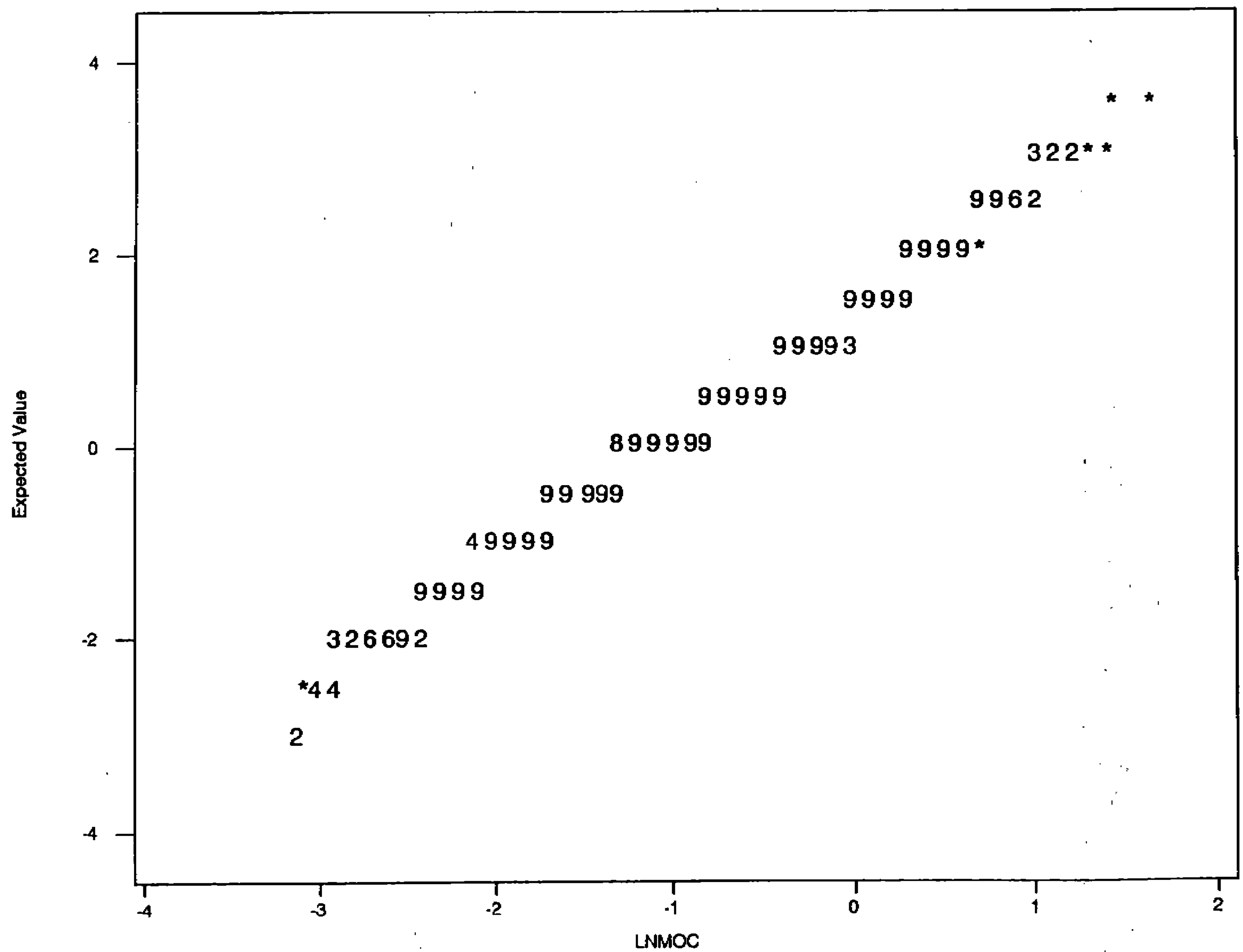


Figure 5-4. Cumulative frequency distribution for 1989 ln(NMOC) data.

2793539R

TABLE 5-1. SUMMARY STATISTICS FOR 1989 MORNING NMOC SITES, BY MONTH

Sample Month 1989	Minimum NMOC ppmC	Median NMOC ppmC	Mean NMOC ppmC	Maximum NMOC ppmC	Standard Deviation NMOC ppmC	Cases
June	0.059	0.396	0.510	3.693	0.403	419
July	0.052	0.428	0.542	3.443	0.420	426
August	0.043	0.405	0.540	3.134	0.451	503
September	0.046	0.530	0.718	5.013	0.637	436

cah.172f

observations given in Section 5.1 which conclude that the frequency distribution of NMOC concentrations in ambient air are logarithmic normal distributed. Comparison of Tables 2-2 and 2-3 containing site average concentrations for the Gaussian and lognormal distributions, respectively, emphasize that the lognormal means may be less than, equal to, or greater than the respective arithmetic means. In all cases the means are within 10% of one another. Either the arithmetic means, or the mean of the lognormal distribution may be used as a measure of central tendency of the data. Table 5-1 also gives monthly minima, medians, and maxima. These latter three statistics are independent of the probability distribution from which they derive.

Figures 5-5 through 5-8 give the stem-and-leaf plots of the NMOC data for June, July, August, and September 1989, respectively. All the plots show the general shape of lognormal distribution. The data for June, July, August, and September may be considered typical of the sites tested during the indicated time period. Monthly mean NMOC emissions are plotted in Figure 5-9 for 1984, 1985, 1986, 1987, 1988, and 1989. No general trends are evident for the years shown. For five of the six years, September means are higher than August means, and for four of the six years, July means are less than June means. At present, however, it must be concluded that random behavior is responsible for apparent month-to-month changes.

During the six years of the NMOC Monitoring Program, three sites participated in the program for all six years. Two sites have been in the program 4 years; 7 sites for 3 years; 18 sites for 2 years; and 61 sites for only 1 year. In all cases the sites were urban sites, but it is difficult to draw conclusions from year to year because of the difference in yearly site participation.

The April and May NMOC monitoring data for 1988 were from only four Florida sites, MIFL, M2FL, T1FL, and T2FL. The remainder of the points located on the 1988 trend line included data from 45 NMOC Monitoring Program sites.

5.3 SPECIAL STUDY

This section summarizes the results of a special study designed to characterize, compare, and qualify NMOC monitoring data from 1984 through

```
 0      56677 999
 1      00000 11111 22222 22333 33344 44445 55555 55555 55566 66666 77777 77888 88888 88999 99999 9
 2  H   00000 00000 11111 22222 22222 33333 33344 44445 55566 66777 78888 88999 999
 3  M   00000 00000 01111 12222 22333 33334 44455 56666 66666 77777 77888 89999
 4      00011 11223 33333 33445 55556 77777 88899
 5      00011 11111 12222 22233 34444 55555 66667 99
 6  H   00000 01112 23333 44455 56666 67778 88999
 7      00111 22222 23345 55566 77889 9999
 8      00002 24456 77788
 9      00111 22233 45556 6
10      00113 34479
11      00014 78
12      0368
13      23567
13      8
14      28
15      9
16      1
17      348
18      7
19      69
21      4
22      5
36      9
```

NMOC, ppmC	
Cases	419
Minimum	0.058
Maximum	3.693
Mean	0.510
Standard Deviation	0.402
Standard Error	0.019
Skewness	2.414
Kurtosis	10.890
Lower Hinge (H)	0.220
Median (M)	0.395
Upper Hinge (H)	0.684

2793526R

Figure 5-5. Stem-and-leaf plot of the morning NMOC data for June, 1989.

```
 0     56888 88999
 1     00011 11222 22222 33344 45555 66667 77778 88888 88888 89999 99999 9999
 2 H   00000 00000 01111 11111 22222 22333 34444 44444 44555 55566 66667 77788 88888 88899 9
 3     00000 00001 11111 22222 23333 33444 44444 45566 66777 78889 99999 99999 99
 4 M   00011 11122 22333 33344 44444 45567 77788 88899 99999 9
 5     00000 11111 11112 22222 23444 55556 66777 77888 88999 999
 6     00000 11223 34555 56788 9
 7 H   00111 22334 47777 8899
 8     00122 45556 66778 8999
 9     00022 23445 55666 788
10     00344 57778 999
11     11123 55567 8
12     03346 6789
13     355
14     119
15     347
16     4568
17     59
21     3
24     49
34     4
```

	NMOC, ppmC
Cases	426
Minimum	0.051
Maximum	3.443
Mean	0.542
Standard Deviation	0.419
Standard Error	0.020
Skewness	2.138
Kurtosis	7.596
Lower Hinge (H)	0.245
Median (M)	0.427
Upper Hinge (H)	0.712

2793527R

Figure 5-6. Stem-and-leaf plot of the morning NMOC data for July, 1989.

```
0       44555 56777 77888 88889 999
1       00000 00000 11111 11222 22233 33333 44444 44455 55556 66666 66666 77777 77888 88889 99999 9
2  H    00000 00000 00111 11122 22233 33333 44444 44455 55555 56666 66666 77777 77777 78888 88999 99999
3       00000 00011 11111 11111 22223 33333 33344 45555 55555 66666 66777 77788 88999 9999
4  M    00000 00001 11111 11222 22223 34444 45555 66777 77788 9999
5       00001 12222 22333 33445 55566 66666 67777 88889 99
6  H    00000 01111 22223 33333 34444 44455 66777 889
7       00011 22333 33444 55556 67779 99
8       00012 33346 66666 77777 89
9       01111 13456 66667 89
10      00011 77899 99
11      02456 9
12      11467
13      44578
13      9
14      00144 9
15      499
16      47
17      03478 9
18      01467 8
19      58
20      49
23      2
24      9
26      6
31      3
```

	NMOC, ppmC
Cases	503
Minimum	0.043
Maximum	3.134
Mean	0.540
Standard Deviation	0.450
Standard Error	0.020
Skewness	1.929
Kurtosis	4.792
Lower Hinge (H)	0.233
Median (M)	0.404
Upper Hinge (H)	0.697

2793528R

Figure 5-7. Stem-and-leaf plot of the morning NMOC data for August, 1989.

0		44455 55666 78889 99999 9
1		00122 22333 33444 44555 55666 66666 66666 67788 88999
2	H	00011 11111 22222 22333 44444 46666 66667 77777 77889 99
3		00000 01111 22222 22333 33334 44555 55666 66677 77778 99999 99
4		00000 12222 33335 55566 66677 88889 9
5	M	01111 11112 22222 33333 33344 44444 55555 55556 66677 78899 99
6		00000 00011 22335 56666 66788 889
7		00012 22344 66667 77888 8
8		01123 33345 77889
9	H	00112 22333 34666 7888
10		01112 23446 7899
11		11223 34556 6779
12		01222 22344 45567 89
13		01225 55557 79
14		01344 77
15		00134 68
16		03455 67
17		03
18		68
19		23456 67
21		28
22		1
23		2
24		5
25		15
26		1
27		9
28		35
29		9
32		2
39		9
40		4
50		1

	NMOC, ppmC
Cases	436
Minimum	0.046
Maximum	5.012
Mean	0.717
Standard Deviation	0.637
Standard Error	0.030
Skewness	2.316
Kurtosis	8.416
Lower Hinge (H)	0.282
Median (M)	0.538
Upper Hinge (H)	0.973

2793529R

Figure 5-8. Stem-and-leaf plot of the morning NMOC data for September,1989.

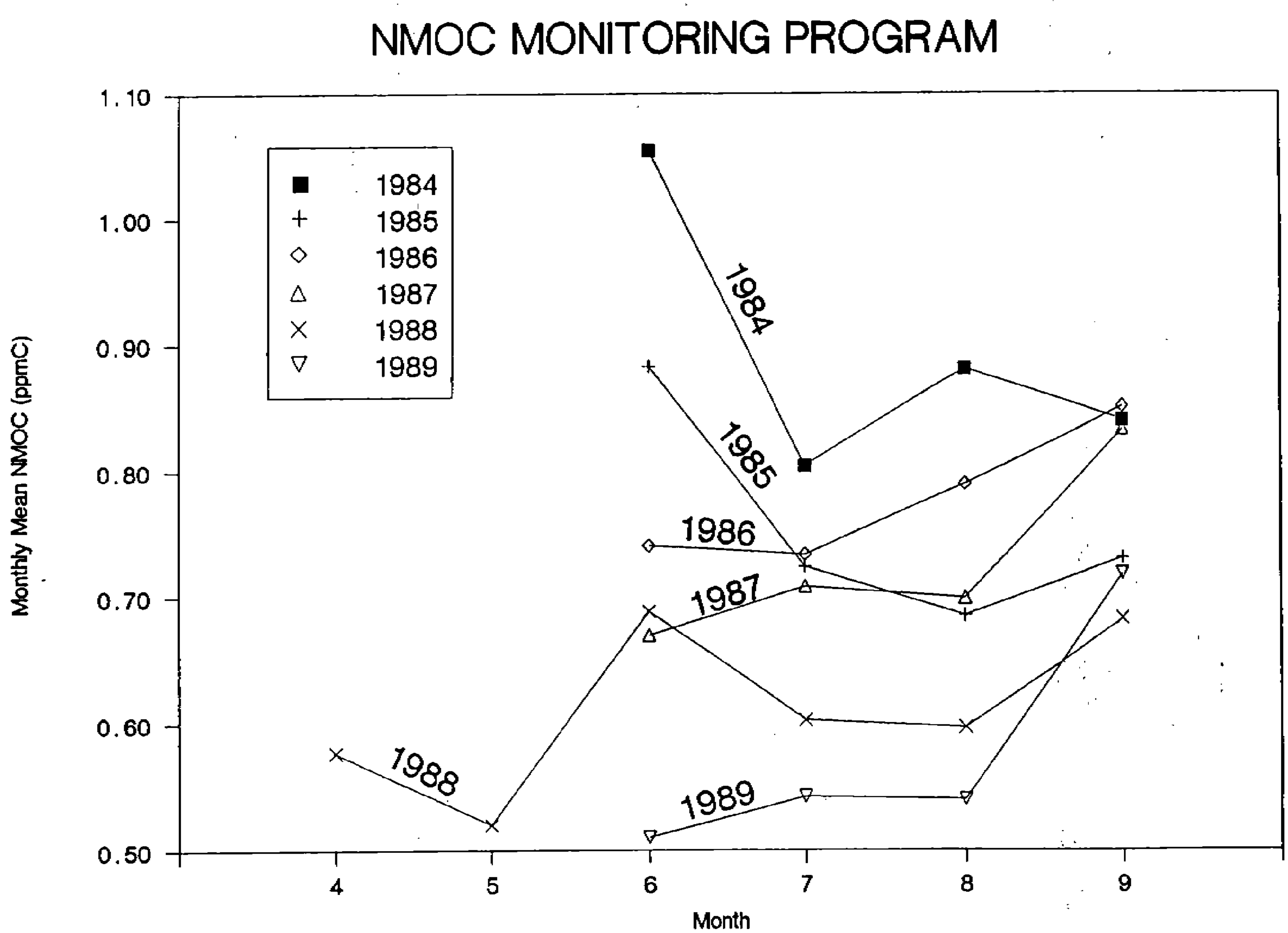


Figure 5-9. Monthly mean NMOC emissions for 1984 through 1989.

1988. Task 1 compared monthly average NMOC concentrations for 1988 with monthly average NMOC concentrations at the same site for years 1984 through 1987. A total of 18 sites participated in the NMOC Monitoring Program for the specified time periods.

Thirty-two monthly average NMOC concentrations were available for comparing 1984 data with 1988 data. In 28 out of 32 comparisons, monthly averages in 1988 were less than corresponding monthly averages in 1984. Thirty-nine monthly averages were available to compare 1985 with 1988; 34 out of 39 monthly averages in 1988 were less than corresponding monthly averages in 1985. Conclusions reached in Task 1 are that NMOC monthly average concentrations in 1988 were lower than corresponding monthly averages in 1984and 1985. The magnitude and pattern of the decreases for the 1988 data are site specific and specific to the years of the comparisons. It should be emphasized that even though the locations of the sites are the same from year to year, site average concentrations given in this study do not reflect the effects of meterological variables, wind speed and direction, solar radiation (presence of clouds), temperature, humidity, and changes in the topography that surrounds the site. Drawing conclusions relative to "average" site NMOC concentrations should be avoided without taking into account all of the meterological and topographical factors.

Comparison of 1988 monthly average NMOC concentrations with monthly average concentrations at the same site in 1986 and 1987 showed that no trends were discernable at the sites tested. Twenty-nine monthly comparisons were possible in 1986 and 48 in 1987.

Task 2 investigated correlation of maximum daily ozone concentrations with 6 a.m. to 9 a.m. NMOC concentrations for June and July 1988 at five urban centers -- New York, Newark, Plainfield, Houston, and Chicago. Maximum daily ozone concentrations at the urban site and at selected ozone receptor sites were plotted versus NMOC concentration at the urban source. Linear, quadratic, and cubic polynomial correlations were tested. Data involving Chicago were not useful in this study because there were insufficient data for the chosen time period. The remainder of the correlations showed significant linear relationships despite linear coefficients of regression lower than 0.550.

Task 3 was designed to relate canister age to NMOC concentration, at urban sites, and subsequently to maximum ozone at receptor sites, should measured NMOC concentration be a function of canister age. However, analysis of NMOC concentrations measured from duplicate sample canisters confirmed that no correlation existed between NMOC concentration and canister age.

5.3.1 Task 1

Task 1 compared monthly averages of NMOC concentrations for sites in the 1988 program with corresponding monthly averages for the same site that participated in the programs one or more previous years. Table 5-2 gives monthly NMOC concentration averages for June, July, August, and September for each site listed, showing the years the site participated in the monitoring program. Table 5-2 also shows the number of cases included in each monthly average. The number of cases at each site differed from year to year. For some sites there were considerable differences in the number of cases.

Certain of the monthly averages were derived from data obtained by Region III[12,13] and these data are flagged in Table 5-2. The remainder of the results in Table 1 were derived from data obtained by Radian Corporation.[3,5,6,7]

The Arlington, Virginia site data for 1987[13] were modified upon the recommendation of Region III.[14] There were three values of NMOC reported to be greater than 3.0 ppmC (3.621 on July 28, 9.061 on August 3, and 4.599 on September 23). Region III personnel have reason to believe that the sampling system was contaminated with acetone on those three days and recommended[14] that the values be removed from the data base for that reason.

Figures 5-10 through 5-27 display graphically the averages listed in Table 5-2. In general, the monthly average NMOC concentrations in 1985 are higher than the averages for 1988. The monthly averages for 1986 and 1987, on the other hand, show few trends when compared to the 1988 monthly averages. It is clear that any trends in the 1984 through 1988 monthly average NMOC concentrations are site specific. For example 1984 monthly averages for Beaumont, TX; Dallas, TX; El Paso, TX; Philadelphia, PA; and Washington, DC are clearly higher than 1988 monthly averages. Richmond, VA; Charlotte, NC; and Miami, FL on the other hand show a mixed comparison between 1984 and 1988.

TABLE 5-2. MONTHLY AVERAGE NONMETHANE ORGANIC COMPOUND CONCENTRATIONS

	June		July		August		September	
Year	Cases	Avg. NMOC Conc., ppmC	Cases	Avg. NMOC Conc., ppmC	Cases	Avg. NMOC Conc., ppmC	Cases	Avg. NMOC Conc., ppmC
Beaumont, TX (BMTX)								
1988	21	0.662	24	0.635	20	0.664	26	0.925
1987	25	0.590	26	0.757	23	0.548	27	0.823
1986	22	0.796	22	0.552	24	0.810	21	1.036
1985	22	1.992	25	2.103	25	1.558	21	1.391
1984	8	1.524	17	0.785	22	1.086	19	0.495
Dallas, TX (DLTX)								
1988	22	0.643	24	0.425	26	0.493	24	0.559
1987	21	0.836	23	0.531	20	0.518	21	0.687
1986	--	-	11	0.583	22	0.975	24	0.558
1985	19	1.112	22	0.737	22	0.892	19	0.735
1984	11	1.184	20	0.880	23	1.059	20	0.832
El Paso, TX (ELTX)								
1988	20	0.391	24	0.378	23	0.441	23	0.604
1987	24	0.369	23	0.362	23	0.430	23	0.589
1986	23	0.348	23	0.521	22	0.546	20	0.539
1985	22	0.862	33	0.673	25	0.578	21	0.735
1984	9	1.083	20	0.835	21	0.816	19	1.068
Philadelphia, PA (PHPA/P1PA)								
1988[a]	17	0.424	18	0.576	19	0.632	10	0.652
1987[a]	13	0.641	22	0.653	19	0.542	15	0.571
1986	23	0.443	22	0.488	24	0.421	--	-
1985	20	0.713	25	0.691	24	0.555	2	0.886
1984	2	0.940	20	1.030	24	0.896	17	1.191

(Continued)

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TABLE 5-2. (Continued)

Year	June		July		August		September	
	Cases	Avg. NMOC Conc., ppmC	Cases	Avg. NMOC Conc., ppmC	Cases	Avg. NMOC Conc., ppmC	Cases	Avg. NMOC Conc., ppmC
Washington, DC (WDC)								
1988	20	0.375	19	0.500	22	0.468	11	0.569
1987	22	0.519	22	0.478	20	0.476	17	0.509
1986	22	0.385	25	0.351	22	0.330	2	0.222
1985	11	0.890	24	0.608	25	0.653	3	0.865
1984	2	0.760	21	0.758	22	0.869	18	0.834
Houston, TX (H1TX)								
1988	12	1.208	22	0.980	26	1.032	23	1.113
1987	26	0.814	27	1.014	22	0.856	24	1.239
1986	22	1.130	25	0.823	21	1.215	23	1.333
1985	12	1.262	22	0.743	11	1.067	22	0.784
Baltimore, MD (BLMD)								
1988[a]	21	0.545	20	0.571	23	0.668	12	0.641
1987[a]	22	0.620	23	0.606	20	0.578	21	0.640
1986	17	0.565	24	0.588	21	0.534	--	-
New York, NY (MNY)								
1988	17	0.763	26	0.773	16	0.659	18	0.795
1987	17	0.751	22	0.764	21	0.784	19	0.724
1986	23	0.544	25	0.636	20	0.606	23	0.673

(Continued)

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TABLE 5-2. (Continued)

	June		July		August		September	
Year	Cases	Avg. NMOC Conc., ppmC	Cases	Avg. NMOC Conc., ppmC	Cases	Avg. NMOC Conc., ppmC	Cases	Avg. NMOC Conc., ppmC
Richmond, VA (RVA)								
1988[a]	21	0.321	18	0.359	22	0.140	10	0.601
1985	19	0.699	23	0.458	25	0.491	--	-
1984	2	0.950	19	0.543	25	0.503	18	0.515
St. Louis, MO (SLMO)								
1988	19	0.783	23	0.585	24	0.642	23	0.667
1987	23	1.316	23	1.031	24	0.662	26	0.642
1985	22	0.758	21	0.793	21	0.645	23	0.669
Charlotte, NC (CHNC)								
1988	10	0.496	11	0.459	22	0.482	22	0.443
1984	--	-	15	0.377	25	0.490	20	0.716
Memphis, TN (MTN/M1TN)								
1988	20	1.046	20	0.977	20	0.895	24	0.883
1984	--	-	11	1.140	20	1.402	21	1.614
Miami, FL (MIF[illegible]								
1988		0.978	19	0.801	23	1.320	27	1.153
1984	--	-	--	-	12	1.622	19	1.121
Cleveland, OH (CLOH)								
1988	18	0.681	22	1.010	23	0.862	24	0.713
1985	12	0.818	22	0.728	26	0.889	22	0.984

(Continued)

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TABLE 5-2. (Continued)

Year	June		July		August		September	
	Cases	Avg. NMOC Conc., ppmC	Cases	Avg. NMOC Conc., ppmC	Cases	Avg. NMOC Conc., ppmC	Cases	Avg. NMOC Conc., ppmC
Philadelphia, PA (P2PA)								
1988[a]	20	0.502	20	0.597	23	0.627	44	0.548
1985	18	0.582	21	0.721	21	0.778	2	1.034
Arlington, VA (ARVA)								
1988[a]	19	0.387	14	0.362	20	0.485	11	0.498
1987[a]	22	0.628	18	0.874	17	0.732	15	0.878
Boston, MA (B2MA)								
1988	18	0.858	23	0.646	23	0.494	27	0.592
1987	25	0.541	26	0.798	23	0.894	27	0.490
Newark, NJ (NWNJ)								
1988	21	0.876	21	0.868	25	0.755	26	0.707
1987	23	0.645	22	0.646	22	0.887	25	0.890

[a]Data from Region III study.

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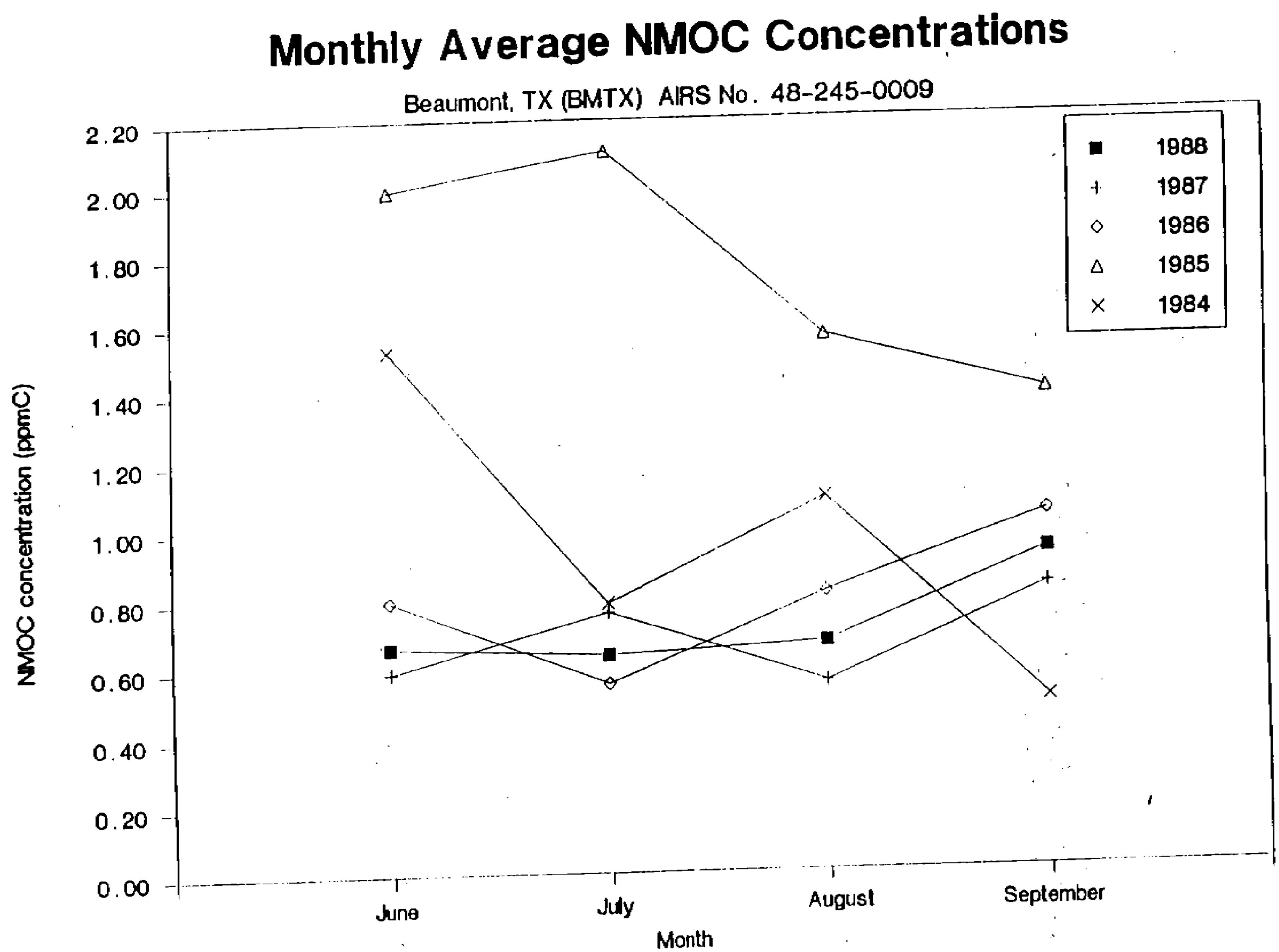

Figure 5-10. Monthly average NMOC concentrations for Beaumont, TX site.

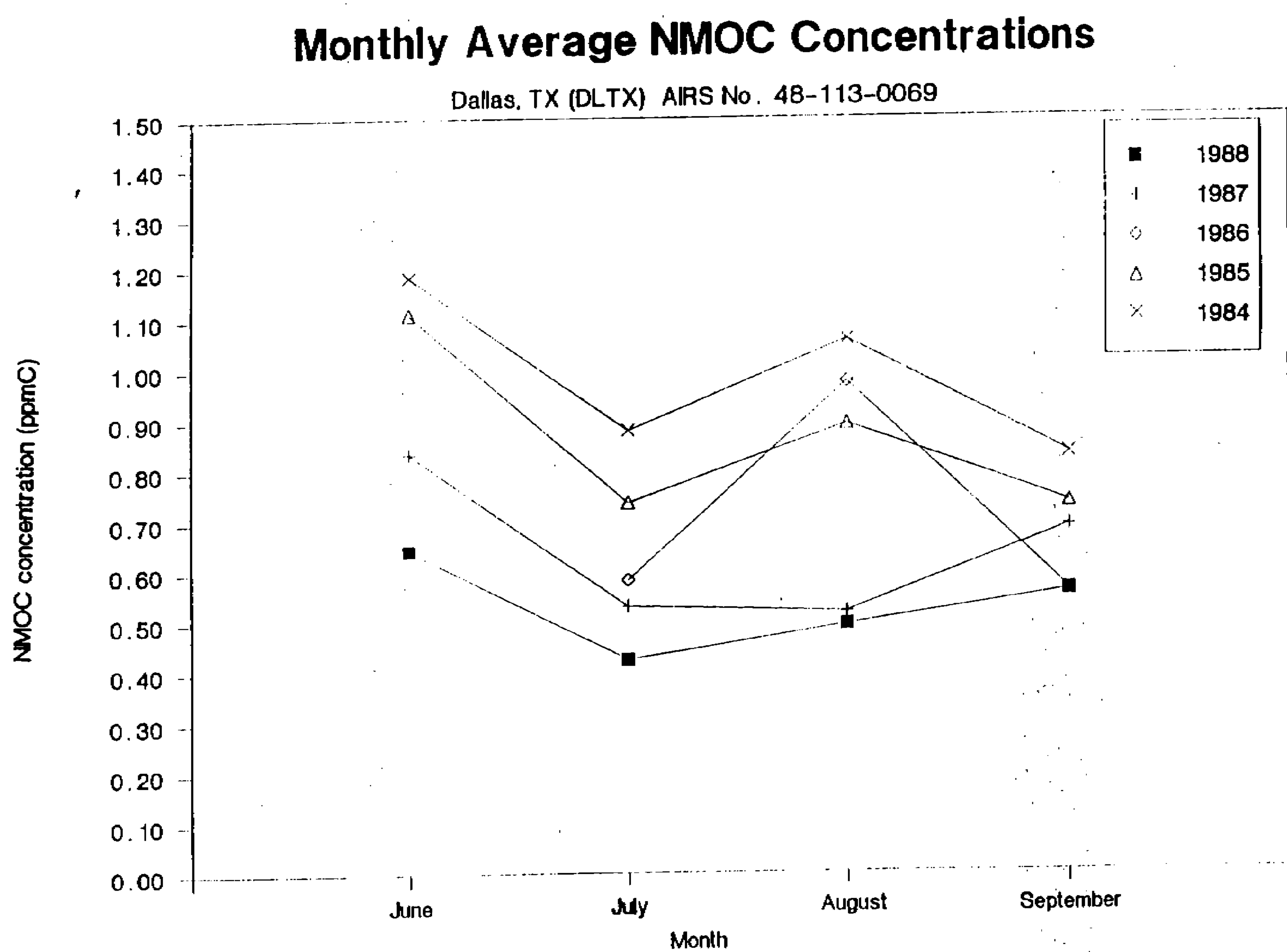

Figure 5-11. Monthly average NMOC concentrations for Dallas, TX site.

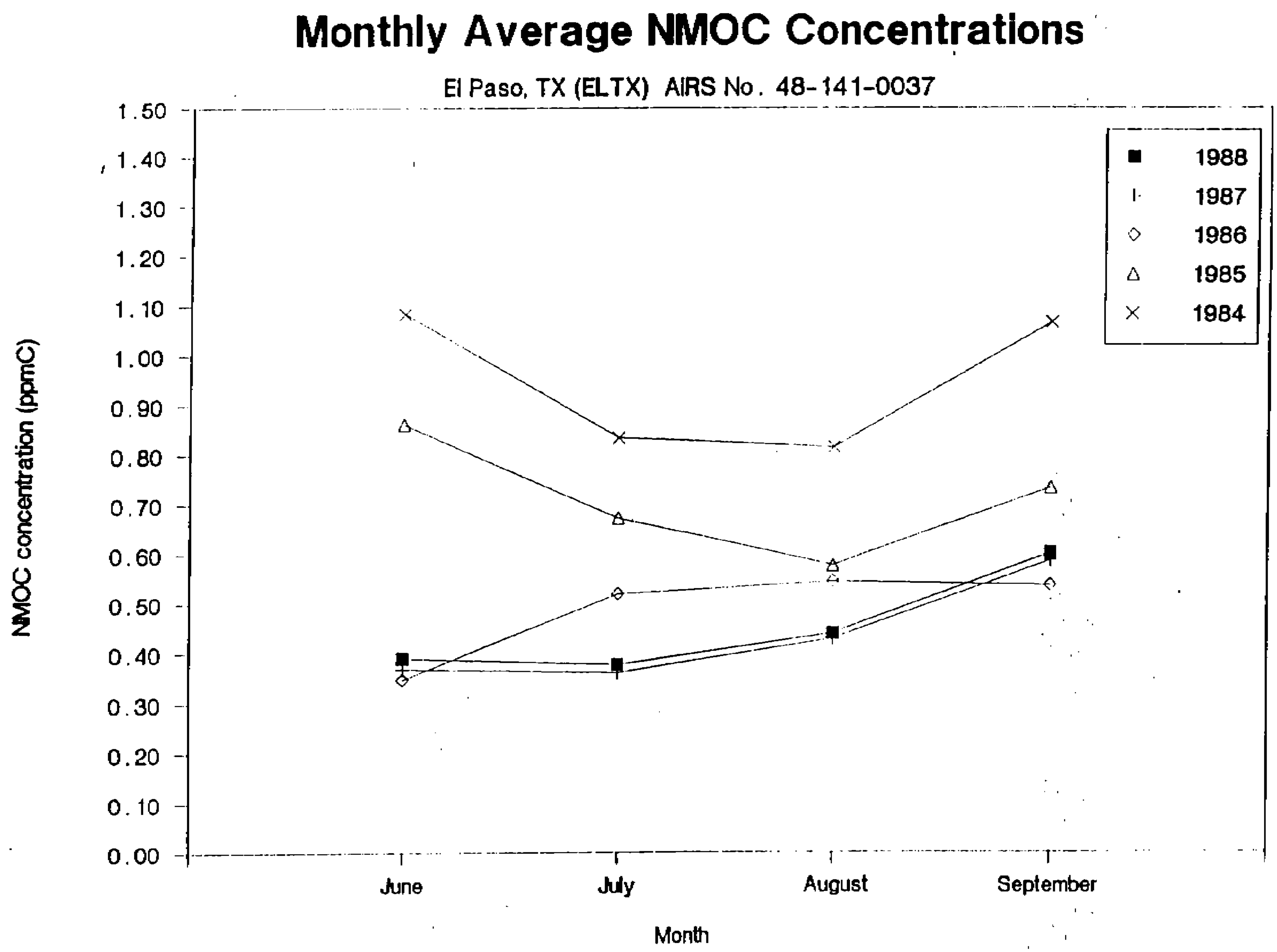

Figure 5-12. Monthly average NMOC concentrations for El Paso, TX site.

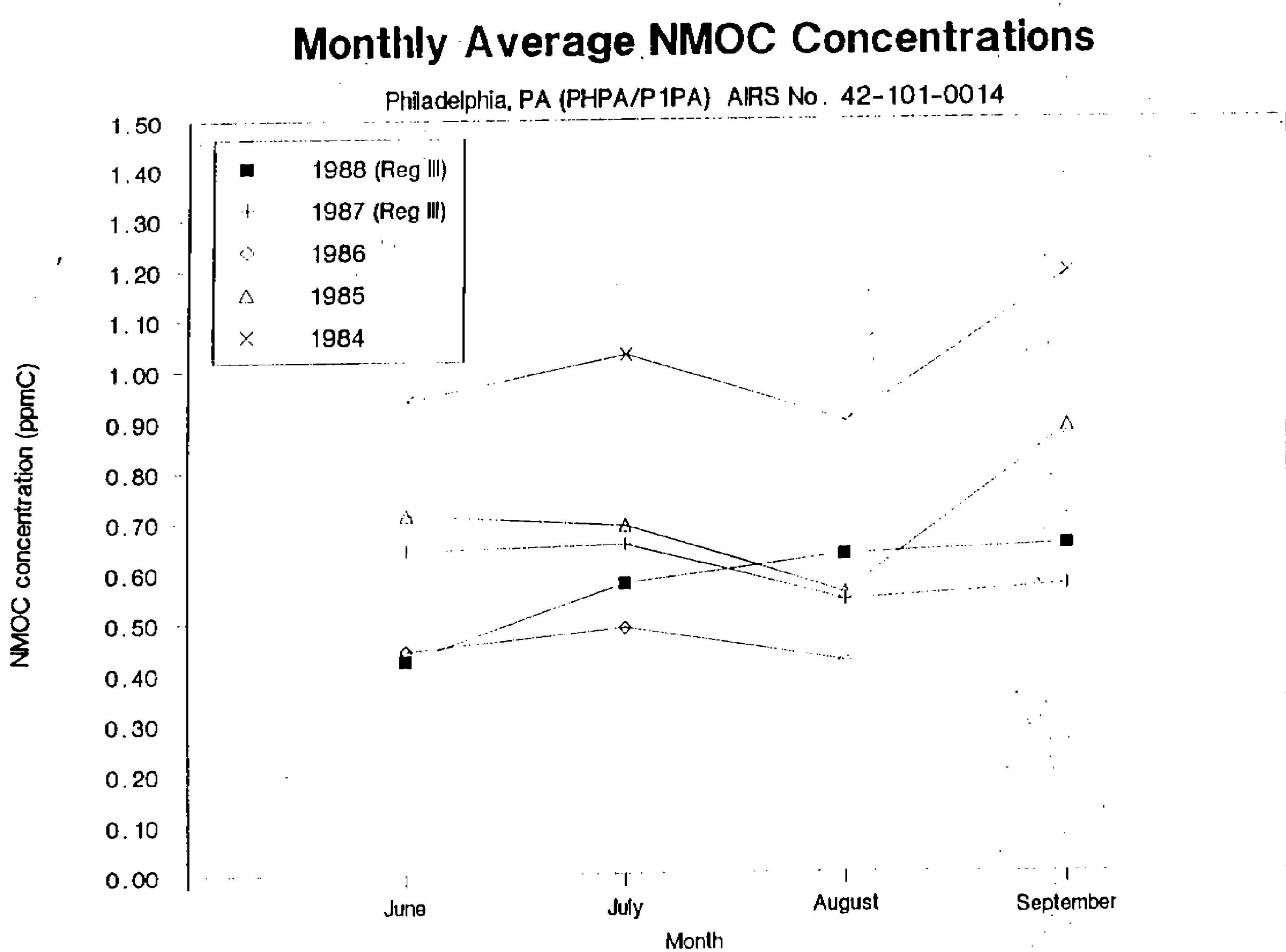

Figure 5-13. Monthly average NMOC concentrations for Philadelphia, PA site.

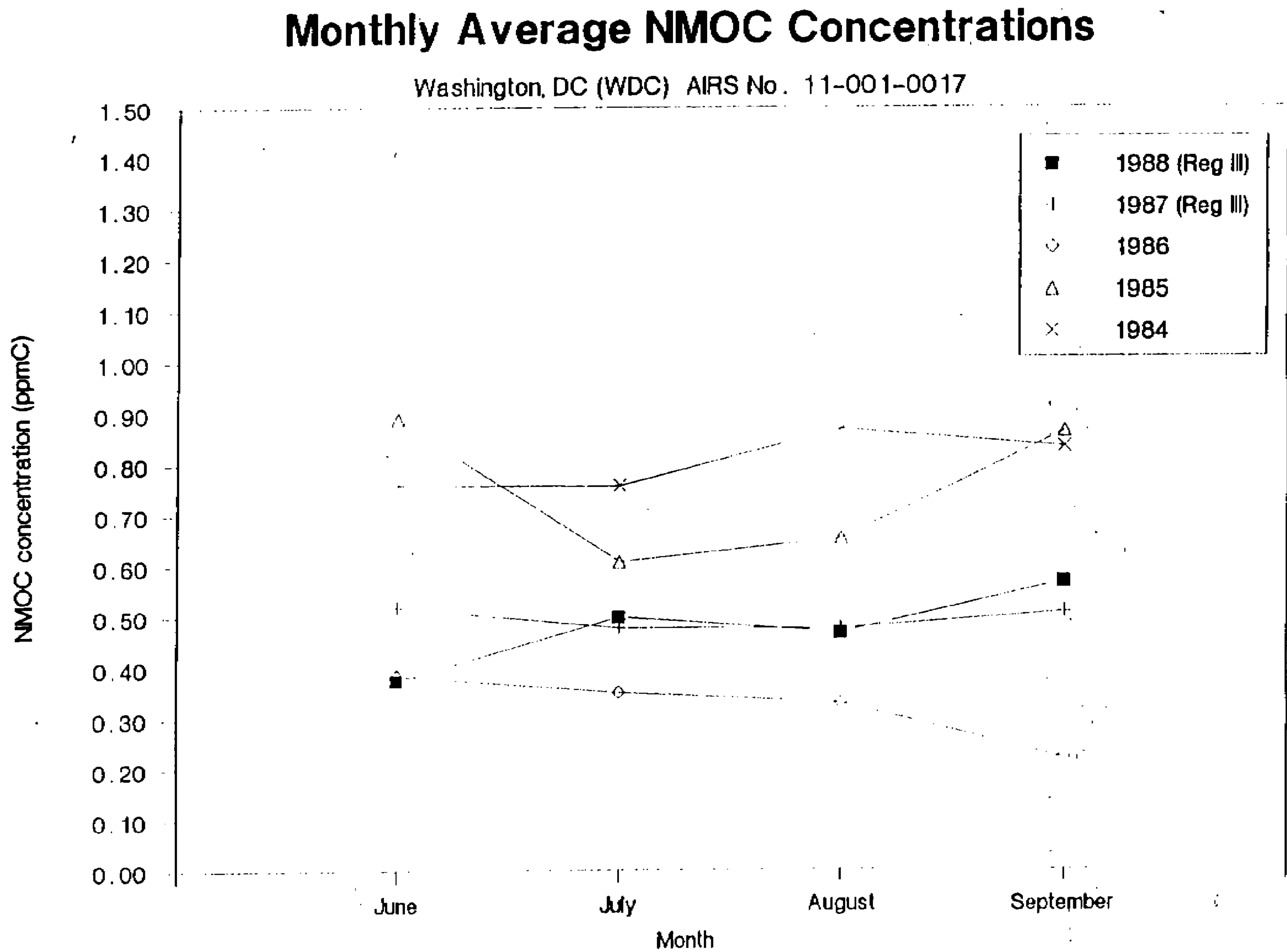

Figure 5-14. Monthly average NMOC concentrations for Washington, DC site.

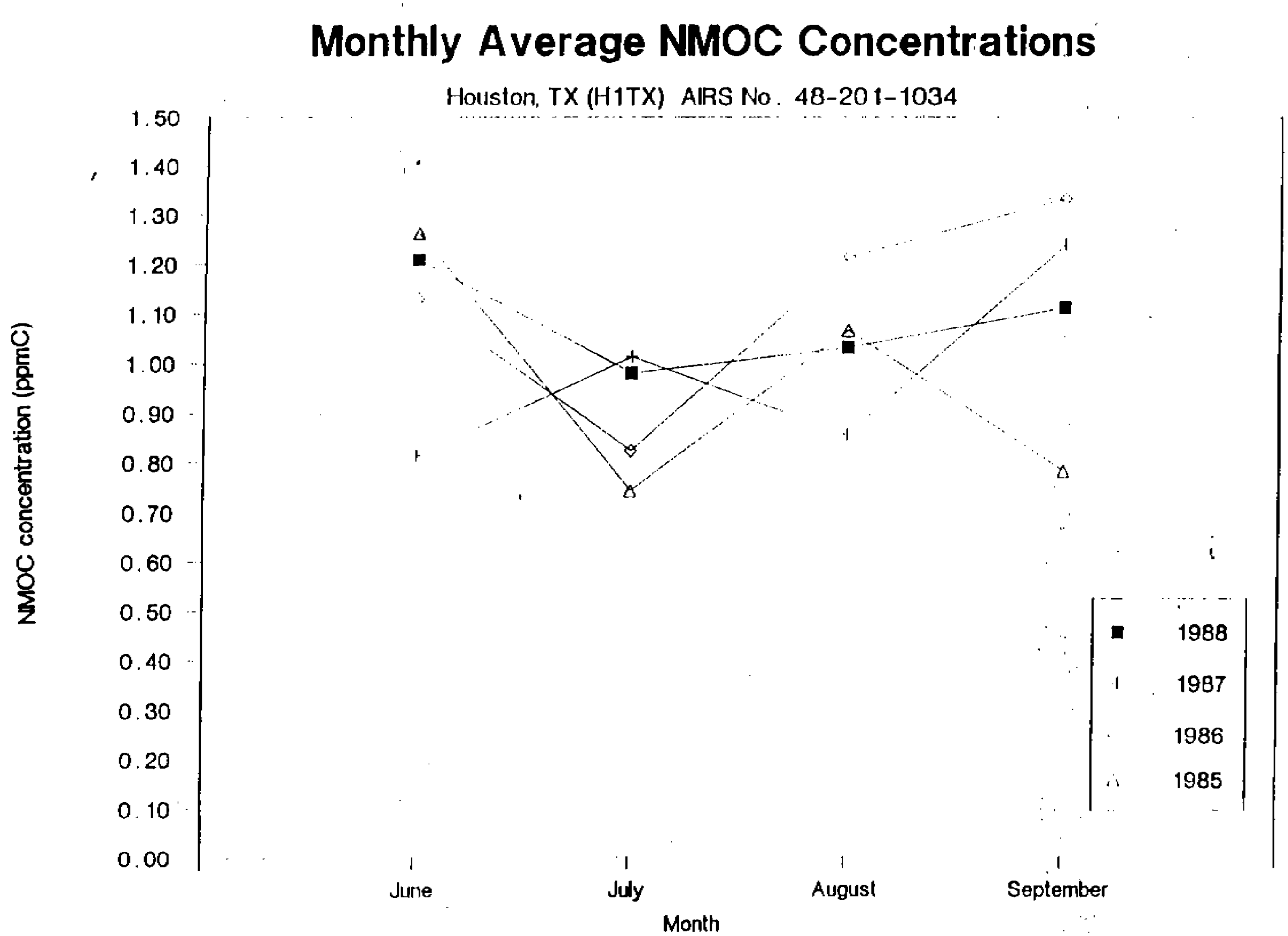

Figure 5-15. Monthly average NMOC concentrations for Houston, TX site.

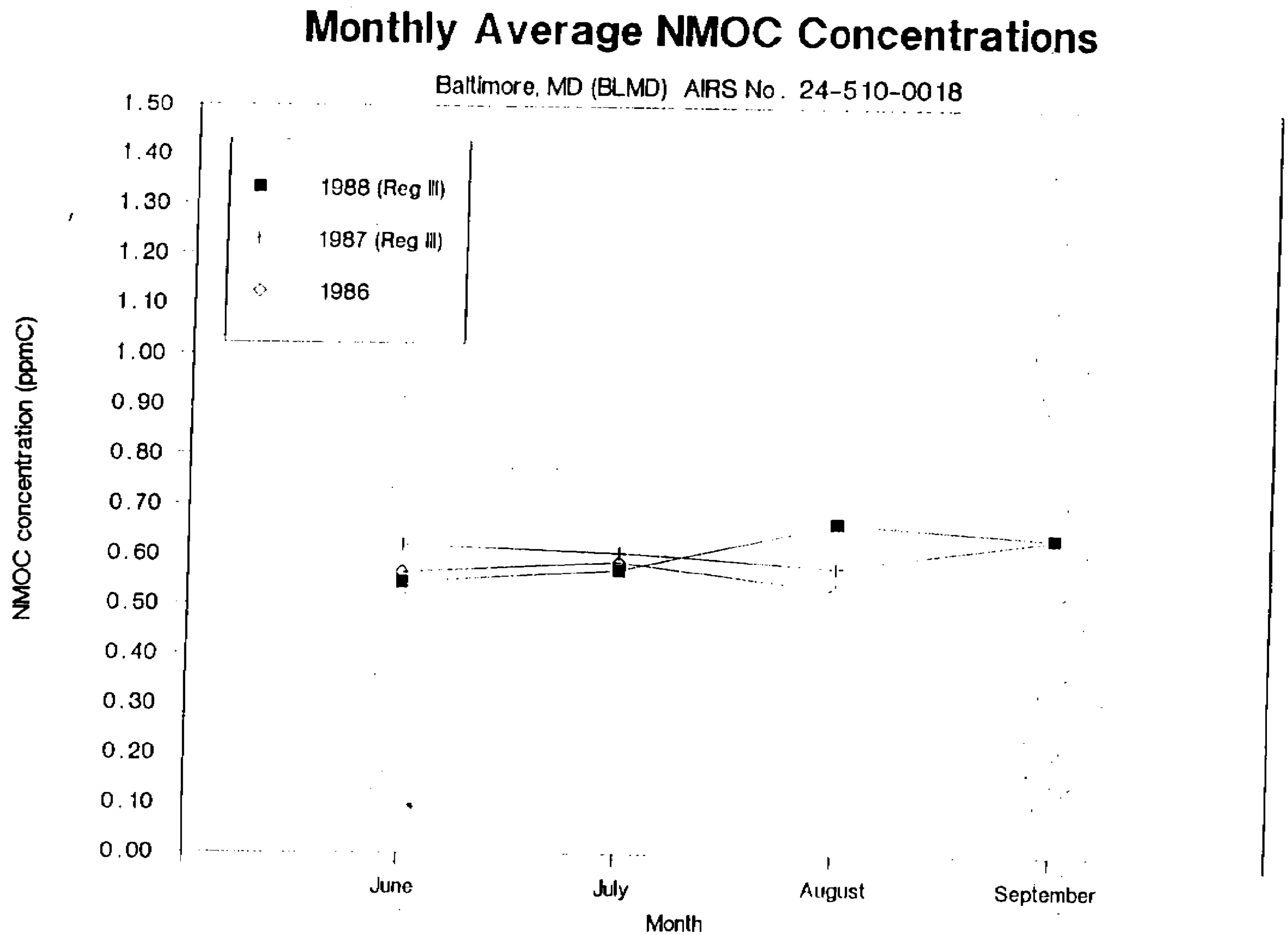

Figure 5-16. Monthly average NMOC concentrations for Baltimore, MD site.

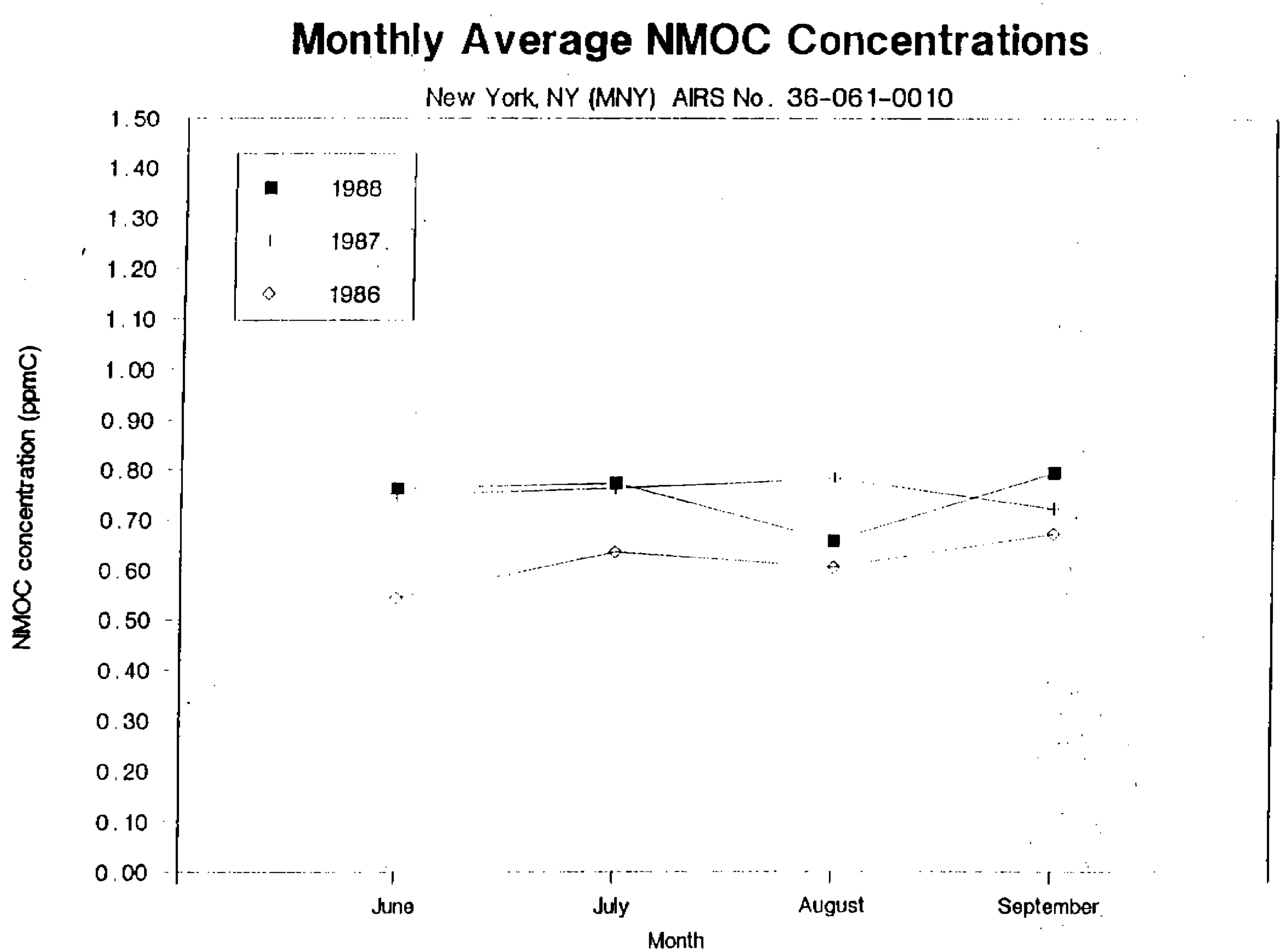

Figure 5-17. Monthly average NMOC concentrations for New York, NY site.

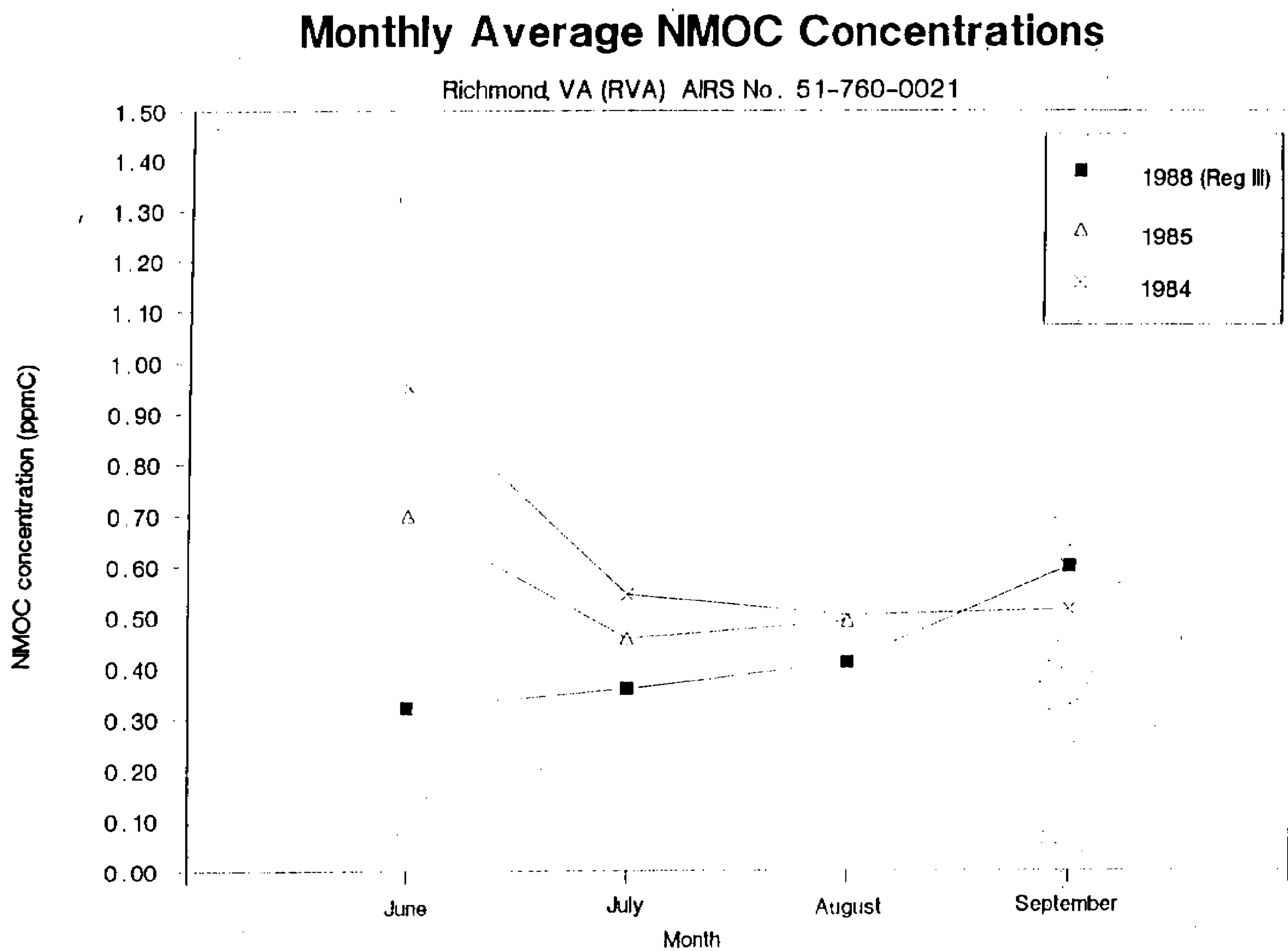

Figure 5-18. Monthly average NMOC concentrations for Richmond, VA site.

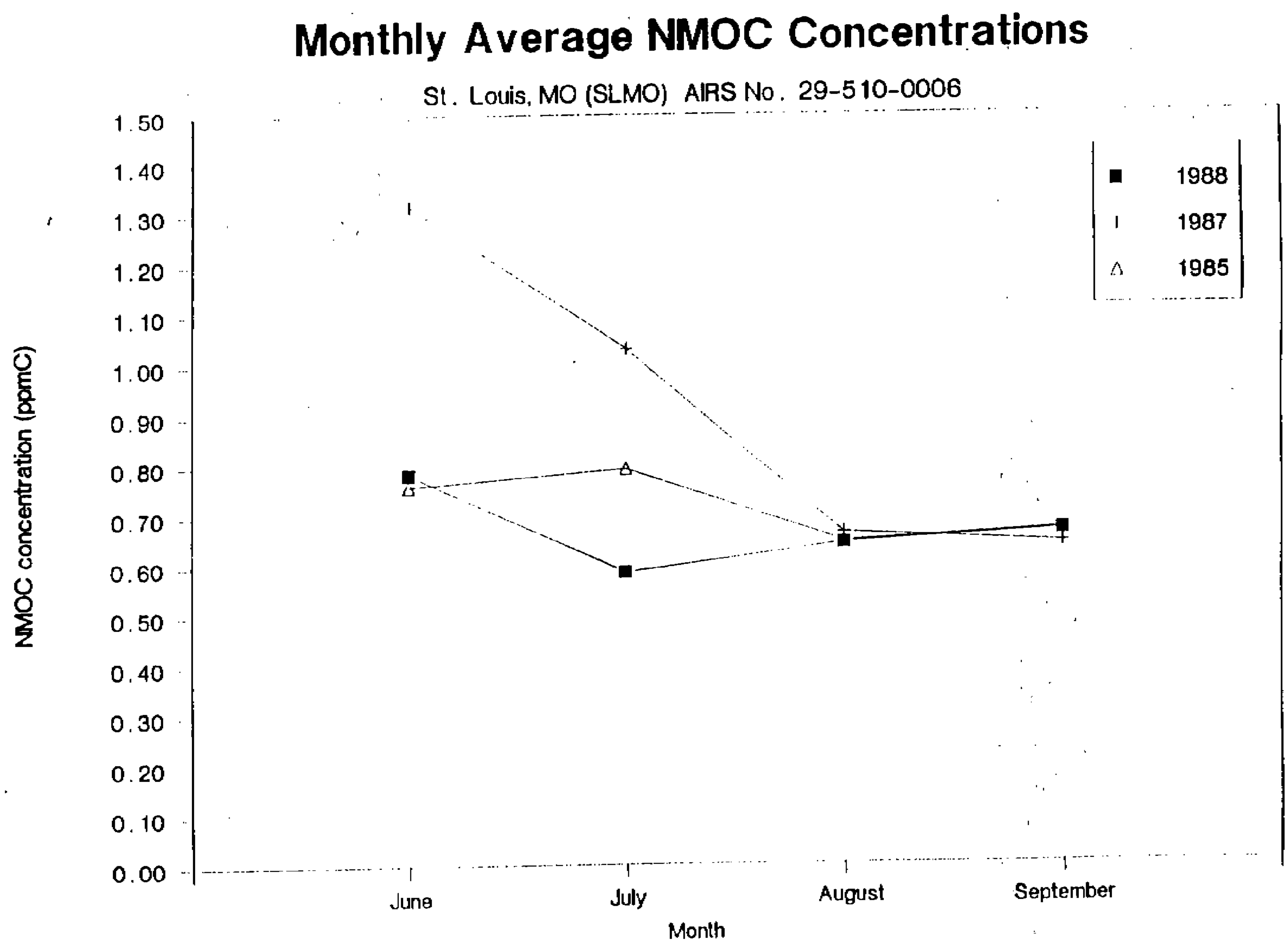

Figure 5-19. Monthly average NMOC concentrations for St. Louis, MO site.

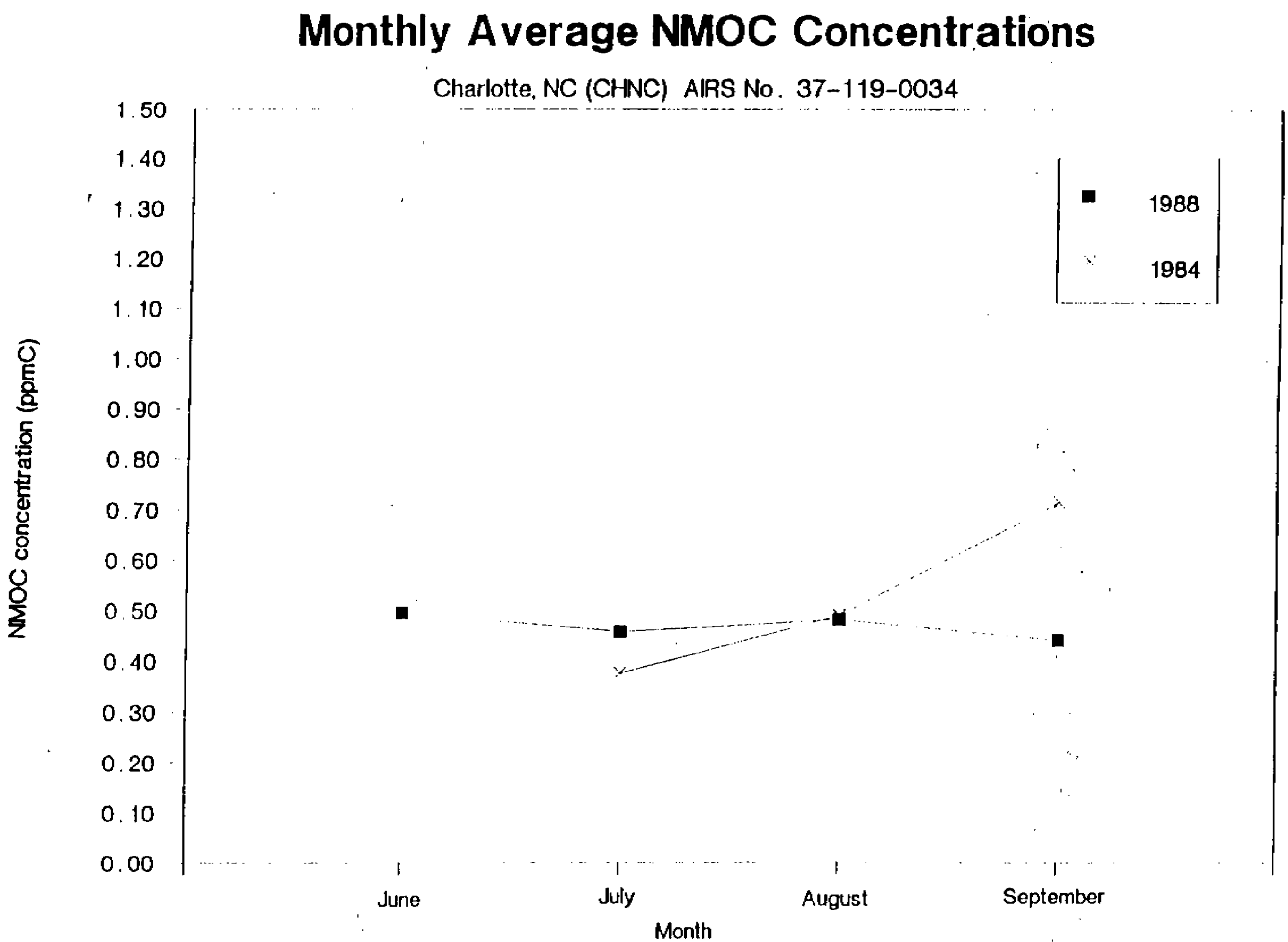

Figure 5-20. Monthly average NMOC concentrations for Charlotte, NC site.

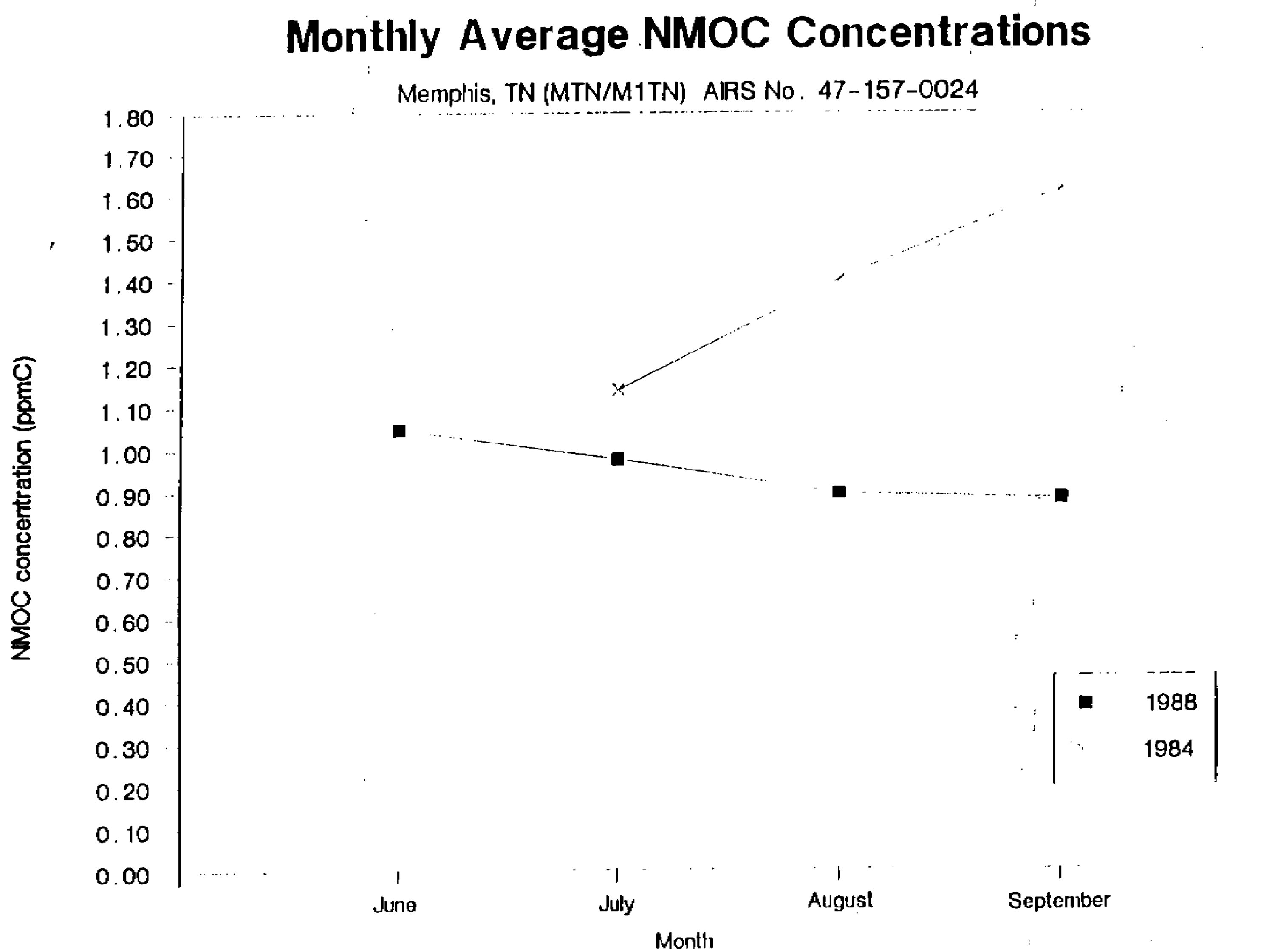

Figure 5-21. Monthly average NMOC concentrations for Memphis, TN site.

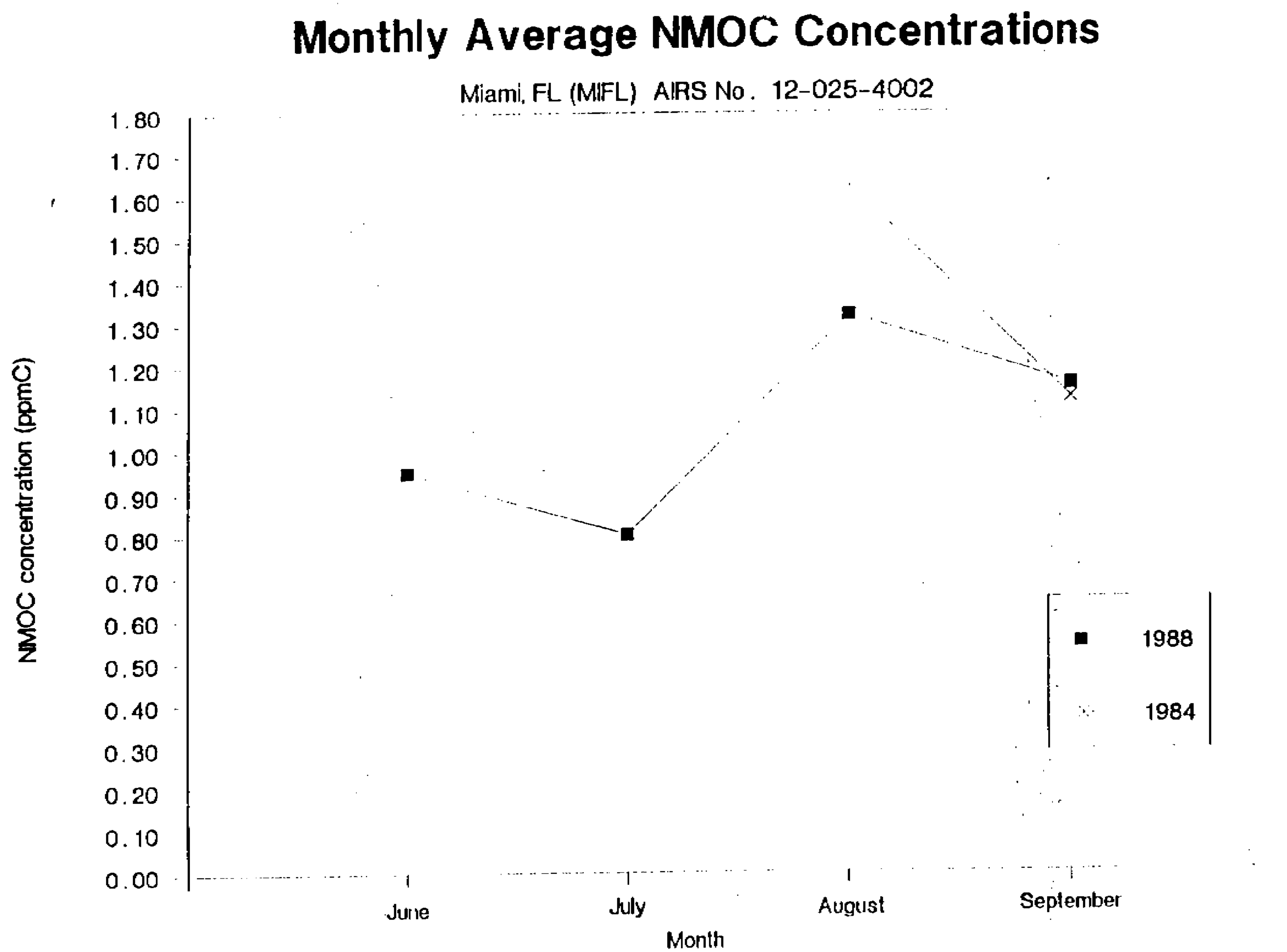

Figure 5-22. Monthly average NMOC concentrations for Miami, FL site.

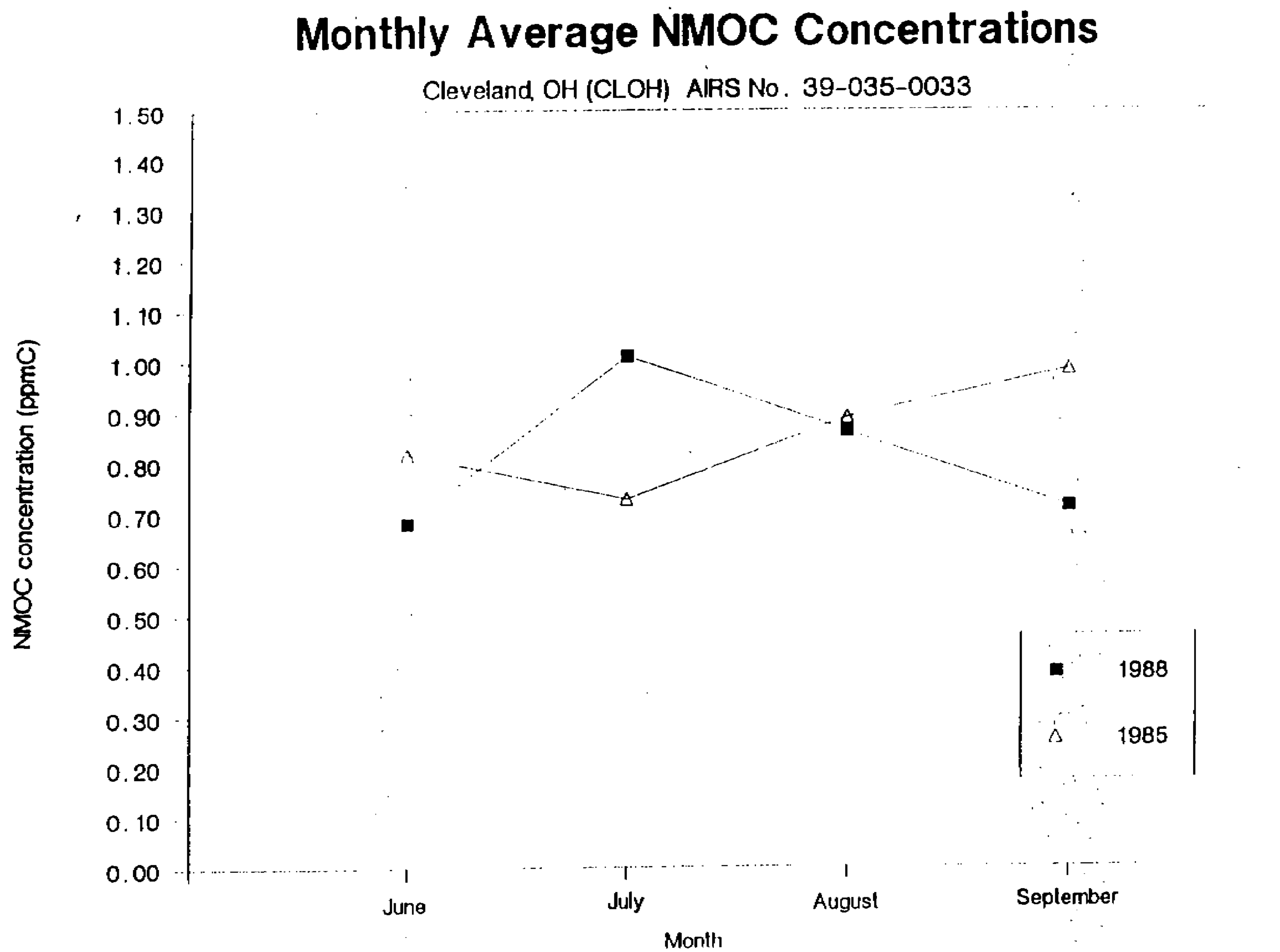

Figure 5-23. Monthly average NMOC concentrations for Cleveland, OH site.

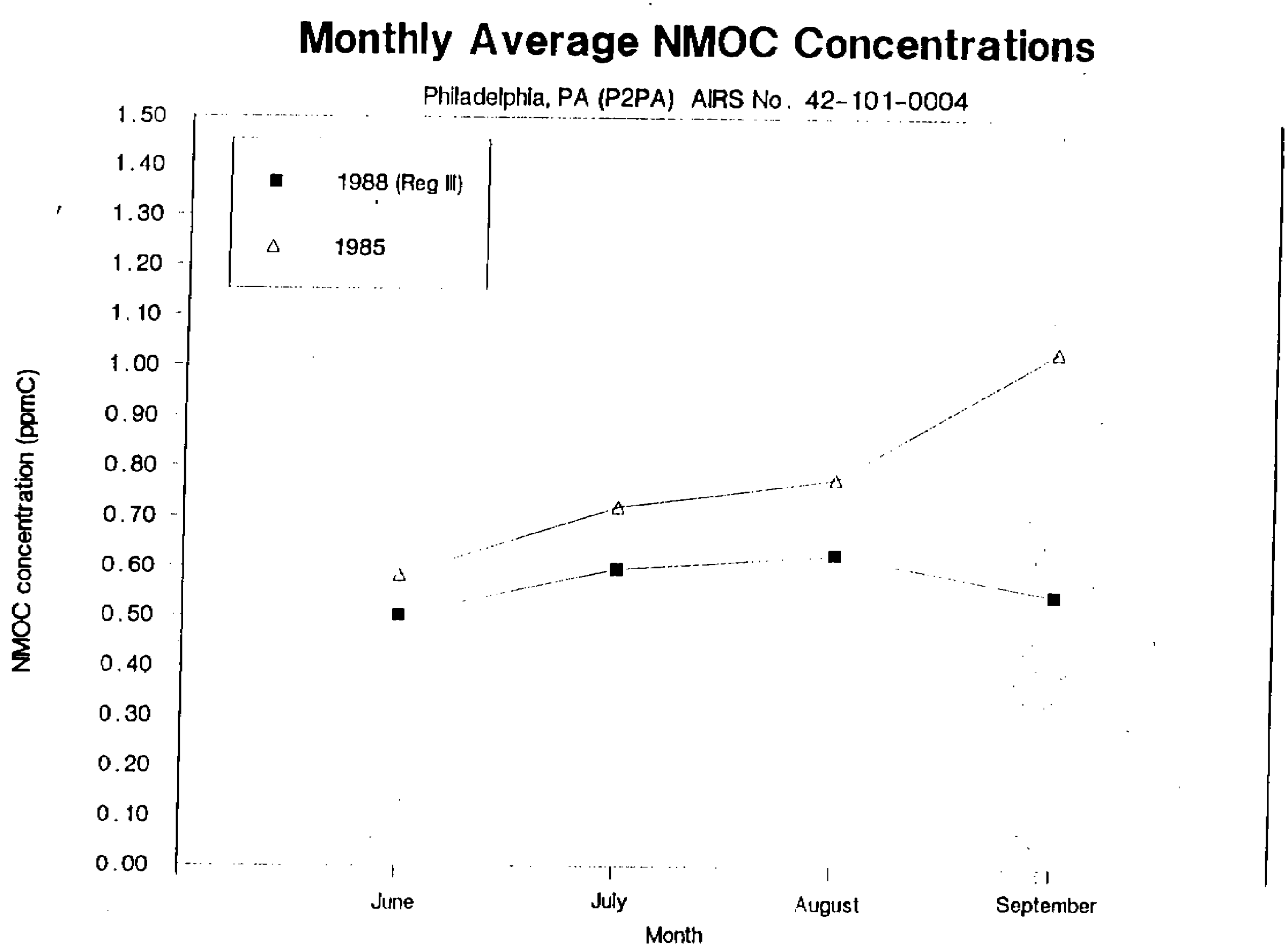

Figure 5-24. Monthly average NMOC concentrations for second Philadelphia, PA site.

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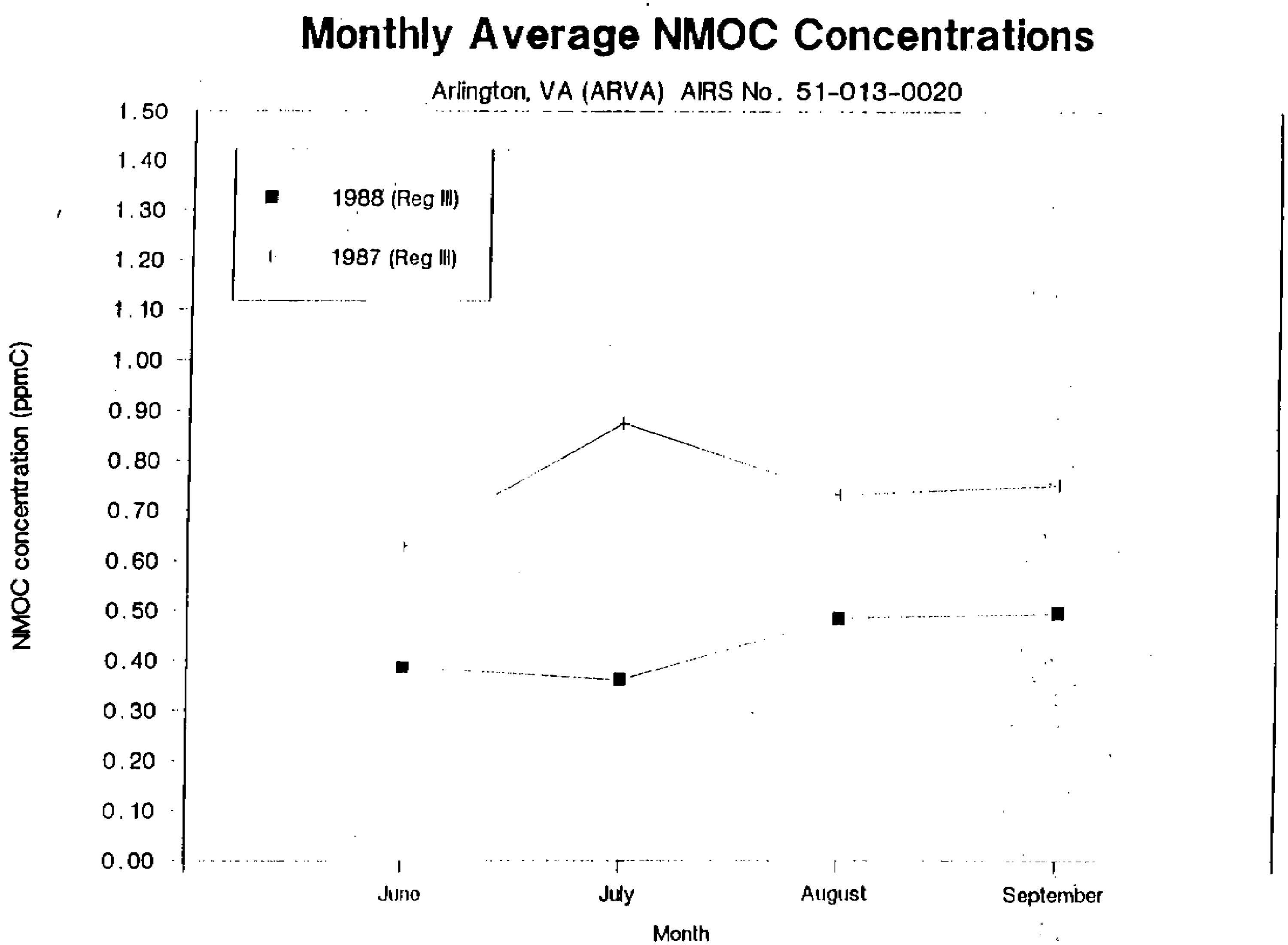

Figure 5-25. Monthly average NMOC concentrations for Arlington, VA site.

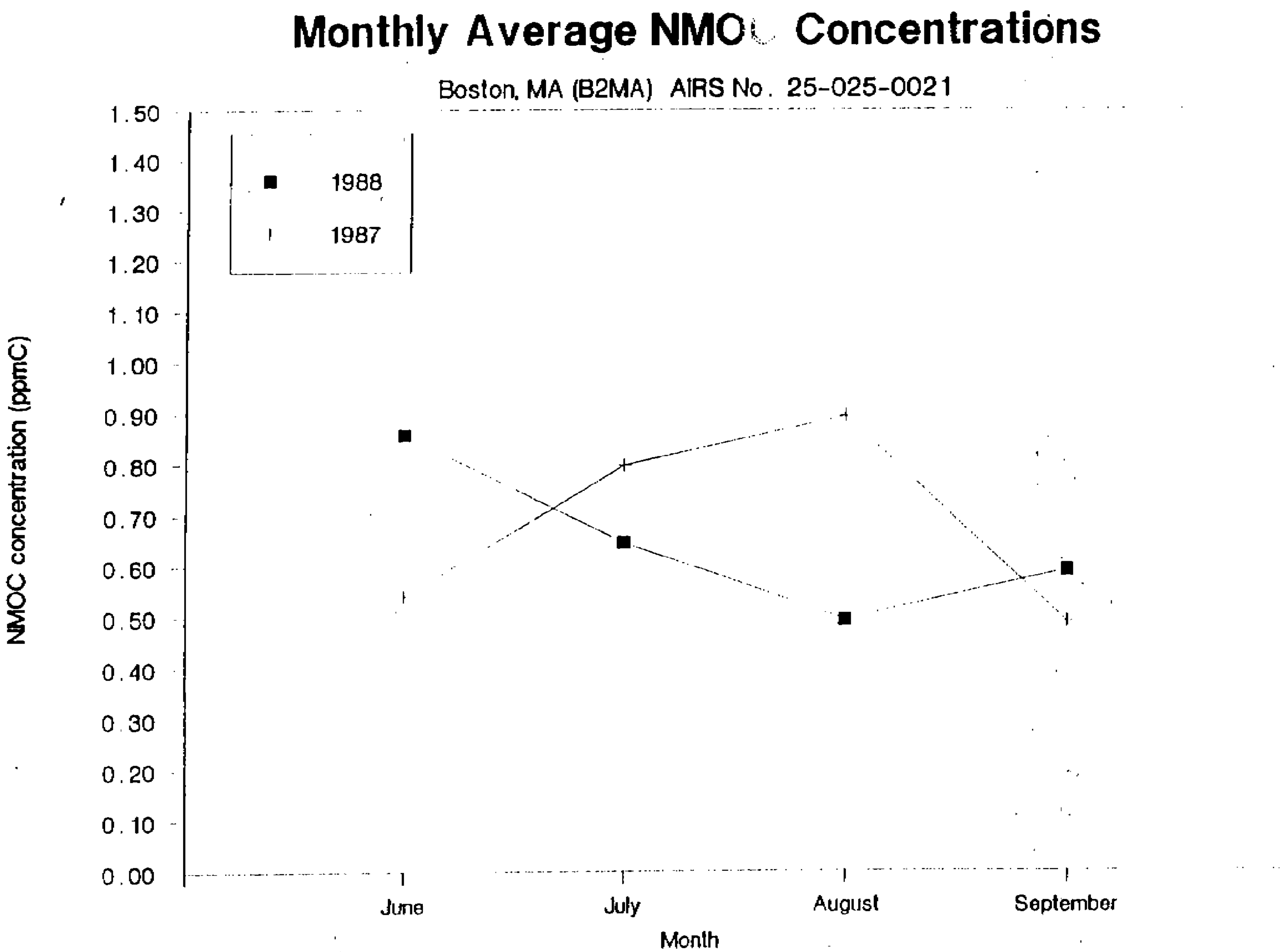

Figure 5-26. Monthly average NMOC concentrations for Boston, MA site.

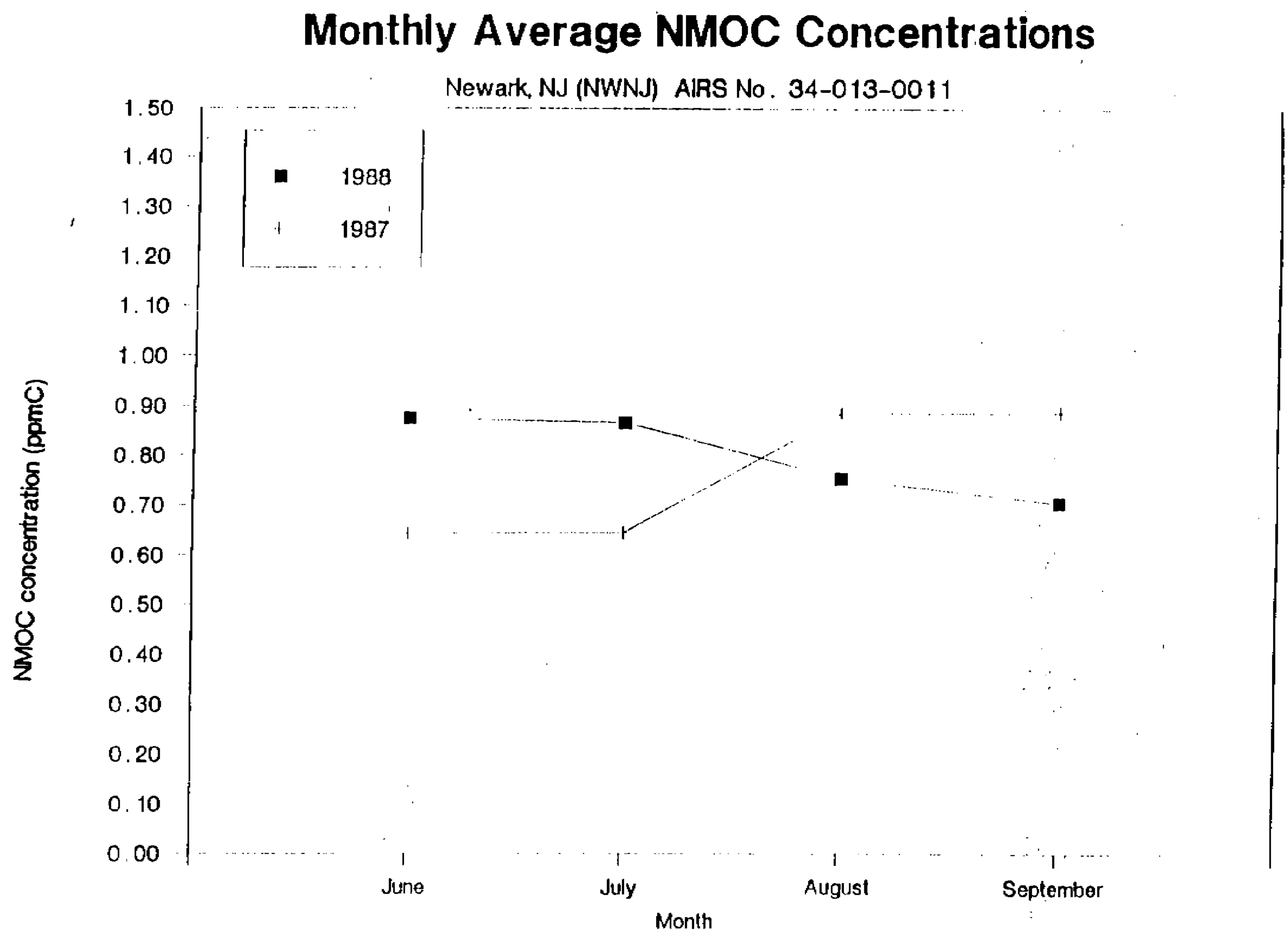

Figure 5-27. Monthly average NMOC concentrations for Newark, NJ site.

Comparing the 1985 results with the 1988 results emphasizes the strongly site-specific nature of the data.

The 1986 and 1987 data show virtually random behavior with respect to the 1988 data. These observations are summarized in Table 5-3, which shows a comparison of monthly average NMOC concentrations between 1988 and comparison years 1984, 1985, 1986, and 1987. Table 5-3 shows the number of months in 1988 for which the corresponding month in the comparison year showed a higher (or lower) monthly average NMOC concentration. The final column in Table 5-3 shows the probability that y or fewer months in 1988 had higher average monthly NMOC concentrations in the comparison year by random processes. It shows that in 1984, the four (or fewer) lower monthly average NMOC concentrations could not have occurred at random, with a 99.99903% probability. Similarly the fact that in 1985, the monthly average NMOC concentration occurred 5 (or fewer) times out of 37 comparisons could not have happened at random, with a 99.999987% probability.

Comparing 1986 data with 1988 and 1987 data with 1988 shows about an equal probability, so that no trends are readily apparent among the 1986, 1987, and 1988 monthly average NMOC concentrations.

5.3.2 Task 2

The purpose of this task was to correlate the daily maximum ozone concentration at a receptor site to the 6 a.m. to 9 a.m. NMOC integrated average concentration at a source site for June and July 1988. NMOC source and ozone receptor sites used for this study are listed in Table 5-4. Maximum daily ozone concentrations in ppmv were used as the dependent variable, while NMOC concentration in ppmC (and/or its square, and/or its cube) was used as the independent variable. Correlations tested were:

$$(O_3)_{max} = a_1 + b_1 \text{ (NMOC)}, \quad (1)$$

$$(O_3)_{max} = a_2 + b_2 \text{ (NMOC)} + c_2 \text{ (NMOC)}^2, \text{ and} \quad (2)$$

$$(O_3)_{max} = a_3 + b_3 \text{ (NMOC)} + c_3 \text{ (NMOC)}^2 + d_3 \text{ (NMOC)}^3. \quad (3)$$

The results of the data analysis are given in Figures 5-28 through 5-35 and in Table 5-5. The figures plot daily maximum ozone concentration (ppmv) as the ordinate and the 6 a.m. to 9 a.m. integrated average NMOC

TABLE 5-3. COMPARISON OF MONTHLY AVERAGE NMOC CONCENTRATIONS

Comparison Year	No. Months in 1988 < Corresponding Month in Comparison year, x	No. Months in 1988 > Corresponding Month in Comparison year, y	n= x+y	$P(z \le y)$[a]
1984	28	4	32	9.651×10^{-6}
1985	34	5	39	1.215×10^{-6}
1986	13	16	29	0.7709
1987	25	23	48	0.4427

[a] $P(z \le y)$ is the probability that y (or fewer) cases could occur by random processes.

$P(y) = \binom{n}{y} p^y q^{n-y}$, the binominal probability that y occurred out of n cases. Quantities p and q for the comparisons made in this study equal 0.5.

TABLE 5-4. SITES FOR JUNE AND JULY 1988 OZONE-NMOC CORRELATION

NMOC Site Code	NMOC Site Location	Modeled Ozone Receptor Site	Receptor Site AIRS Number
C6IL	Chicago, IL	Evanston, IL	17-031-7002
		Waukegan, IL	17-097-1002
H1TX	Houston, TX (Mae Drive)	Aldine, TX	48-201-0024
		NW Harris Co.	48-201-0029
		Mae Drive	48-201-1034
MNY	New York, NY (Mable Dean)	Greenwich, CT	09-001-0017
		Bayonne, NJ	34-017-0006
		Mable Dean	36-061-0010
NWNJ	Newark, NJ	Bayonne, NJ	34-017-0006
		Plainfield, NJ	34-035-1001
		Newark, NJ	34-013-0011
PLNJ	Plainfield, NJ	Bayonne, NJ	34-017-0006
		Newark, NJ	34-013-0011
		Plainfield, NJ	34-035-1001
PLNJ & NWNJ & MNY[a]	Plainfield, NJ, Newark, NJ, and New York, NY	Greenwich, CT	09-001-0017
		Bayonne, NJ	34-017-0006
NWNJ & PLNJ[b]	Newark and Plainfield, NJ	Bayonne, NJ	34-017-0006

[a]NMOC daily concentrations are averaged for Plainfield, Newark, and New York.

[b]NMOC daily concentrations are averaged for Newark and Plainfield, NJ.

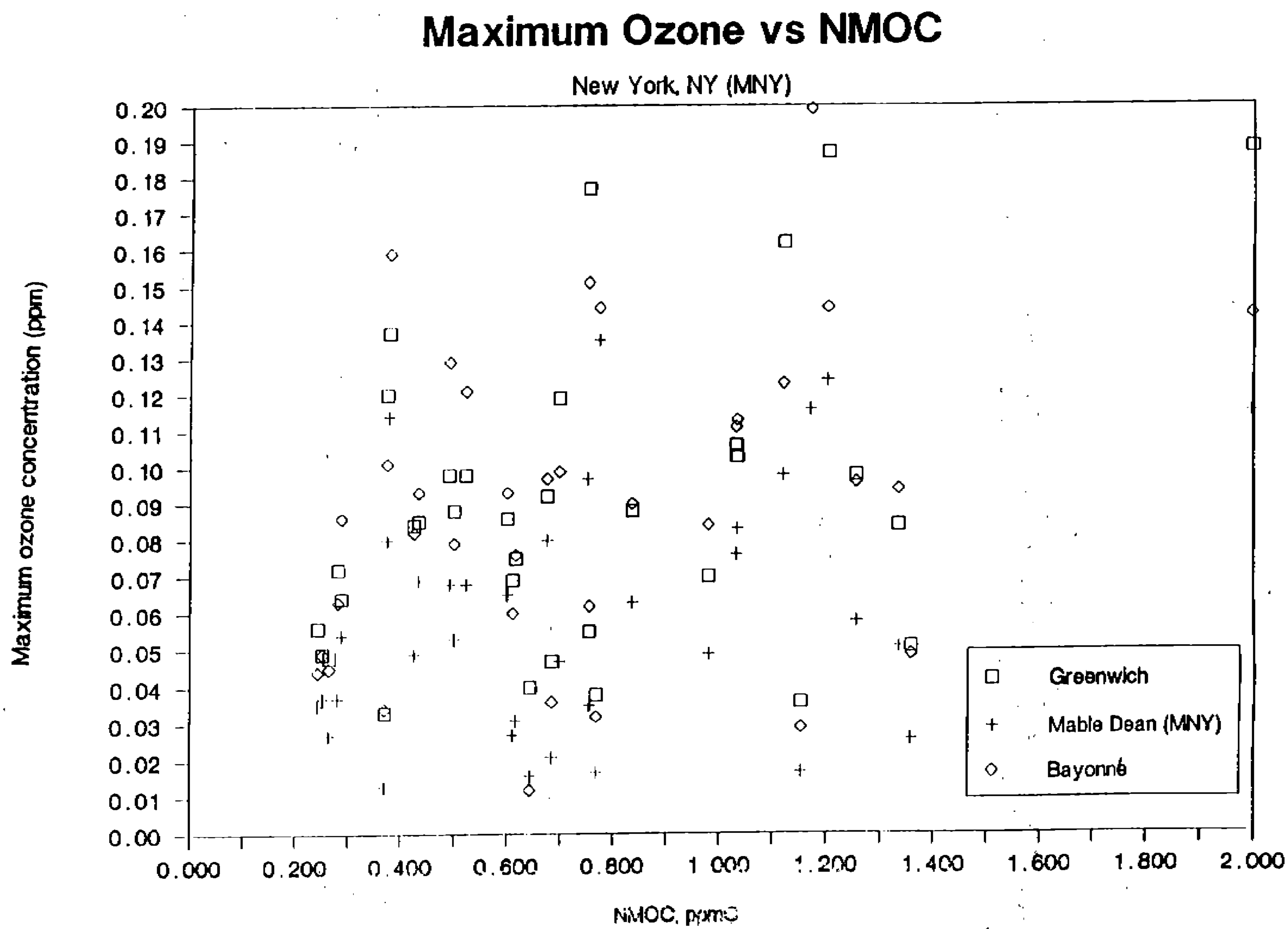

Figure 5-28. Maximum ozone versus NMOC concentration for New York, NY site.

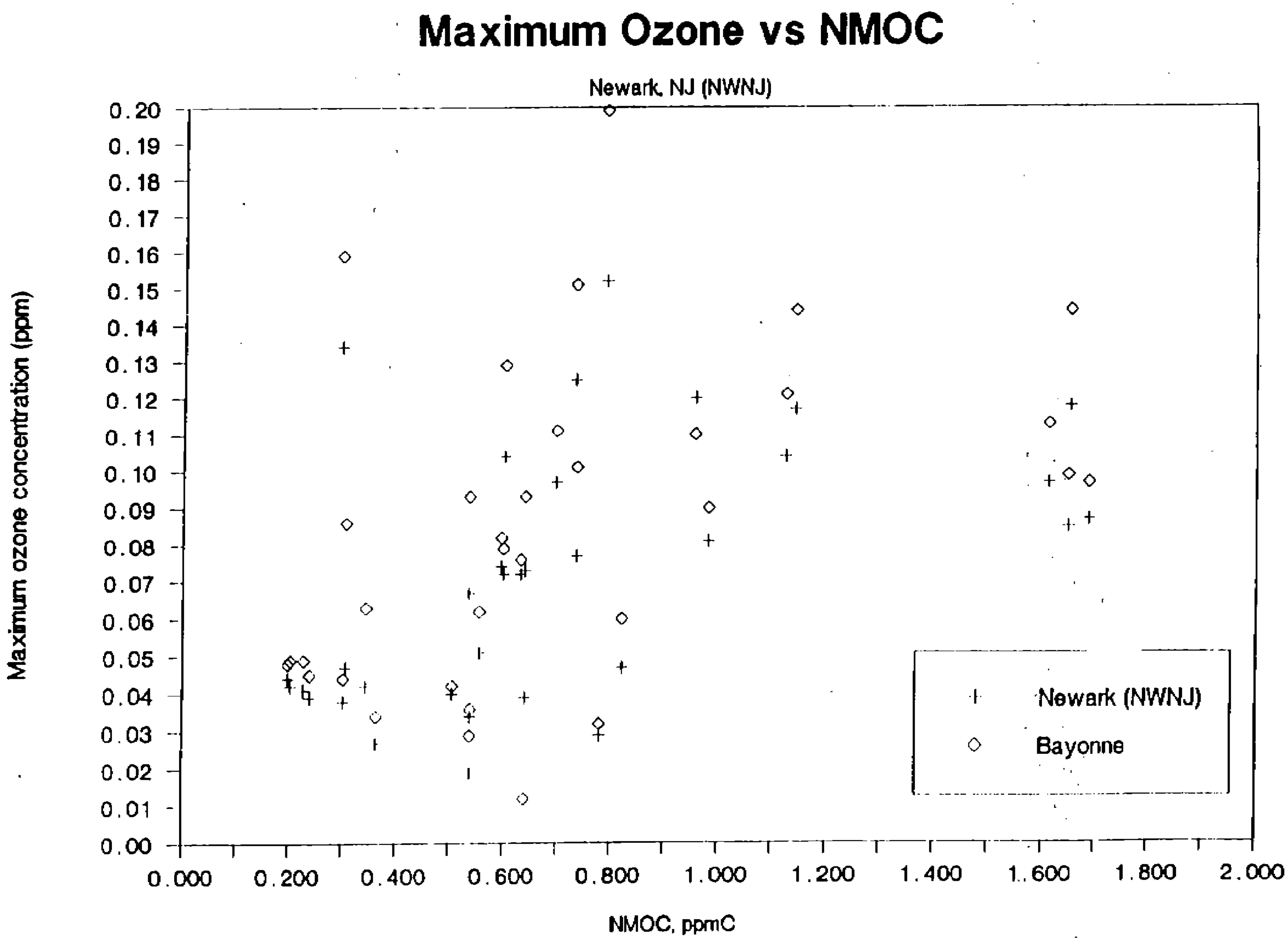

Figure 5-29. Maximum ozone versus NMOC concentration for Newark, NJ site.

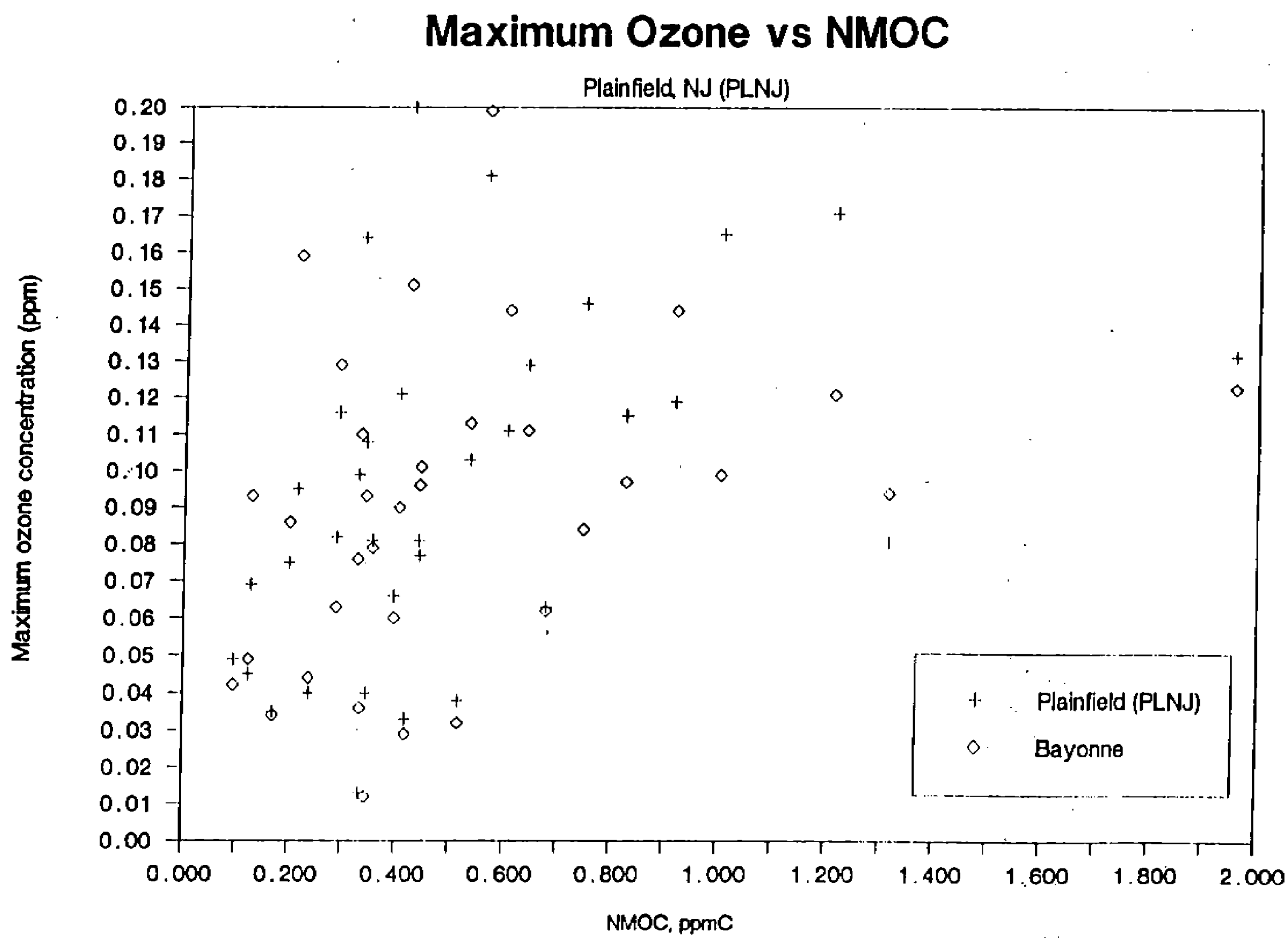

Figure 5-30. Maximum ozone versus NMOC concentration for Plainfield, NJ site.

Maximum Ozone vs NMOC

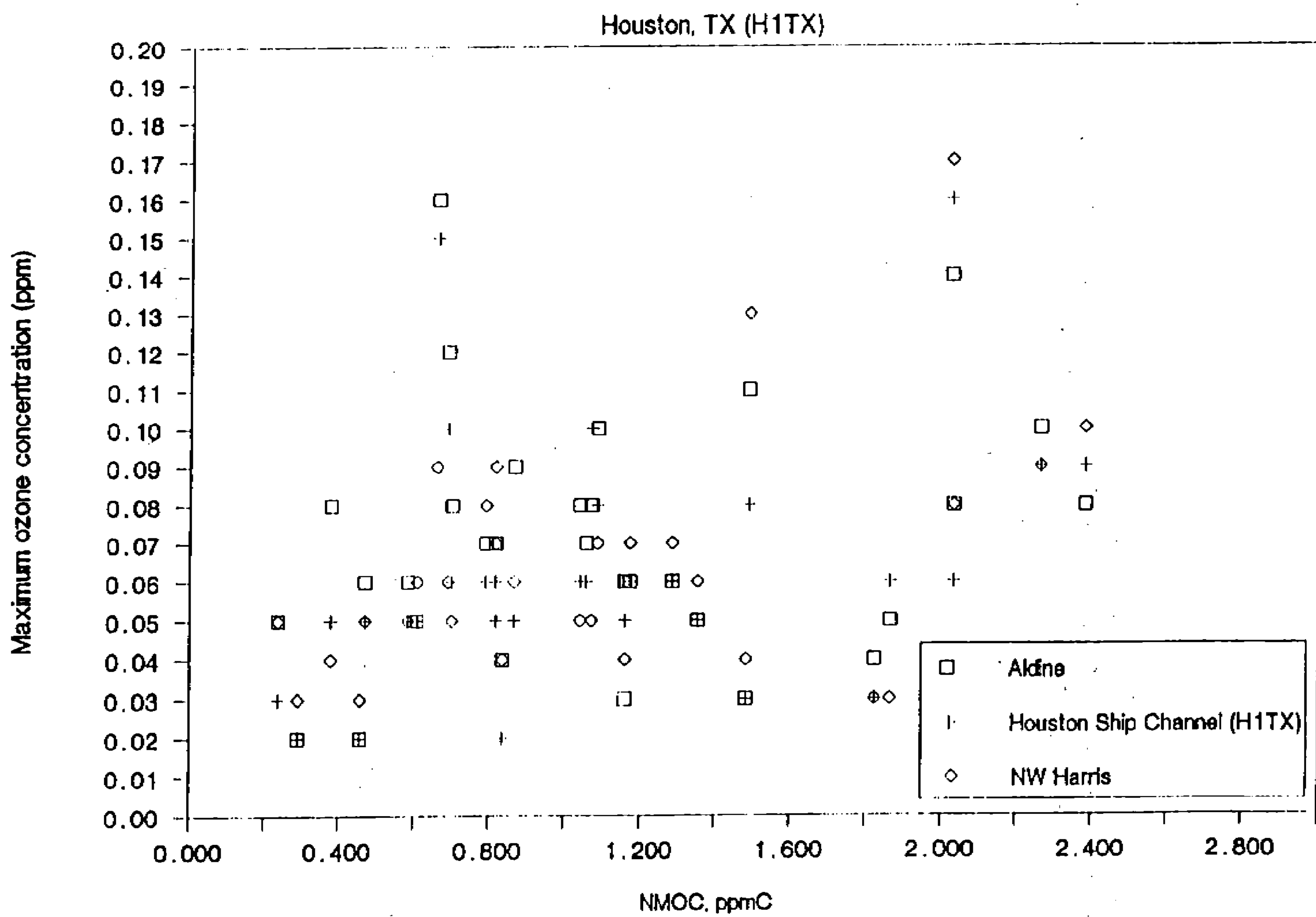

Figure 5-31. Maximum ozone versus NMOC concentration for Houston, TX site.

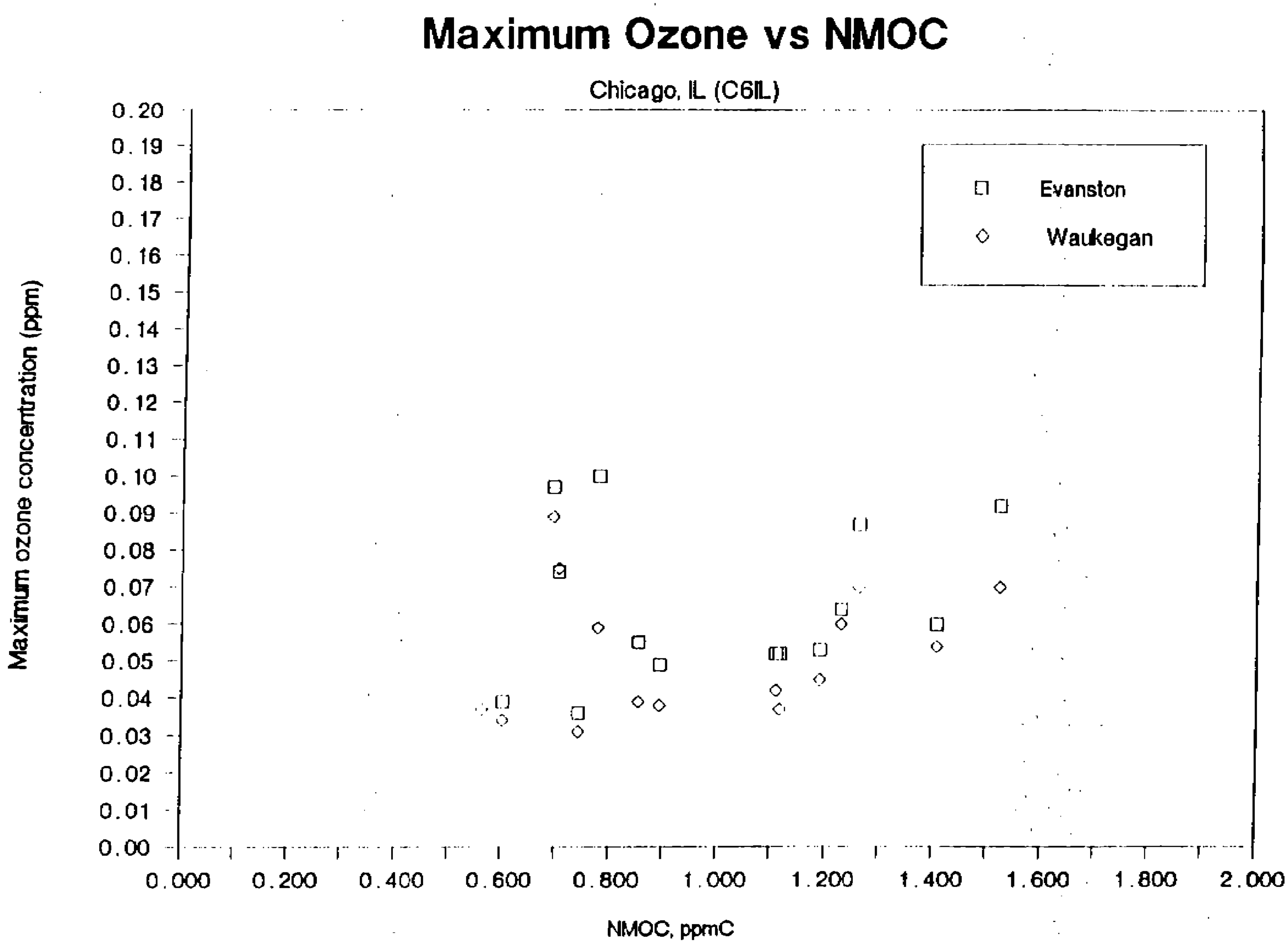

Figure 5-32. Maximum ozone versus NMOC concentration for Chicago, IL site.

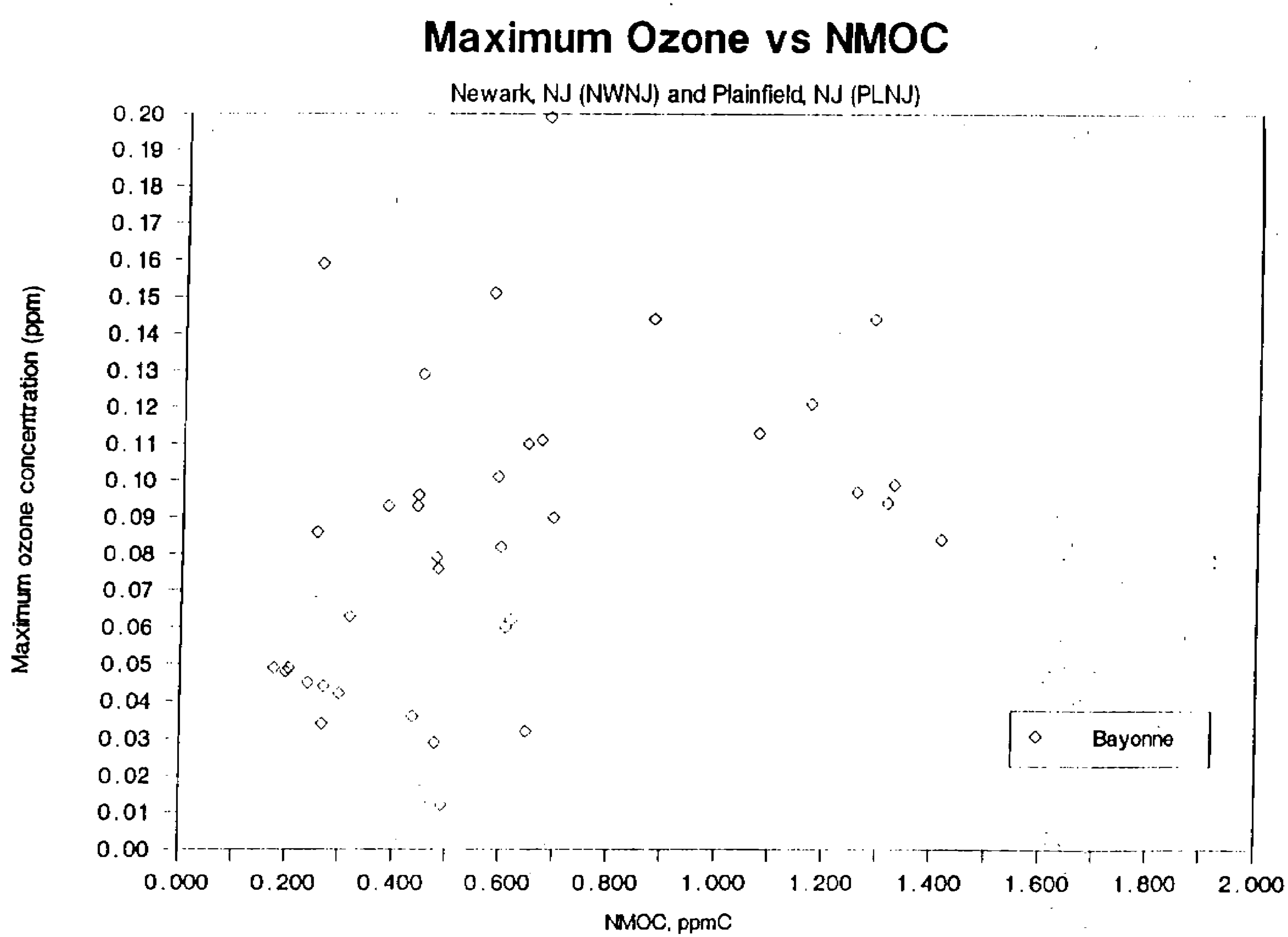

Figure 5-33. Maximum ozone vs NMOC concentration for Newark, NJ and Plainfield, NJ site.

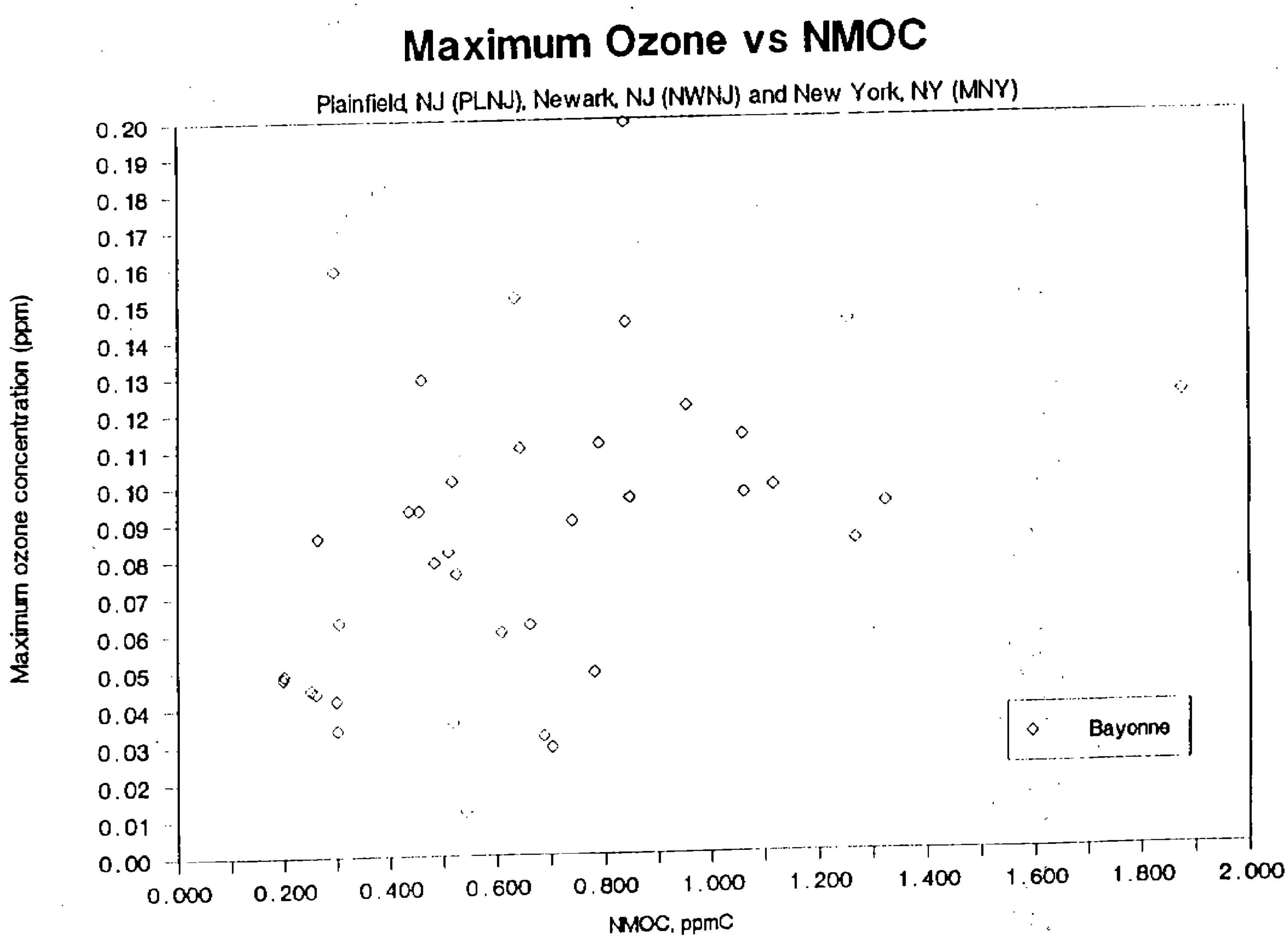

Figure 5-34. Maximum ozone versus NMOC concentraton for pooled Plainfield, NJ, Newark, NJ and New York, NY site.

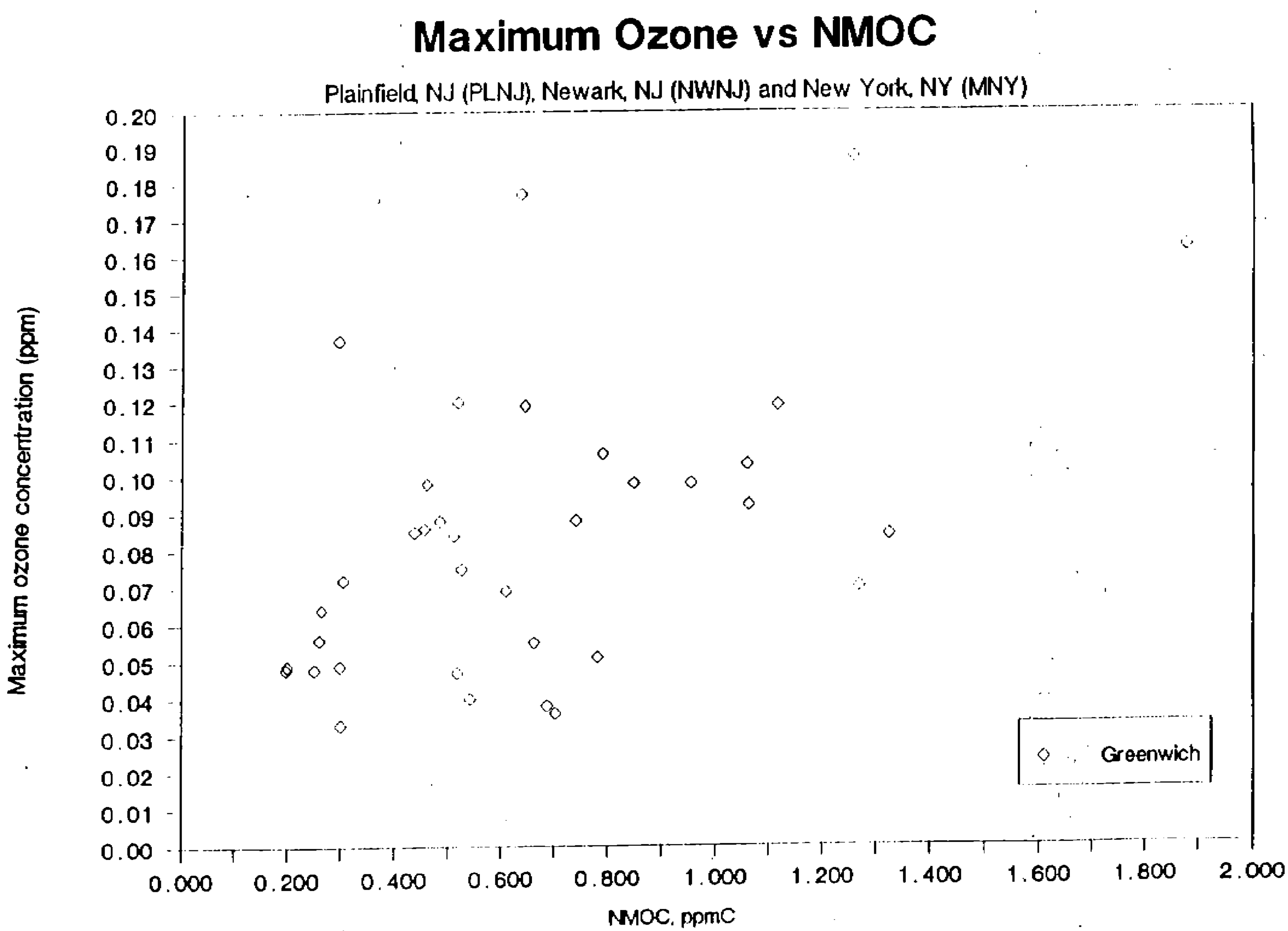

Figure 5-35. Maximum ozone versus NMOC concentration for pooled Plainfield, NJ, Newark, NJ and New York, NY site.

TABLE 5-5. MAXIMUM OZONE vs. NMOC CORRELATIONS

NMOC Source Site	Receptor Site for Ozone Maximum	Cases	Regression Coefficients a	b	c	d	P(a=0.0)	P(b=0.0)	P(c=0.0)	P(d=0.0)	Coefficient of Regression R
C6IL	Evanston, IL	14	0.05305	0.01186	-	-	0.03150	0.57966	-	-	0.162
		14	0.13456	-0.15719	0.08117	-	0.16223	0.40585	0.36947	-	0.313
		14	-0.19970	0.86386	-0.90903	0.30699	0.60348	0.45779	0.41698	0.37658	0.411
	Waukegan, IL	16	0.02231	0.02884	-	-	0.10245	0.04239	-	-	0.512
		16	0.00684	0.07714	-0.02949	-	0.71096	0.09234	0.25435	-	0.579
		16	-0.00056	0.19796	-0.24526	0.09598	0.97548	0.04431	0.10948	0.14898	0.667
H1TX	Aldine, TX	33	0.05093	0.01657	-	-	0.00015	0.09759	-	-	0.293
		33	0.03732	0.04644	-0.01225	-	0.07078	0.21315	0.40266	-	0.328
		33	0.00090	0.20954	-0.18433	0.04849	0.97138	0.01425	0.02479	0.03260	0.489
	NW Harris Co	32	0.03379	0.02679	-	-	0.00208	0.00282	-	-	0.511
		32	0.02784	0.03998	-0.00541	-	0.11450	0.21618	0.66854	-	0.515
		32	0.00482	0.14306	-0.11410	0.03061	0.82863	0.05567	0.11079	0.12227	0.572
	H1TX	33	0.03560	0.02331	-	-	0.00298	0.01550	-	-	0.418
		33	0.02674	0.04275	-0.00797	-	0.16530	0.02245	0.56218	-	0.429
		33	-0.00327	0.17717	-0.14979	0.03996	0.89177	0.02955	0.05528	0.06473	0.525
MNY	Greenwich, CT	36	0.05025	0.05789	-	-	0.00165	0.00241	-	-	0.490
		36	0.04505	0.07337	-0.00868	-	0.06568	0.21134	0.77893	-	0.492
		36	0.00674	0.26511	-0.24445	0.07829	0.84292	0.05837	0.12196	0.12805	0.544
	Bayonne, NJ	36	0.06377	0.03446	-	-	0.00012	0.05611	-	-	0.321
		36	0.06189	0.03960	-0.00276	-	0.02523	0.52889	0.93183	-	0.322
		36	0.03487	0.15293	-0.12913	0.03945	0.50855	0.44628	0.54717	0.55109	0.337
	MNY	37	0.03406	0.03318	-	-	0.00368	0.01649	-	-	0.392
		37	0.03117	0.04169	-0.00478	-	0.08592	0.33483	0.83460	-	0.393
		37	0.00821	0.15661	-0.14643	0.04712	0.74858	0.13185	0.21476	0.22100	0.439
NWNJ	Bayonne, NJ	38	0.05802	0.03213	-	-	0.00000	0.00231	-	-	0.480
		38	0.03688	0.08213	-0.01824	-	0.02972	0.01311	0.10372	-	0.536
		38	0.01466	0.16820	-0.09504	0.01747	0.52336	0.02122	0.10260	0.17634	0.570
	Plainfield, NJ	38	0.05453	0.04244	-	-	0.00001	0.00017	-	-	0.573
		38	0.01953	0.12525	-0.03021	-	0.22187	0.00021	0.00697	-	0.676
		38	0.00353	0.18724	-0.08551	0.01258	0.87472	0.00940	0.13153	0.31583	0.687
	NWNJ	38	0.04680	0.03013	-	-	0.00000	0.00044	-	-	0.542
		38	0.02960	0.07084	-0.01485	-	0.02787	0.00738	0.09502	-	0.591
		38	0.00696	0.15852	-0.09309	0.01780	0.69638	0.00607	0.04210	0.07941	0.637

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TABLE 5-5. (Continued)

NMOC Source Site	Receptor Site for Ozone Maximum	Cases	Regression Coefficients a	b	c	d	P(a=0.0)	P(b=0.0)	P(c=0.0)	P(d=0.0)	Coefficient of Regression R
PLNJ	Bayonne, NJ	36	0.06674	0.04001	-	-	0.00000	0.01113	-	-	0.418
		36	0.04883	0.10251	-0.03201	-	0.00673	0.04106	0.18262	-	0.468
		36	0.02730	0.23378	-0.21285	0.06086	0.26138	0.04913	0.15171	0.21530	0.506
	Newark, NJ	36	0.05458	0.03576	-	-	0.00000	0.00607	-	-	0.449
		36	0.04344	0.07462	-0.01990	-	0.00349	0.07106	0.31513	-	0.475
		36	0.01896	0.22390	-0.22555	0.06921	0.33508	0.02167	0.06409	0.08597	0.543
	PLNJ	36	0.06675	0.04926	-	-	0.00000	0.00385	-	-	0.470
		36	0.03597	0.15666	-0.05501	-	0.04386	0.00301	0.02783	-	0.573
		36	0.01848	0.26332	-0.20195	0.04945	0.45601	0.03174	0.18382	0.32412	0.591
PL & NW & M[a]	Greenwich, CT	39	0.04581	0.06090	-	-	0.00022	0.00006	-	-	0.598
		39	0.03924	0.07893	-0.00852	-	0.03476	0.05821	0.63801	-	0.602
		39	0.01997	0.17126	-0.11411	0.03066	0.45034	0.09541	0.28947	0.31951	0.616
	Bayonne, NJ	39	0.05849	0.04085	-	-	0.00001	0.00478	-	-	0.443
		39	0.04524	0.07505	-0.01569	-	0.02676	0.08981	0.40768	-	0.460
		39	0.03543	0.11648	-0.06002	0.01243	0.31148	0.36511	0.64457	0.73030	0.463
NW & PL[b]	Bayonne, NJ	39	0.06325	0.03484	-	-	0.00000	0.00473	-	-	0.443
		39	0.04688	0.07841	-0.01841	-	0.00901	0.04668	0.23756	-	0.477
		39	0.01975	0.19923	-0.13367	0.03012	0.51867	0.09503	0.22333	0.28758	0.502

[a]Average of Newark, Plainfield, and New York NMOC concentrations for June and July 1988.

[b]Average of Newark and Plainfield, NJ NMOC concentrations for June and July 1988.

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concentration in ppmC as the abscissa. For Figures 5-33, 5-34, and 5-35, the daily average NMOC concentrations were averaged for the NMOC source sites shown. Table 5-5 lists the correlation statistics for equations (1), (2), and (3) for the various site combinations shown. NMOC source sites are symbolized in the first column. The second column shows the ozone receptor sites tested. Column 3 gives the number of days in June and July 1988 for which both ozone and NMOC data were available. The next four columns give the regression coefficients for equations (1), (2), and (3).

The first row in Table 5-5 (C6IL vs. Evanston, IL) gives a and b for equation 1; the second row, a, b, and c for equation 2; and the third row, a, b, c, and d for equation 3. Columns 8 through 11 give probabilities that the constants indicated are zero, i.e., in the first row P(a=0.0) = 0.03150 indicates that the probability that a is zero equals 0.03150; and P(b=0.0) = 0.57966 indicates that the probability that b is zero equals 0.57966. A regression coefficient is taken to be "significant" (i.e., significantly different from zero), if the probabilities are equal to or less than 0.05.

For the correlation (between ozone and NMOC) to be significant, a, b, c, or d needs to be different from zero. Therefore, for the Chicago-Evanston data, the first three rows in Table 5-5, none of the correlations is significant. On the other hand, there is a good linear correlation between ozone and NMOC concentrations for the MNY-Greenwich, CT, site pair [P(a=0.0) = 0.00165, and P(b=0.0) = 0.00241].

The final column in Table 5-5 gives the coefficient of regression, R, for each combination tested. The values of R range from 0.162 to 0.687. Even for the MNY-Greenwich, CT, data pair cited above, the correlation coefficient for the linear regression is only 0.490, despite the significance of the regression coefficients a and b. This information emphasizes the fact that NMOC alone explains only about 49% of the variation of maximum ozone with NMOC concentration. This fact implies that other independent variables, in addition to NMOC concentration, are required adequately to predict ozone concentrations--possibly parameters involving NO_x concentration, meteorological data, temperature, and/or radiation intensity.

The data for the Chicago, Illinois, NMOC source site (C6IL) for June and July 1988 are spotty and do not follow the pattern evident in the remaining sites. The pattern shows that in virtually all other combinations tested, a significant linear relationship exists between maximum ozone concentration at a receptor site (or a NMOC source site) and NMOC concentration at a source site. Quadratic and cubic relations (equations 2 and 3) do not show significant correlations. As explained above, significant relationships are obtained where the probabilities that the regression coefficients, a, b, c, and/or d are equal to or less than 0.05.

Conclusions reached in Task 2 are:

- The C6IL NMOC source data for June and July 1988 are not useful in this study because of the limited data;
- A linear relationship exists between daily maximum ozone concentration and 6 a.m. to 9 a.m. NMOC ambient air concentration for the sites studied in June and July 1988; and
- No significant quadratic or cubic trend exists between daily maximum ozone concentration and 6 a.m. to 9 a.m. NMOC concentration for the sites studied using the June and July 1988 monitoring data.

5.3.3 Task 3

The purpose of this task was to investigate whether canister age affected the measured NMOC concentration. If such a correlation could be discerned, it would then be possible to correct the measured NMOC concentration to remove the canister age effect, and, in turn, to improve the correlation between maximum ozone at a receptor site and the NMOC concentration at an urban site.

To explore the effect of canister age on measured NMOC concentration, the 1988 duplicate sample NMOC concentration results were used. For each duplicate sample, a difference in the measured NMOC concentration from samples taken from each canister was paired with the difference between the ages of the duplicate canisters. If canister age affected the measured NMOC concentration significantly, a plot of NMOC concentration difference (or percent difference) between duplicate would show a trend when plotted versus the paired differences in canister age for the duplicate canisters.

Figure 5-36 shows a plot of NMOC percent difference versus canister age for the 1988 duplicate sample canisters. The age difference is shown to be positive and negative indicating that the age difference was calculated by

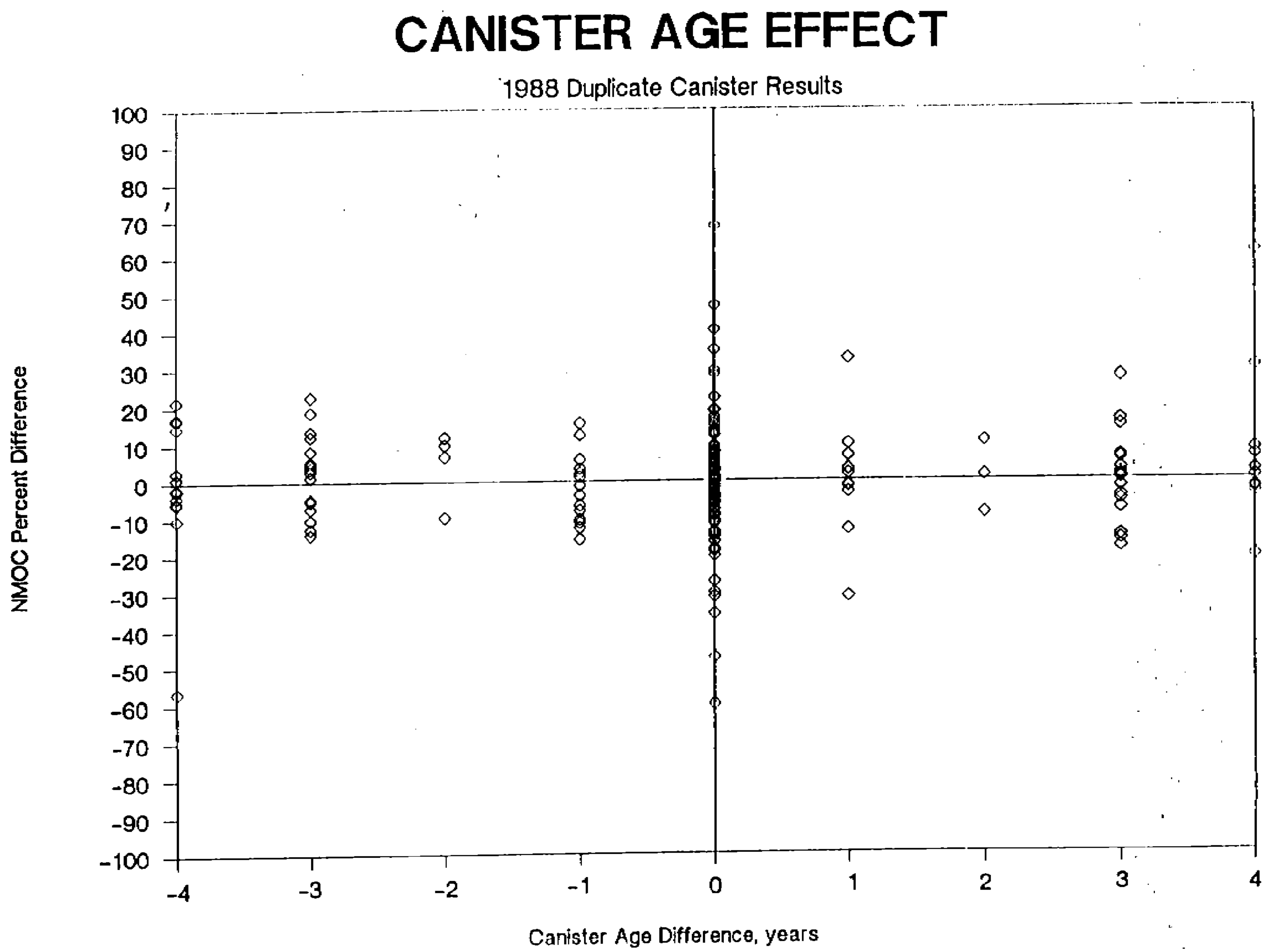

Figure 5-36. Percent NMOC as a function of canister age difference, by chronological analysis number.

chronological analysis number rather than by canister age. The same data were replotted in Figure 5-37 using for canister age difference the older canister age minus the younger canister age. The NMOC % difference was calculated in the same "direction" as the canister age.

Both these plots show that there is no significant correlation between measured NMOC concentration difference and canister age difference. These data implies that the internal surfaces of the SUMMA®-treated canisters remains passivated for at least four years, and probably longer when the canisters are used for ambient air samples.

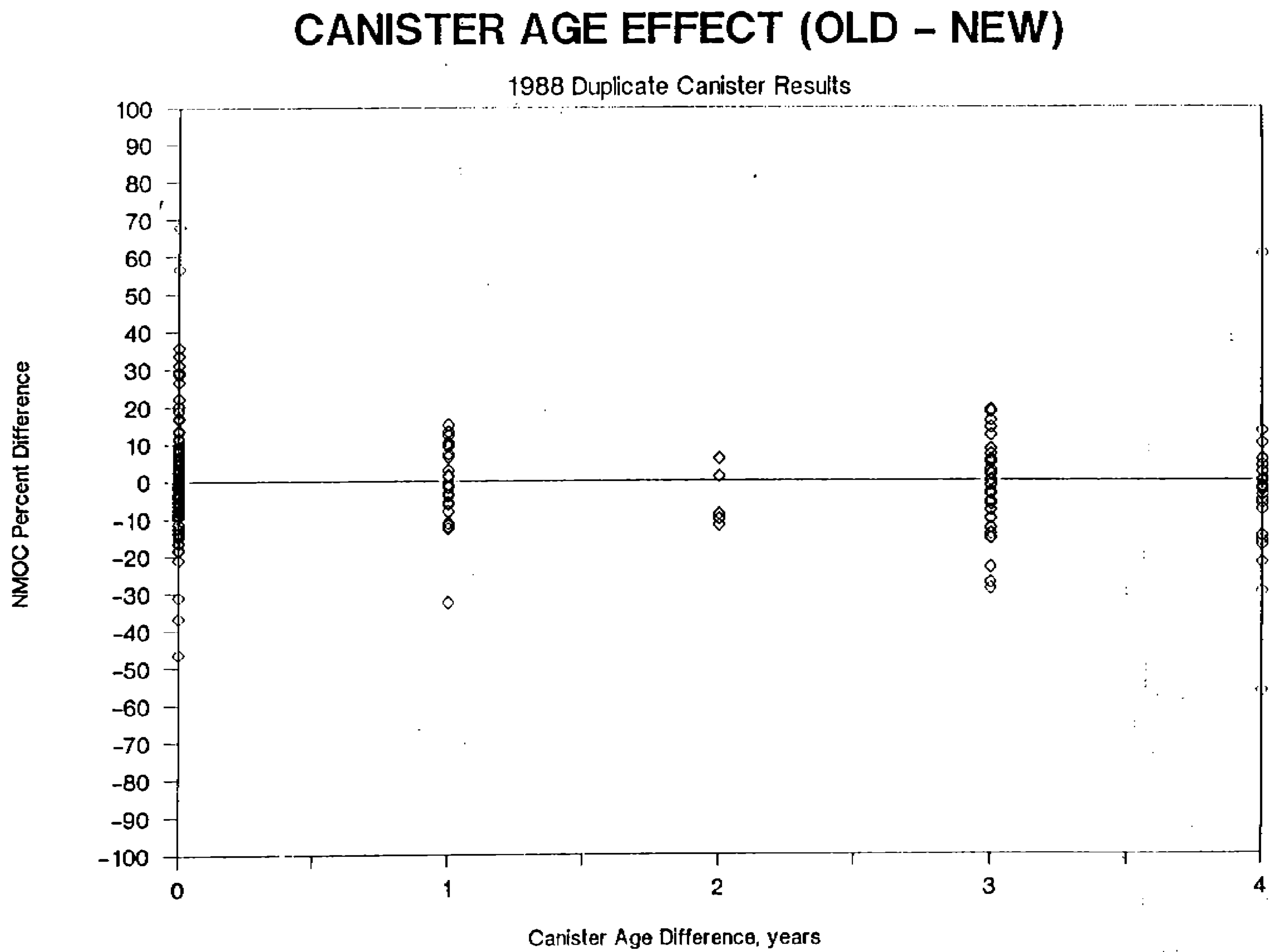

Figure 5-37. Percent NMOC as a function of canister age difference, by canister age.

6.0 RECOMMENDATIONS, NMOC MONITORING PROGRAM

Based on the experiences and results of the 1989 NMOC Monitoring Study, certain recommendations can be made with respect to equipment design and validation procedures.

6.1 OPERATING PROCEDURE CHANGES

Current operating procedures call for the use of dry propane standards and external audit samples. The experimental design recommended would cover the present NMOC span of 0 to 9 ppmC, and at least 3 levels of humidity: zero, low (~10%), and medium (~30%) relative humidity. The effect of humidity on propane calibration (and audit) results is currently unknown and should be determined.

6.2 VERTICAL STRATIFICATION STUDY

In 1987, 1988, and 1989 ambient air samples were taken at ground level (3 to 10 meters) and at the 1197-foot (364.9 meter) level. In 1988, an additional site was located on top of the World Trade Center in New York, a height of over 1000 ft. It is recommended that the study be continued at these sampling locations and that at least one more level (at 100 meters or some other appropriate height above ground level) be sampled at the same location. At the same time, barometric pressure and wind velocity and direction data should be obtained at each sampling level. These samples should be analyzed for NMOC content as well as for the air toxics compound concentrations. The information gained from such a study would be useful in validating various atmospheric model predictions.

6.3 SEASONAL NMOC STUDIES

Data derived in a study qualifying NMOC and NO_x in seasons other than summer could be useful in understanding the relationship of NMOC to NO_x and meteorological conditions. Currently a year-round study for 24-hour air toxics ambient air samples is being conducted. No study is currently in progress to determine seasonal NMOC concentration changes.

6.4 DIURNAL STUDIES

It is proposed that a diurnal study be made at an appropriate monitoring site to measure NMOC concentrations 24-hours per day, seven days per week, for at least four weeks. An appropriate site for such a study would be one at which the NMOC concentration averaged 0.800 ppmC or greater, and one at which meterological as well as NO_x data were available. Sampling plans could include both continuous NMOC measurement, and collection of integrated samples at various times through the day.

6.5 CANISTER CLEANUP STUDIES

Additional cleanup studies are proposed to determine more specifically the carryover of organic material after cleaning, and to determine how storage of cleaned, evacuated canisters affects NMOC concentration of a sample. Storage effects up to three months under vacuum and under pressure should be included in the study.

Additional studies are proposed to compare cleanup procedures at room temperature with cleanup procedures involving heating of the canisters.

After July 14, 1988, the canister procedure was revised to eliminate steps 4 and 5. If in Step 6 for either of the cleanup procedures, the NMOC concentration was greater than 0.030 ppmC, the cleaning procedure was repeated until the acceptance criterion was met.

Radian has proposed[7] initiation of several studies to determine whether the present canister cleanup procedure is adequate to prevent significant carryover of organic compounds from one canister to the next. These studies are needed since equilibration in a canister may take a week or longer.

The effect of sample pressure on the measured NMOC concentration is not clear. Ambient air samples are sufficiently humid so that at 15 psig, liquid water condenses inside the canister. Migration of liquid water to the canister walls affects the adsorption equilibrium, and at the same time, provides a medium for further depletion of the vapor phase organic compounds because of the solubility of the organics in water. Equilibration under these conditions would take longer, perhaps 30 days or more, and the effect on the measured air sample NMOC (and UATMP target compound) concentration has not been determined. These effects, however, are probably not significant for the NMOC measurements, but could affect 3-hour air toxics measurements.

Radian has proposed undertaking a study to ensure a better understanding and measurement of the effectiveness of the canister cleanup procedure. The present canister cleanup procedure appears to be adequate for the NMOC program, since the concentrations of interest are at the ppmC level. However, the 3-Hour Air Toxics and UATMP, the concentration levels are at the ppbv levels, i.e., 0.01 to 50 ppbv, and the present canister cleanup procedure may not be sufficient to prevent significant carryover of target compounds from one sample to the next.

6.6 COORDINATED SAMPLING AT NMOC SITES

It is recommended that where possible the following sampling take place at NMOC sites for the 1990 monitoring programs:

- NMOC samples;
- Aldehyde samples;
- 3-hour air toxics compounds; and
- UATMP sampling (at least 38 target compounds).

This kind of program would effect some economy in setting up and monitoring the sampling program, and also provide some opportunity for cross-correlation of the results.

Coordinated sampling would be most meaningful at sites where NMOC and/or UATMP monitoring occurred the previous year (or years).

6.7 FIELD AUDIT

It is recommended that a field audit be designed and conducted at several NMOC sites during the 1990 Monitoring Program. It is suggested that one field audit per month be performed at an NMOC site during June, July, August, and September 1989. The field audit should use at least one standard of known NMOC concentration and should collect duplicate samples plus a zero-air blank for each site.

6.8 DUPLICATE SAMPLE AND REPLICATE ANALYSIS

During the 1990 NMOC Monitoring Program records should be kept of (1) the NMOC concentration in a duplicate canister before cleanup, and (2) the zero-air NMOC concentration at the time of the third pressurization with clean, humidified zero air. The duplicate samples should be scheduled so that the same amount of time elapses between sampling and analysis for all duplicate samples.

7.0 THREE-HOUR AIR TOXICS DATA SUMMARY

The 1989 NMOC Program included three-hour air toxics samples at 7 NMOC urban sites (See Table 7-1) located in the contiguous United States. Overall concentration results are reported in parts per billion by volume (ppbv) in Section 7.1, and site-specific results are given in Section 7.2.

Analyses were done by a GC/MD system using flame ionization detection (FID), photoionization detection (PID), and electron capture detection (ECD). Compound identification was made using a combination of retention time, ratios of PID/FID and/or ECD/FID responses, and analyst experience and judgment. Quantitation was done using the FID response, with the exception of halogenated compounds that were quantitated using the ECD. If there was an indication that the quantitation detector response for the target compound had interference from an unknown source quantitation was performed on one of the alternate detectors if applicable. Table 7-1 indicates the number of 3-hour samples taken for GC/MD analyses to speciate for 38 UATMP compounds. About 11 analyses were performed on samples from each site. One duplicate sample was collected from each site, and the analysis of one of the samples from each site was replicated. Two of the samples from each site were analyzed by gas chromatography/mass spectrometry (GC/MS) for confirmation of compound identification.

Three-hour air toxics samples were regular NMOC Monitoring Program samples that were collected in 6-L stainless steel canisters from 6:00 a.m. to 9:00 a.m. The final canister pressure was about 12 psig. The NMOC samples that were speciated by GC/MD were selected at random during the summer. Each selected sample was first analyzed by the PDFID method for its NMOC concentration. Then the canister pressure was bled to atmospheric pressure and the canister bellows valve was closed. The canister was allowed to equilibrate at least 18 hours before the GC/MD analysis was performed.

7.1 OVERALL RESULTS

Concentrations of the air toxic compounds detected are summarized in Table 7-2 for the 1989 3-hour ambient air samples that were speciated. The table shows the number of cases (samples), the percent of cases in which the

TABLE 7-1. THREE-HOUR AMBIENT AIR SAMPLES AND ANALYSES

Site Code	No.	Duplicate Pairs	GC/MD Analyses Replicate	GC/MD Analyses Total	GC/MS Analyses
C3IL	10	1	1	12	2
C6IL	9	1	1	11	2
GRMI	9	1	1	11	2
M1NY	9	1	1	11	2
MNY	9	1	1	11	2
NWNJ	9	1	1	11	2
PLNJ	9	1	1	11	2
Total	64	7	7	78	14

TABLE 7-2. COMPOUND IDENTIFICATION WITH GC/MD FOR ALL 3-HOUR SITES

Cases Compounds	%	No.	Minimum ppbv	Maximum ppbv	Mean ppbv
Acetylene	14	9	1.02	17.33	5.09
Propylene	19	12	1.52	19.46	6.70
1,3-Butadiene	67	43	0.05	1.58	0.42
Chloroethane	6	4	0.05	1.49	0.60
Bromomethane	5	3	0.05	0.07	0.06
Methylene chloride	17	11	0.93	9.94	2.89
Chloroprene	44	28	0.03	1.30	0.24
Chloroform	5	3	0.09	0.10	0.10
1,1,1-Trichloroethane	98	63	0.28	6.87	1.66
Carbon tetrachloride	100	64	0.11	0.23	0.15
Benzene	100	64	0.13	8.78	2.66
Trichloroethylene	80	51	0.03	7.56	0.73
1,2-Dichloropropane	14	9	0.07	1.64	0.80
Bromodichloromethane	2	1	0.08	0.08	0.08
Toluene	100	64	0.24	54.31	8.22
n-Octane/trans-1,3-dichloropropylene	6	4	0.12	1.87	1.03
cis-1,3-Dichloropropylene	11	7	0.22	0.92	0.43
1,1,2-Trichloroethane	13	8	0.01	0.51	0.12
Tetrachloroethylene	59	38	0.04	4.85	1.31
Chlorobenzene	16	10	0.03	1.29	0.31
Ethylbenzene	100	64	0.04	16.48	1.07
m/p-Xylene	100	64	0.18	88.90	5.86
Styrene/o-Xylene	100	64	0.06	18.64	1.82
m-Dichlorobenzene	19	12	0.01	0.13	0.03
p-Dichlorobenzene	44	28	0.05	2.54	0.61
o-Dichlorobenzene	14	9	0.07	0.40	0.20