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1991 NONMETHANE ORGANIC COMPOUND, SPECIATED NONMETHANE ORGANIC COMPOUND, AND THREE-HOUR AIR TOXICS MONITORING PROGRAM



**1991 NONMETHANE ORGANIC COMPOUND,
SPECIATED NONMETHANE ORGANIC COMPOUND,**

AND

**THREE-HOUR
AIR TOXICS MONITORING
PROGRAM**

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SYMBOLS AND ABBREVIATIONS

$A_{k(ij)}$	air aliquot k removed from duplicate canister j, sample i
a.c.	area counts, generated from a gas chromatograph
ADIFF	absolute value of DIFF
AIRS	Aerometric Information Retrieval System
a.m.	ante meridiem
APCDIFF	absolute value of PDIFF
APR	April
AREAL	Atmospheric Research and Exposure Assessment Laboratory
ASTM	American Society for Testing Materials
Aug	August
BMTX	Beaumont, TX - AIRS No. 48-245-0009
BRLA	Baton Rouge, LA - AIRS No. 22-033-0006
Calib.	calibration
Conc.	concentration
cm	centimeter
CRM	Certified Reference Material
CH	State of Chihuahua, Mexico
CT	Connecticut
CV	coefficient of variation
$D_{i(j)}$	duplicate canister sample j (j = 1 or 2) taken from ambient air sample i
DELTA	Radian NMOC concentration - QAD NMOC concentration, ppmC; Radian NMOC concentration - ASRL concentration, ppmC; or AREAL NMOC concentration - QAD NMOC concentration, ppmC
DIFF, Diff.	measured NMOC concentration - calculated NMOC concentration ppmC for in-house quality control samples; (NMOC concentration for the second channel) - (NMOC concentration for the first channel)
DNPH	2,4-dinitrophenyl hydrazine
Dup.	duplicate
e	base of natural logarithm, 2.71828...
ECD	electron capture detector
EPA	United States Environmental Protection Agency
F1FL	Fort Lauderdale, FL - AIRS No. 12-011-2003
F	Friday
F	the F-statistic
FID	flame ionization detector
FL	Florida

SYMBOLS AND ABBREVIATIONS - Continued

GC/FID	gas chromatography flame ionization detector
GC/MD	gas chromatography multidetector
GC/MS	gas chromatography mass spectrometry
HITX	Houston, TX - AIRS No. 48-201-1034
H	Thursday
H	hinge (25th percentile or 75th percentile)
He	helium
hg	mercury
HP-5880	Hewlett-Packard Model 5880
HPLC	high performance liquid chromatography
i.d.	inside diameter
ID	identification
Inj.	injection
JUMX	Juarez-CH, Mexico - AIRS No. 80-006-0001
KI	potassium iodide
L	liter
LA	Louisiana
LCL	lower control limit
LINY	Hempstead, NY (Long Island) - AIRS No. 36-059-0005
m	meter
M	Monday
M	median
Max	maximum
MDL	method detection limit
Min	minimum
min	minute
mL	milliliter
mm	millimeter
MNY	New York, NY - AIRS No. 36-061-0010
MU	mean of ln(NMOC)

SYMBOLS AND ABBREVIATIONS - Continued

NAAQS	National Ambient Air Quality Standards
NC	North Carolina
NIST	National Institute of Standards and Technology
NMOC	Nonmethane organic compound
NO _x	oxides of nitrogen
NWNJ	Newark, NJ - AIRS No. 34-013-0011
NJ	New Jersey
NY	New York
o.d.	outside diameter
PBPL	West Palm Beach, FL - AIRS No. 12-099-1004
PCDIFF	percent difference = DIFF/calculated NMOC concentration x 100, for in-house QC samples
PDFID	preconcentration, direct flame ionization detection
PLNJ	Plainfield, NJ - AIRS No. 34-035-1001
ppbv	parts per billion by volume
ppm	parts per million
ppmC	parts per million by volume as carbon
ppmv	parts per million by volume
psig	pounds (force) per square inch gauge
PSNMOC	photochemical speciated nonmethane organic compound
QA	quality assurance
QAD	Quality Assurance Division (EPA)
QAPP	Quality Assurance Project Plan
QC	quality control
RINC	Raleigh, NC - AIRS No. 37-183-0015
R	response factor range, (RF _{i+1} - RF _i)
RF	response factor
RTP	Research Triangle Park
S	standard deviation
S _i	sample i
SAROAD	Storage and Retrieval of Aerometric Data
SOP	standard operating procedure
SO _x	oxides of sulfur
SIGMA	standard deviation of ln(NMOC)
Std Dev	standard deviation

SYMBOLS AND ABBREVIATIONS - Continued

T	Tuesday
TX	Texas
THC	total hydrocarbon
UATMP	Urban Air Toxics Monitoring Program
UCL	upper control limit
U.S.	United States
UTM	Universal Transverse Mercator
vs.	versus
W	Wednesday
W	Shapiro-Wilk statistic
WSNC	Winston-Salem, NC - AIRS No. 37-067-0022
XBAR	estimate of the sample mean
"	inch(es)
°C	degrees Celsius
$\epsilon_{(ijk)}$	residual (or error, assumed to be due to analysis) l from aliquot k, duplicate canister j, and air sample i
°F	degrees Fahrenheit
%CV	percent coefficient of variation
μ	micron
μ	population mean
μg	microgram

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 1991 NMOC Monitoring Program.

Between June 3 and September 27, 1991, Radian analyzed 687 ambient air samples, including 74 duplicate samples, collected in SUMMA® polished stainless steel canisters at 8 sites. These NMOC analyses were performed by the cryogenic preconcentration, direct flame ionization detection (PDFID) method.¹ Based on the 1984 through 1990 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 1991 study confirmed these findings and supported the conclusion that the PDFID method is the method of choice to measure total 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 1991, air toxic analyses were conducted on 3-hour ambient air samples taken at two sites at which NMOC samples were taken. Air toxics monitoring was a component of the 1987, 1988, 1989, 1990, and 1991 programs. 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. A related monitoring program, the 1990 Urban Air Toxics Monitoring Program (UATMP), began sampling in March 1990 at urban sites and extended through

February 1991. The samples from the latter program were 24-hour integrated ambient air samples taken every twelve days and are referred to as UATMP samples throughout this report. The final report for the 1991 UATMP will be presented under separate cover.

Beginning with the 1989 monitoring season, selected carbonyls were measured and reported. In 1989, 24-hour samples were taken and analyzed for selected carbonyls -- formaldehyde, acetaldehyde, and acetone. In the 1990 monitoring season, ozone scrubbers were added to the sampling assemblies to scavenge any ozone present in the ambient air sampled, prior to its being drawn through the 2,4-dinitrophenylhydrazine (DNPH) cartridges. In the 1991 monitoring season, Radian Corporation prepared the DNPH cartridges, supervised the ambient air sampling, and performed the analyses. In 1991, carbonyl samples were taken from 6:00 a.m. to 9:00 a.m. at five sites and analyzed for 14 carbonyls -- formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, butyr/isobutyraldehyde, benzaldehyde, isovaleraldehyde, valeraldehyde, tolualdehyde, hexanaldehyde, and 2,5-dimethylbenzaldehyde.

Beginning in 1991, photochemical speciated nonmethane organic compound (PSNMOC) concentrations were measured at several sites. Sixty-nine hydrocarbons are speciated and quantitated in this analysis. Chlorinated and oxygenated species in the ambient air are not identified in the PSNMOC procedure. The PSNMOC sampling apparatus is identical with the NMOC sampling apparatus. Three-hour samples are collected in cleaned, evacuated stainless steel canisters from 6:00 to 9:00 a.m. under final pressures of about two atmospheres absolute pressure. The samples are cryogenically preconcentrated and split to be analyzed in two gas chromatographic columns by flame ionization detectors (FIDs). One column separates the C₂-hydrocarbons, ethane, ethene, and acetylene. The other column separates the remaining 66 target hydrocarbons.

The Final Report for the 1991 Nonmethane Organic Compound Monitoring Programs are included in Sections 1.0 through 12.0. Sections 1.0 through 6.0 report the data, procedures, and assessment of the NMOC portion of the monitoring program. Sections 7.0 through 10.0 report the data, procedures,

and assessment of the 3-hour air toxics portion of the monitoring program. Section 11.0 lists references.

The sampling sites for the 1991 NMOC Monitoring Program are listed in Appendix A. Appendix A also gives the EPA Regions for each site, the Radian Site Code, the Aerometric Information Retrieval System (AIRS) site code and site information, and indicates whether or not 3-hour air toxics analyses or PSNMOC analyses were performed on selected ambient air samples from the site.

Appendix B contains the detailed instructions on the PDFID method. Appendix C lists the 1991 NMOC Monitoring Program site data. Appendix D lists the 1991 NMOC Monitoring Program Invalidated and Missing Samples information. Appendix E gives PDFID Integrator Programming Instructions. Appendix F gives 1991 NMOC Daily Calibration Data. Appendix G gives 1991 In-House Quality Control Samples, and Appendix H gives Multiple Detector Speciated Three-Hour Site Data Summaries.

1.1 NMOC MONITORING PROGRAM

1.1.1 Introduction and Data Summary

The sampling schedule is given in the 1991 NMOC Quality Assurance Project Plan (QAPP).² For all the sites in the 1991 NMOC Monitoring Program, sampling occurred from 6:00 a.m. to 9:00 a.m. local time, Monday through Friday from June 3, 1991 through September 27, 1991 with the exception of the Raleigh, NC (RINC) site, which collected samples until October 4, 1991. Site codes for the 1991 NMOC Monitoring Program are listed in Appendix A. 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 94.1% in 1991 compared to 95.8% in 1990, 95.5% in 1989, 93.4% in 1988, 95.0% in 1987, 96.8% in 1986, 95.8% in 1985, and 90.6% in 1984. Percent completeness for 1991 ranged from 87.1 at Plainfield, NJ (PLNJ), to 100.0 for Newark, NJ (NWNJ). Statistics for the NMOC concentrations in parts per million carbon (ppmC) by volume are listed in Table 1-2. This table also includes all duplicate sample concentration statistics.

Table 1-1

1991 NMOC Completeness Results

Site Location	Radian Site Code	Scheduled Sampling Days	Total Scheduled Duplicate Samples	Total Scheduled Samples	Total Valid Duplicate Samples	Total Valid Samples	Percent Complete
Fort Lauderdale, FL	F1FL	82	9	91	8	88	96.70
Long Island, NY	L1NY	83	9	92	9	90	97.83
New York, NY	M1NY	76	9	85	11	79	92.94
Newark, NJ	N1NJ	84	9	93	6	93	100.00
West Palm Beach, FL	PBFL	83	9	92	9	87	94.57
Plainfield, NJ	PLNJ	84	9	93	12	81	87.10
Raleigh, NC	R1NC	83	9	92	7	81	88.04
Winston-Salem, NC	WSNC	83	9	92	9	88	95.65
OVERALL		658	72	730	71	687	94.11

Table 1-2
 NMOC Overall Statistics, by Site

Site	Cases	Concentration, ppmC							v ^a
		Min	Max	Median	Mean	Std Dev	Skewness	Kurtosis	
F1FL	88	0.042	3.134	0.359	0.490	0.529	3.047	12.105	0.698
L1NY	90	0.058	1.321	0.273	0.326	0.235	1.897	4.917	0.832
MNY	79	0.155	1.790	0.404	0.493	0.309	1.954	4.604	0.816
NMNJ	93	0.129	1.520	0.393	0.462	0.251	1.439	3.162	0.892
PBFL	87	0.094	1.515	0.510	0.542	0.272	0.770	0.888	0.953
PLNJ	81	0.068	3.842	0.292	0.464	0.626	4.168	19.069	0.503
RINC	81	0.056	0.983	0.214	0.298	0.221	1.415	1.157	0.815
WSNC	88	0.050	1.120	0.182	0.261	0.232	2.253	5.061	0.716
OVERALL	687	0.042	3.842	0.318	0.417	0.373	3.974	26.816	0.707

^aShapiro-Wilk statistic to test normality of data.

1.1.2 Calibration and Drift

Each Radian PDFID channel was calibrated, 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 -8.4% to +6.8 percent. The absolute value of the percent drift of the daily calibration factors ranged from zero to +8.4 percent.

1.1.3 NMOC Precision

Analytical precision was determined by repeated analyses of 121 site samples. Percent differences between the second and the first analysis averaged -1.43 percent. The average of the absolute values of the percent difference was 14.3% with a standard deviation of 20.0 ppmC. The analytical precision includes the variability between Radian channels and within Radian channels. The data quality objective for this measurement as published in the QAPP² was 15%, based on previous NMOC program experience³ with this measurement.

Overall precision, including sampling and analysis variability, was determined by analysis of 74 duplicate site samples, simultaneously collected in two canisters from a common sampling system. Percent difference for Radian's analyses of the duplicates averaged 0.836 percent. The average absolute percent difference was 15.8% with a standard deviation of 15.7 ppmC. The data quality objectives for this measurement was 20%, based on previous experience.³

1.1.4 Accuracy

Because the NMOC measurements encompass a range of mixtures of organic compounds whose individual concentrations are unknown, 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. Periodically, 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 propane Certified Reference Material (CRM) 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. Quality control samples of propane were mixed from a propane standard certified by referenced to NIST propane Certified Reference Material (CRM) 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 0.000 to 3.042 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 through their QA contractor, ManTech. The propane samples were referenced to NIST propane Certified Reference Material (CRM) 1667B or 1665B. The audit samples were given Radian ID Numbers upon receipt. The average percent bias for the Radian channels was 4.07%, ranging from +1.9 to +8.9 percent. Table 1-4 shows the external audit results.

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 over 150 separate determinations, percent cleanup averaged 99.747 percent. Cleanup was defined in terms of the percent of the NMOC concentration that was removed in the cleanup cycle.

IN-HOUSE PROPANE QC RESULTS Channel A

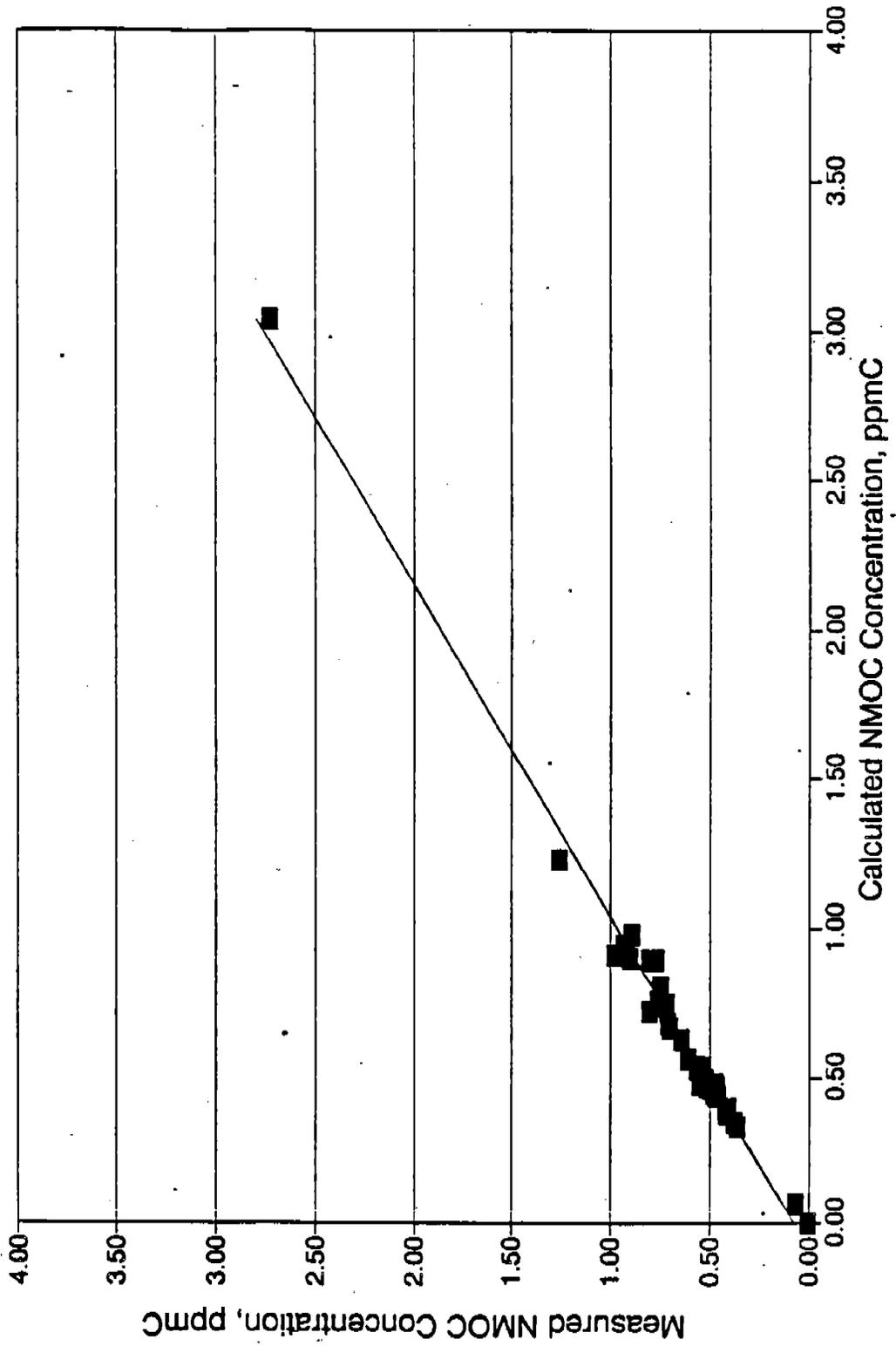


Figure 1-1. In-house quality control results, Channel A.

IN-HOUSE PROPANE QC RESULTS

Channel B

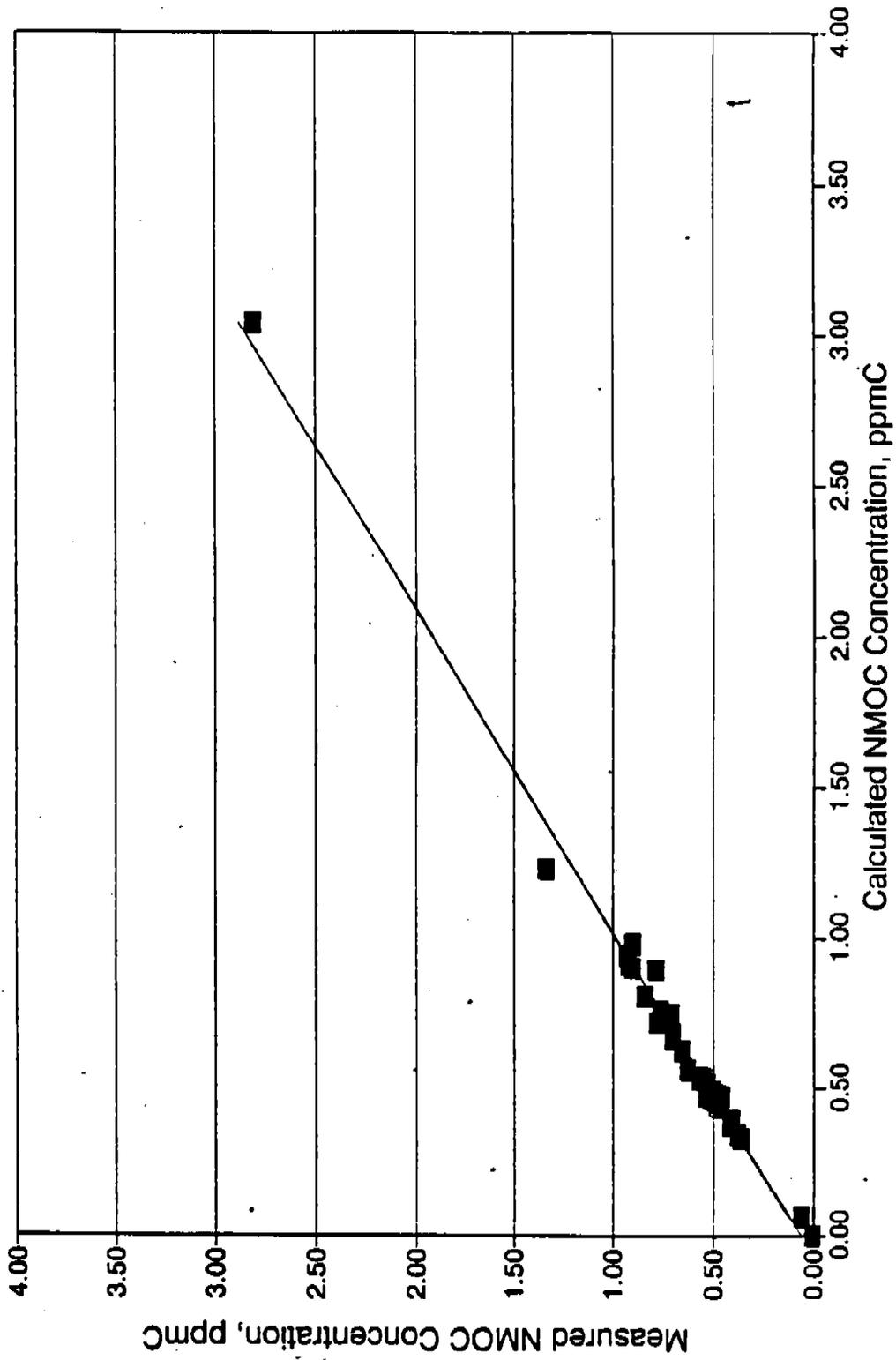


Figure 1-2. In-house quality control results, Channel B.

IN-HOUSE PROPANE QC RESULTS

Channel C

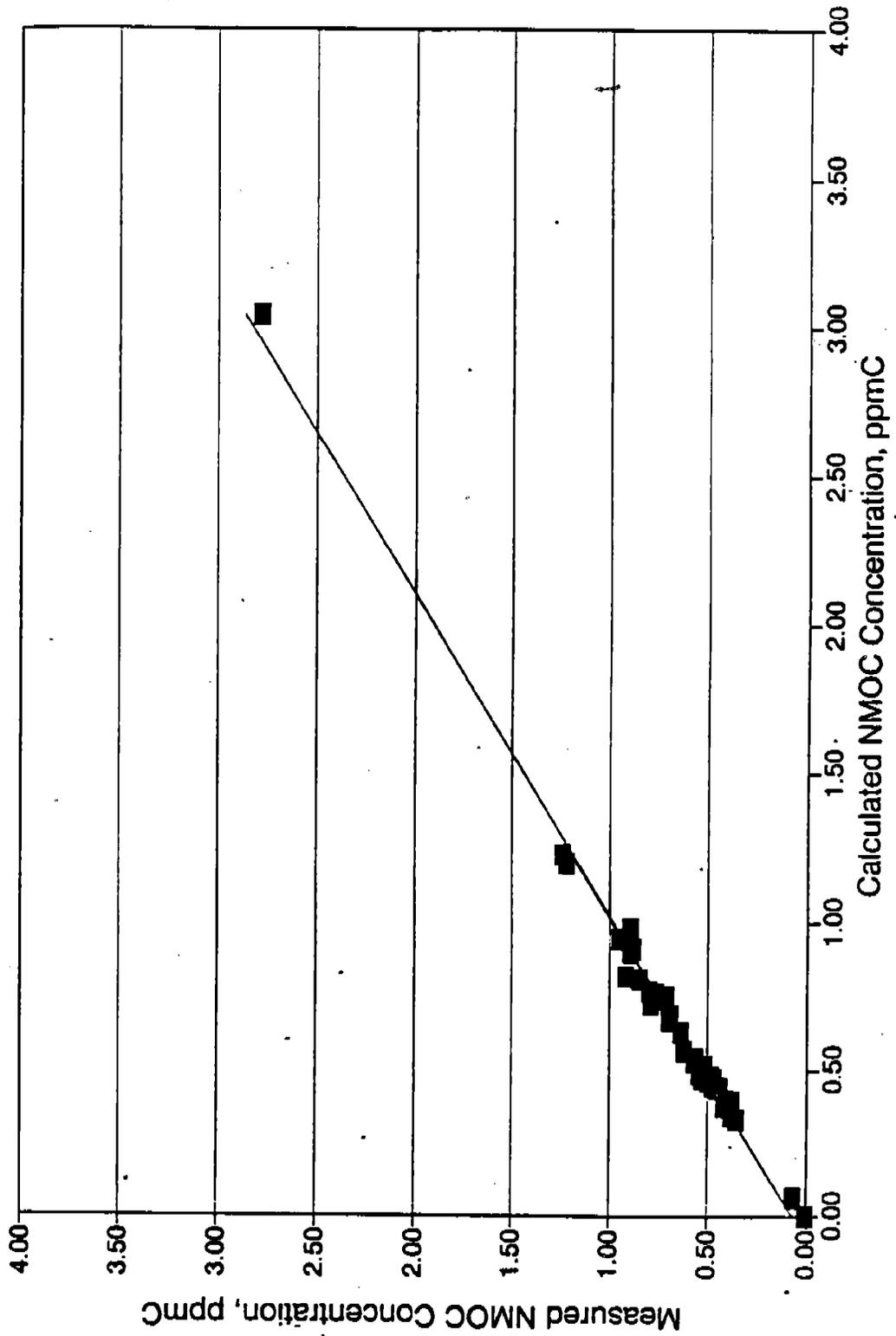


Figure 1-3. In-house quality control results, Channel C.

IN-HOUSE PROPANE QC RESULTS

Channel D

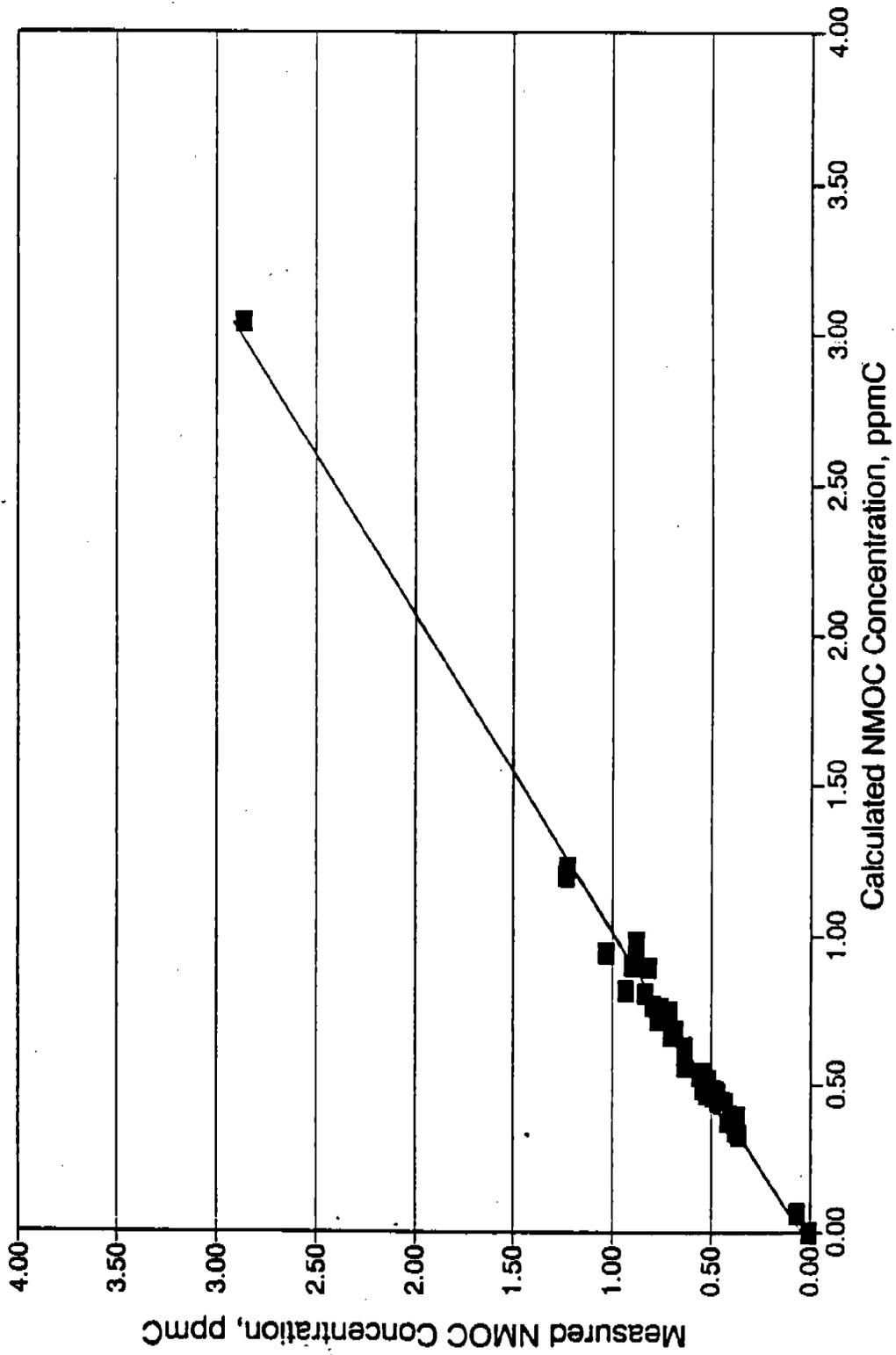


Figure 1-4. In-house quality control results, Channel D.

Table 1-3

Linear Regression Parameters for In-House Quality Control Data

Radian Channel	Cases	Intercept	Slope	Coefficient of Correlation
A	47	0.072788	0.893984	0.994696
B	46	0.059017	0.925588	0.995561
C	47	0.061009	0.920621	0.996163
D	48	0.045389	0.943950	0.995771

Table 1-4
External NMOC Audit Samples

Canister No.	Concentration, ppnC					
	Theoretical	Analysis				
		ManTech	Radian A	Radian B	Radian C	Radian D
014	1.248	1.515	1.544	1.551	1.553	1.553
185	1.200	1.500	1.550	1.542	1.539	1.529
625	1.119	1.095	1.095	1.192	1.178	1.161
722	1.911	2.157	2.157	1.835	1.820	1.800

Ten percent (10%) 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 0.932 percent. All errors that were found were corrected.

1.2 THREE-HOUR AIR TOXICS MONITORING PROGRAM

At two sites, NWNJ and PLNJ, 3-hour NMOC samples were speciated by a GC/MD analytical system for 38 UATMP target compounds for a total of 17 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 both of the sites simultaneously and analyzed individually by GC/MD. Replicate analyses were performed on one duplicate sample per site. A total of 21 GC/MD analyses were performed, including duplicate samples and replicate analyses.

1.2.1 Overall Data Summary

Twenty-five target compounds were identified in the 21 analyses. Benzene, m/p-xylene/bromoform, toluene, ethylbenzene, o-xylene/1,1,2,2-tetrachloroethane carbon tetrachloride, and 1,1,1-trichloroethane were identified in every sample. Concentrations of the target compounds identified ranged from 0.04 ppbv for 1,1,1-trichloroethylene to 169.7 ppbv for acetylene. The overall average concentration of the target compounds identified was 6.64 ppbv, averaged over all sites and target compounds. The air toxics data are tabulated by site code in Section 7 (Table 7-2) showing numbers of cases identified, minima, maxima, and means for all target compounds.

1.2.2 Site Results

Overall site mean concentrations were 6.04 ppbv for NWNJ, and 7.39 ppbv for PLNJ averaged over all target compounds identified. These air toxic data are presented in Section 7.0. The unusually high overall average and site averages result from unusually high averages in the acetylene concentrations seen at the two sites in 1991.

1.2.3 Gas Chromatography/Mass Spectrometry Confirmation Results

Based on three GC/MS analyses of the 3-hour air toxics samples, one from each site location, the following results were obtained. The GC/MS analyses confirmed 80.00% of the GC/MD analyses. The results are summarized in Table 1-5, showing 20.00% positive GC/MD-positive GC/MS confirmation, 15.71% positive GC/MD-negative GC/MS confirmation, 4.29% negative GC/MD-positive GC/MS comparison, and 60.00% negative GC/MD-negative GC/MS comparisons. Comparisons labeled "negative GC/MD-positive GC/MS" refer to specific samples in which a compound was not identified by GC/MD but positively identified by GC/MS analysis. Comparisons labeled "positive GC/MD-negative GC/MS" indicate specific samples in which a compound was positively identified by GC/MD but not identified by GC/MS analysis.

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 11.72 percent.

Analytical precision was estimated by repeated analyses of aliquots from a sample canister. The analytical precision measured by the overall average absolute percent difference was 9.84 percent. Both the sampling and analytical precision results are excellent in view of the concentration range found in this study.

Both the duplicate sample and repeated analyses results are discussed in Section 8.7.

1.2.5 External Audit

The external audit for the 3-hour air toxics compounds is conducted bimonthly on the Urban Air Toxics Program and the results will be reported in the 1991 UATMP Final Report. The audit samples that are used are furnished by the Quality Assurance Division of the U.S. EPA.

Table 1-5

Compound Identification Confirmation

GC/MD versus GC/MS Comparison	Cases	Percentage
Positive GC/MD - Positive GC/MS	14	20.00
Positive GC/MD - Negative GC/MS	11	15.71
Negative GC/MD - Positive GC/MS	3	4.29
Negative GC/MD - Negative GC/MS	42	60.00
Total	70	10.00
Total compound identification confirmation = 20.00% + 60.00% = 80.00%		

1.3 CARBONYL

Carbonyl samples were taken at four sites, NWNJ, PLNJ, MNY, and LINY, for the 1991 monitoring season. Duplicate samples were taken on Monday, June 24 and August 5; Tuesday, July 2 and August 13; Wednesday, July 10 and August 21; Thursday, July 18 and August 29; and Friday, July 26 and September 6, 1991. Three-hour samples were taken from 6:00 a.m. to 9:00 a.m. simultaneously with the NMOC samples at the four sites. The carbonyl sampler has its own inlet manifold, capillary critical orifice and separate Metal-Bellows® pump. The inlet manifold splits in two which leads into duplicate ozone scrubbers ahead of 2,4-dinitrophenylhydrazine (DNPH) coated cartridges.

Carbonyl concentrations ranged from 0.3 ppbv for acrolein at LINY to 12.0 ppbv for acetone at NWNJ. Eight carbonyls, formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, and butyr/iosbutyraldehyde, were identified at one or more of the 1991 sites.

1.4 SNMOC

Five sites, BMTX, BRLA, ELTX, HITX, and JUMX, participated in the speciated nonmethane organic compound monitoring program. These sites collected integrated ambient air samples from 6:00 a.m. to 9:00 a.m., Monday through Friday, from June 3, 1991, through September 27, 1991. Five sites, RINC, PLNJ, PBFL, NWNJ, and F1FL, carried out a limited monitoring program with 10 samples collected during the monitoring season from June through September 1991.

Measured concentrations ranged from 0.37 ppbv for n-nonane to 1032 ppbv for n-pentane with averages ranging from 0.925 ppbv for n-dodecane to 63.447 for isopentane.

2.0 NMOC DATA SUMMARY

This section presents the data summary for the 1991 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 eight 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 1991 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 T0-12¹. 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 1991 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 QAPP². For the 1991 NMOC sites, completeness was over 90%, 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 1991 NMOC Program show 94.1% complete. This compares with 95.8% in 1990, 95.5% in 1989, 93.4% in 1988,

Table 2-1

1991 NMOC Completeness Results

Site Location	Radian Site Code	Scheduled Sampling Days	Total Scheduled Duplicate Samples	Total Scheduled Samples	Total Valid Duplicate Samples	Total Valid Samples	Percent Complete
Fort Lauderdale, FL	FIFL	82	9	91	8	88	96.70
Long Island, NY	LINY	83	9	92	9	90	97.83
New York, NY	MNY	76	9	85	11	79	92.94
Newark, NJ	NWNJ	84	9	93	6	93	100.00
West Palm Beach, FL	PBFL	83	9	92	9	87	94.57
Plainfield, NJ	PLNJ	84	9	93	12	81	87.10
Raleigh, NC	RINC	83	9	92	7	81	88.04
Winston-Salem, NC	WSNC	83	9	92	9	88	95.65
OVERALL		658	72	730	71	687	94.11

95.0% complete in 1987, 96.8% complete in 1986, 95.8% complete in 1985 and 90.6% complete in 1984.^{3,4,5,6,7,8,9}

Completeness was defined as the percentage of samples, scheduled in the QAPP,² that were collected and analyzed as valid samples, beginning with the first valid sample and ending with the last scheduled sample, with the exception of RINC. An unexpected site situation caused RINC to collect its last sample on October 4, 1991.

Table 2-2 summarizes statistics by sites. All sites collected an integrated sample from 6:00 a.m. to 9:00 a.m. The overall average of the NMOC concentration is seen to be 0.417 ppmC. The averages pertain only to the sites for the 1991 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. All the kurtosis figures listed in this report are zero centered, which means that 3.0 has been subtracted from the fourth moment to give a reported kurtosis of 0.0 for a symmetrical distribution. The Shapiro-Wilk statistic (W) tests the normality of the data and ranges from zero to one. The closer the statistic is to one, the better the fit of the data to normality. Comparing W for a site in Tables 2-2 and 2-3 shows that the logarithmic transformation of the NMOC data make the logarithm of NMOC concentrations to be a more nearly normal distribution.

NMOC monitoring data can be better characterized by a lognormal distribution than by a normal distribution, following the findings of previous years.^{3,4,5,6,7,8,9} Table 2-3 summarizes the 1991 NMOC data using the definitions that characterize a lognormal distribution overall and for each site. MU and SIGMA are the mean and standard deviation, respectively, of the

Table 2-2

NMOC Overall Statistics, by Site

Site	Cases	Concentration, ppmC							N ^a
		Min	Max	Median	Mean	Std Dev	Skewness	Kurtosis	
F1FL	88	0.042	3.134	0.359	0.490	0.529	3.047	12.105	0.698
L1NY	90	0.058	1.321	0.273	0.326	0.235	1.897	4.917	0.832
M1NY	79	0.155	1.790	0.404	0.493	0.309	1.954	4.604	0.816
N1W1NJ	93	0.129	1.520	0.393	0.462	0.251	1.439	3.162	0.892
P1B1FL	87	0.094	1.515	0.510	0.542	0.272	0.770	0.888	0.953
P1L1NJ	81	0.068	3.842	0.292	0.464	0.626	4.168	19.069	0.503
R1INC	81	0.056	0.983	0.214	0.298	0.221	1.415	1.157	0.815
W1S1NC	88	0.050	1.120	0.182	0.261	0.232	2.253	5.061	0.716
OVERALL	687	0.042	3.842	0.318	0.417	0.373	3.974	26.816	0.707

^aShapiro-Wilk statistic to test normality of data.

Table 2-3

1991 LNMOc Overall Statistics, by Site

Site	Cases	Concentration, ppmC								N ^a
		Min	Max	Median	Mean ^b	Mu ^c	Sigma ^d	Mode		
FIFL	88	0.042	3.134	0.359	0.499	-1.144	0.947	0.178	0.968	
LINY	90	0.058	1.321	0.273	0.326	-1.345	0.668	0.110	0.980	
MNY	79	0.155	1.790	0.404	0.488	-0.861	0.537	0.341	0.969	
NMNJ	93	0.129	1.520	0.393	0.463	-0.908	0.525	0.181	0.977	
PBFL	87	0.094	1.515	0.510	0.551	-0.751	0.556	0.310	0.965	
PLNJ	81	0.068	3.842	0.292	0.425	-1.144	0.760	0.228	0.934	
RINC	81	0.056	0.983	0.214	0.296	-1.448	0.681	0.102	0.960	
WSNC	88	0.050	1.120	0.182	0.254	-1.617	0.703	0.111	0.954	
OVERALL	687	0.042	3.842	0.318	0.415	-1.153	0.739	0.155	0.983	

^aLNMOc = ln(NMOC), when NMOC is in ppmC.

^bMean = $\exp(\text{Mu} + \text{Sigma}^2/2)$.

^cMu is the mean of ln(NMOC). e^{Mu} is the geometric mean.

^dSigma is the standard deviation of ln(NMOC). e^{Sigma} is called the geometric standard deviation.

^eShapiro-Wilk statistic to test normality of data.

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, the site code used throughout this report, the Aerometric Information Retrieval System (AIRS) Number. Appendix A gives the AIRS printouts for all the sites that are in the system for 1991.

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 1991 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; and
- NMOC concentration in ppmC, determined by Radian.

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

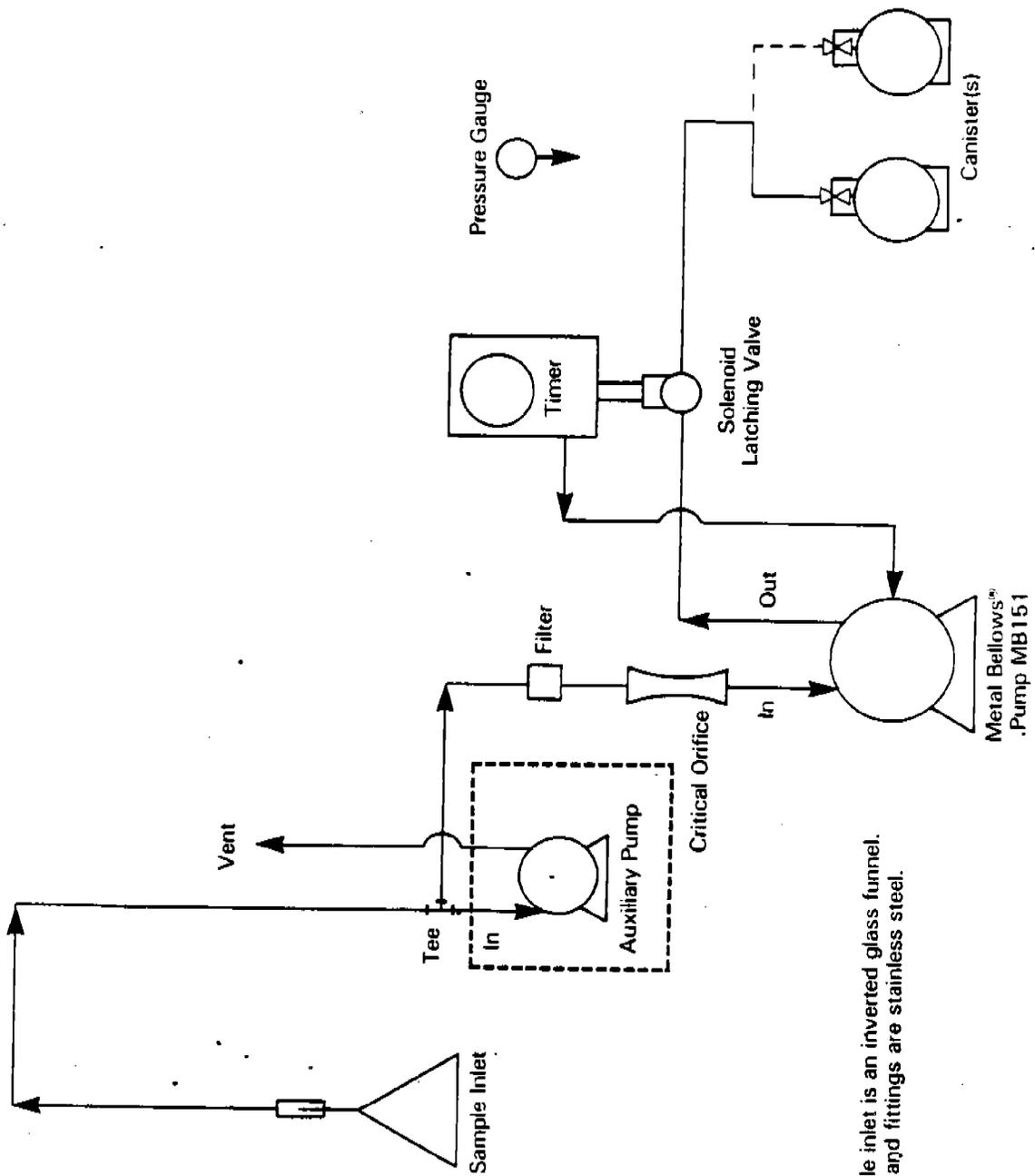
This section summarizes descriptions of the installation and operation of the field sampling equipment, a summary of the analytical equipment and procedures for NMOC measurement, and a description of the canister cleanup equipment and procedures.

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 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 tubing or gas-chromatographic-grade stainless steel tubing and stainless steel fittings 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 eight 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 being sampled. The critical



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

1281787R

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

orifice was sized to maintain a constant flow rate and to fill a 6-L stainless steel canister from the 0.5 mm Hg vacuum to about 15 psig in three 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.

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 ($\pm 15\%$) 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.



NMOC SAMPLING FIELD DATA FORM

Site Code : _____ SAROAD # : _____

Site Location : City: _____ State: _____

Sample Collection Date : _____ Sampling Period : _____

Operator : _____ Elapsed Time : _____

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 : _____

0781189R

Figure 3-2. NMOC Sampling Field Data Form

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.

3.1.4 Sampler Performance for 1991

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 1991 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 1991 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 93.0 percent. The site-specific completeness ranged from 88.0% for RINC to 100.0% for NWNJ.

Invalidated samples were primarily due to operator error and equipment problems. Completeness can be improved at all sites through greater attention to sampling procedure, and by ensuring that trained site personnel are available.

A total of 55 invalidated/missing samples were recorded in the 1991 NMOC Monitoring Program. Appendix D lists the invalidated/missing samples in chronological order, along with the reason for invalidation. Avoidable operator error accounts for 20% and equipment problems account for 60% of the invalidated samples. Thirteen percent were missed sample collections for unknown reasons. The remaining 7% reflects four missed sample collections due to site inaccessibility.

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 B. 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 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

Figure 3-3. NMOC Invalid Sample Form

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 instrument), which is described in Appendix B. The EPA-QAD instrument was used as a reference during this program.

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 in Table 3-1.

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 1991 study according to a project specific Standard Operating Procedure (SOP). Further description is given below to help explain the analytical apparatus and procedure.

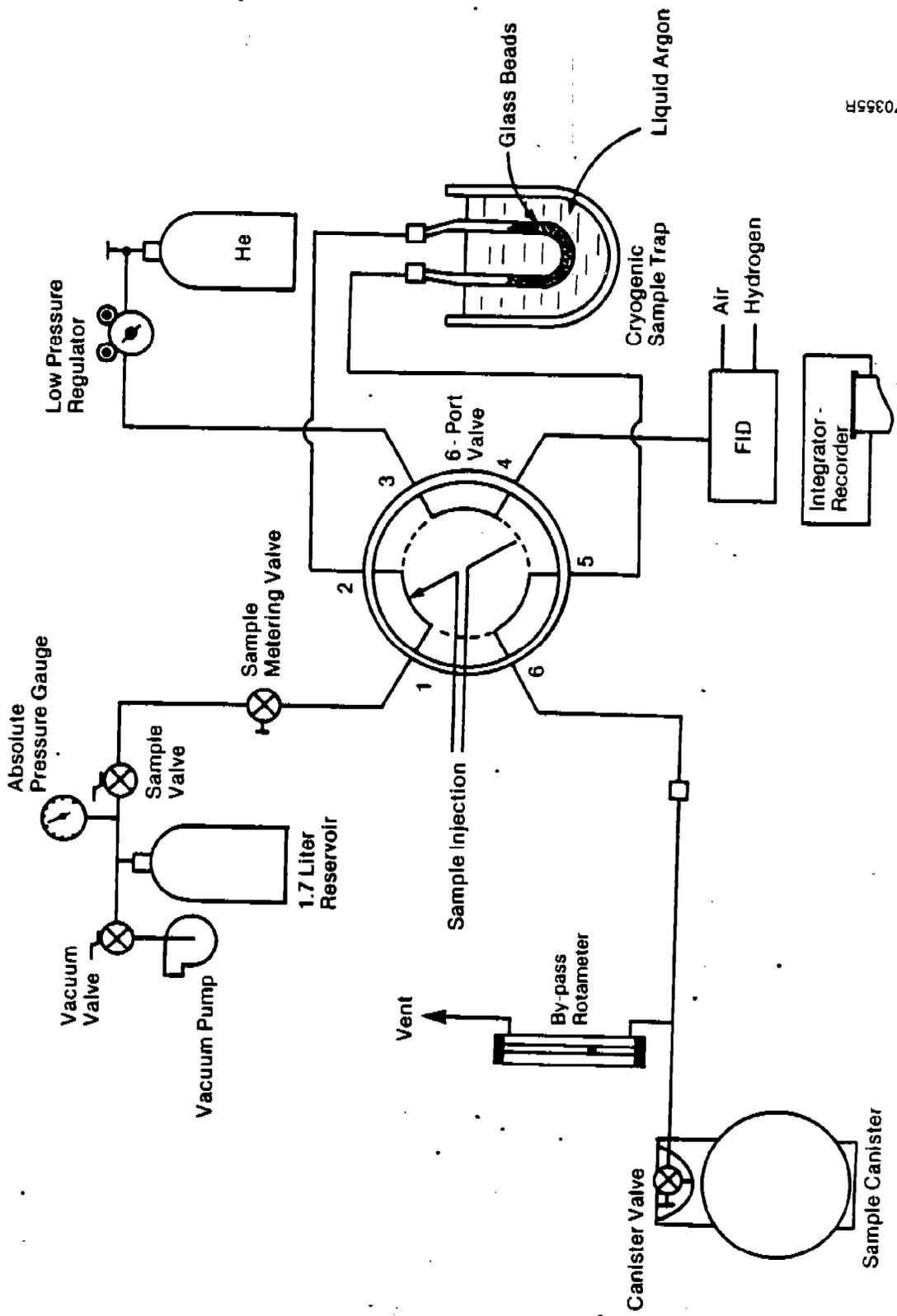
The six-port valve shown in Figure 3-4 was installed in the auxiliary heated zone of the HP-5880 and was pneumatically actuated using chromatographic valve control signals to apply either compressed air or vacuum to the valve. The sample trap itself was located inside the chromatograph's column oven. 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

Table 3-1

Support Gas Operation Conditions

Purpose	Cylinder Composition	Pressure	Mean Flow Rate ^a
Carrier Gas	Helium	30 psig	29.5 mL/min
FID Air	Hydrocarbon-free air	30 psig	300.7 mL/min
FID Fuel	Hydrogen	32 psig	29.0 mL/min

^aFlow rates corrected to standard conditions (1 atmosphere pressure, 20°C).



68703955R

Figure 3-4. NMOG analytical equipment.

of tubing effectively substitutes for the pressure restriction provided by a column, it does not perform the separation function of a column.

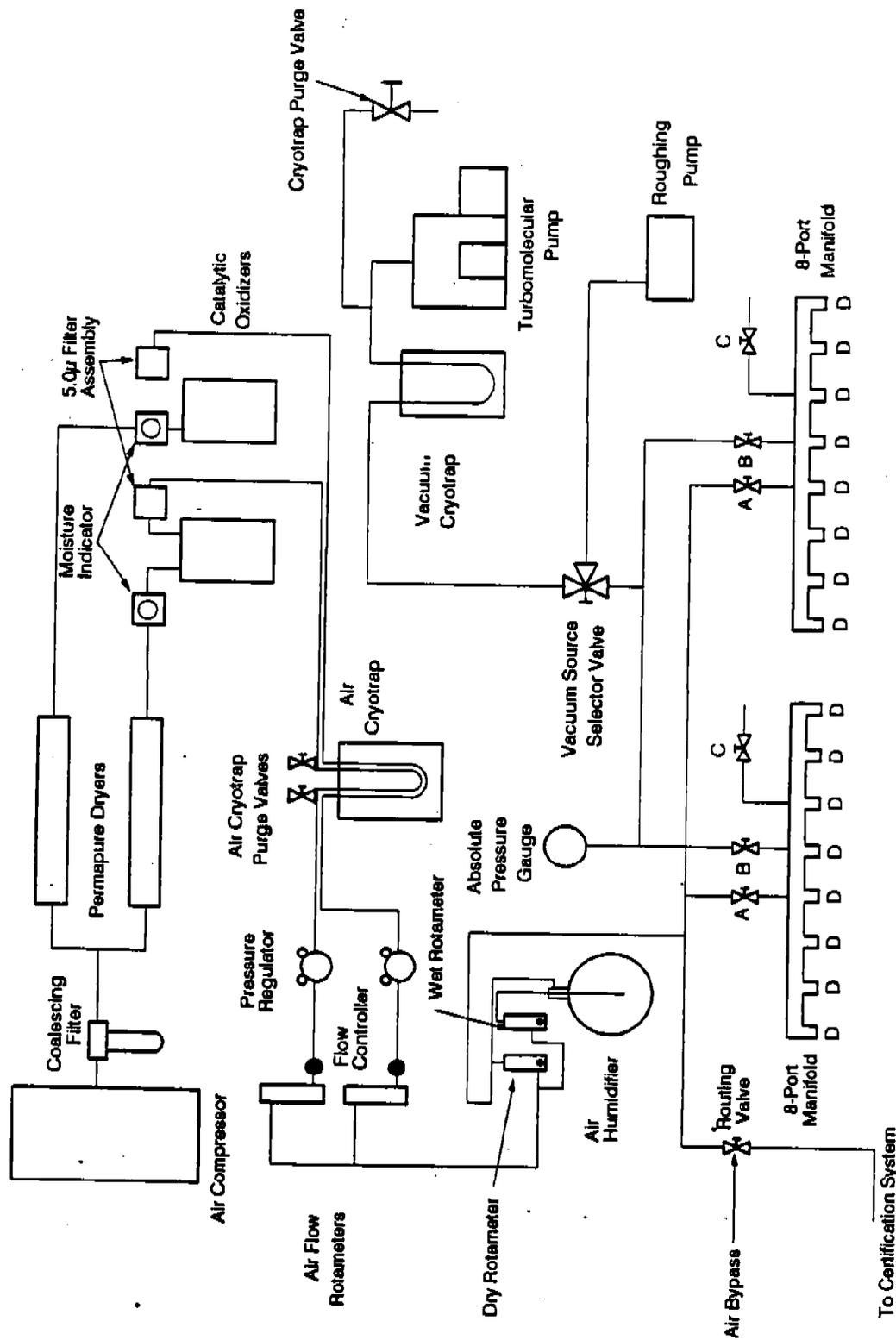
During sample trapping, a slight excess of sample gas flow was maintained. A pressure change of 80 mm Hg in a 1.7-L vacuum reservoir was used to gauge and control the volume of sample gas cryogenically trapped. After the trapping cycle was complete, the HP-5880 program shown in Appendix B was initiated. 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 0.5 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 of 20 ppbC, the canister was evacuated to 0.5 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 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.



- 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

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 1990 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 0.5 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 0.020 ppmC, then the eight canisters on the manifold were considered to be clean. Finally the canisters were again evacuated to 0.5 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 1991 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 of or referenced to an NIST SRM propane by ManTech.

4.1 INTRODUCTION AND CONCLUSIONS

Completeness for the 1991 NMOC study was 94.11 percent. This value indicates that good communication and planning were maintained between the site personnel and the laboratory personnel. Precision for the 1991 NMOC study averaged 14.16% absolute percent difference of repeated analysis and compared to 7.6% for the 1990 study, 14.2% for the 1989 study, 10.1% for the 1988 study, 9.61% for the 1987 study, 9.01% for the 1986 study, and 10% for the 1985 study.

Bias of the Radian channels for the 1991 audit results ranged from +1.9% to +8.9 percent. In 1990 the accuracy determined from the external audit samples ranged from -3.2% to +6.2%, from +1.3% to +4.5% in 1989, from 1.3% to 4.5% in 1988, and from -2.9% to -0.06% in 1987. 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. Daily calibration checks and 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 10% of the 1991 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 1991 are comparable 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 propane CRM No. 1666B. The concentration of the propane used in the performance assessment ranged from 2.47 to 17.49 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 were linear, having coefficients of correlation from 0.999244 to 0.999671. 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 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 determined

Table 4-1

1991 Performance Assessment Summary, Radian Channels

Radian Channel	Cases	Linear Regression Results ^a		
		Intercept	Slope	Coefficient of Correlation
A	20	-356.689	3762.889	0.999549
B	20	-353.754	3690.198	0.999666
C	20	-503.732	3717.716	0.999244
D	20	99.526	3629.419	0.999671

^aFigures 4-1 through 4-4 plot propane area counts vs. concentration in ppmC.

Four-Point Calibration - Channel A

Linear Regression

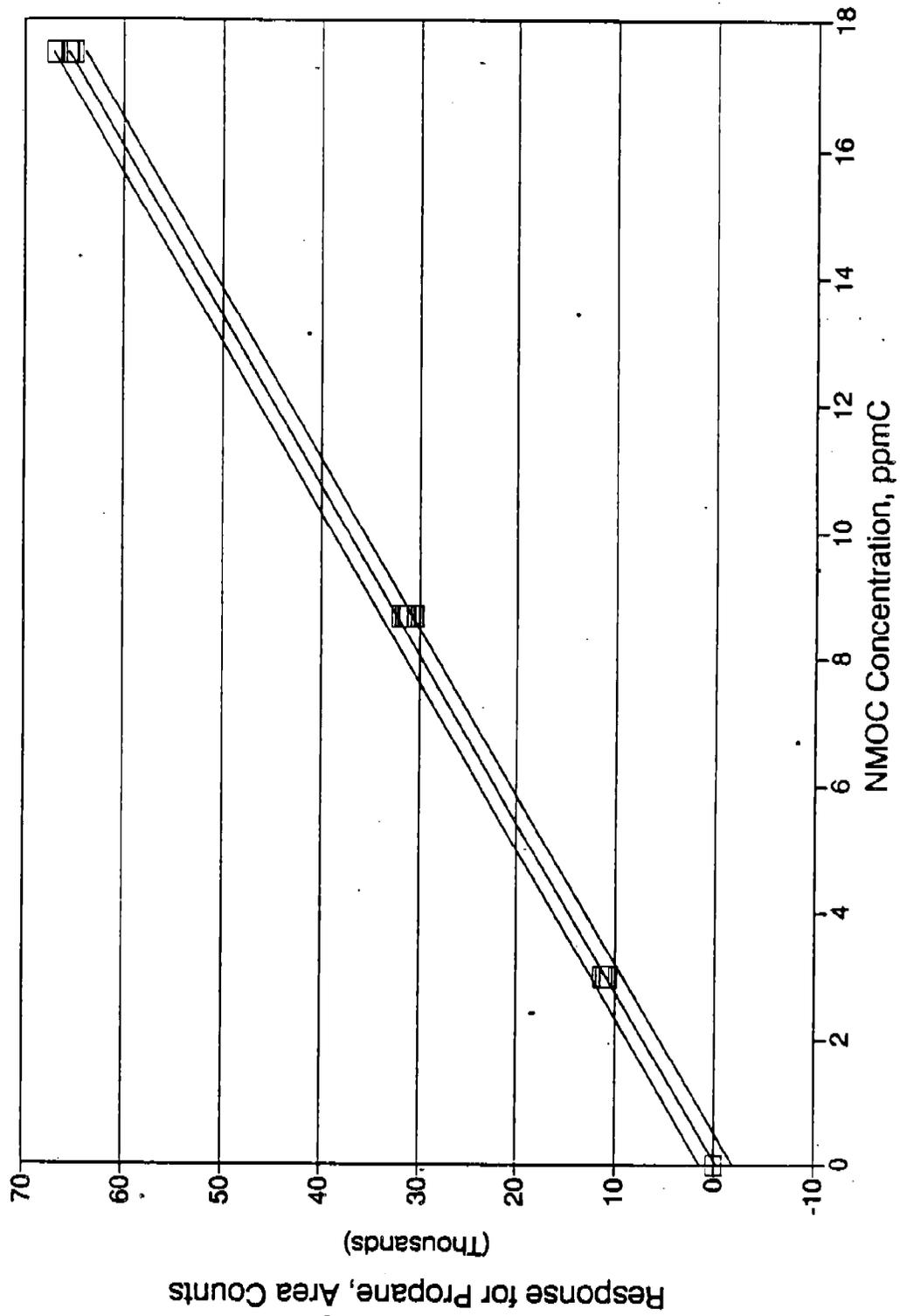


Figure 4-1. NMOc performance results, Channel A.

Four-Point Calibration - Channel B

Linear Regression

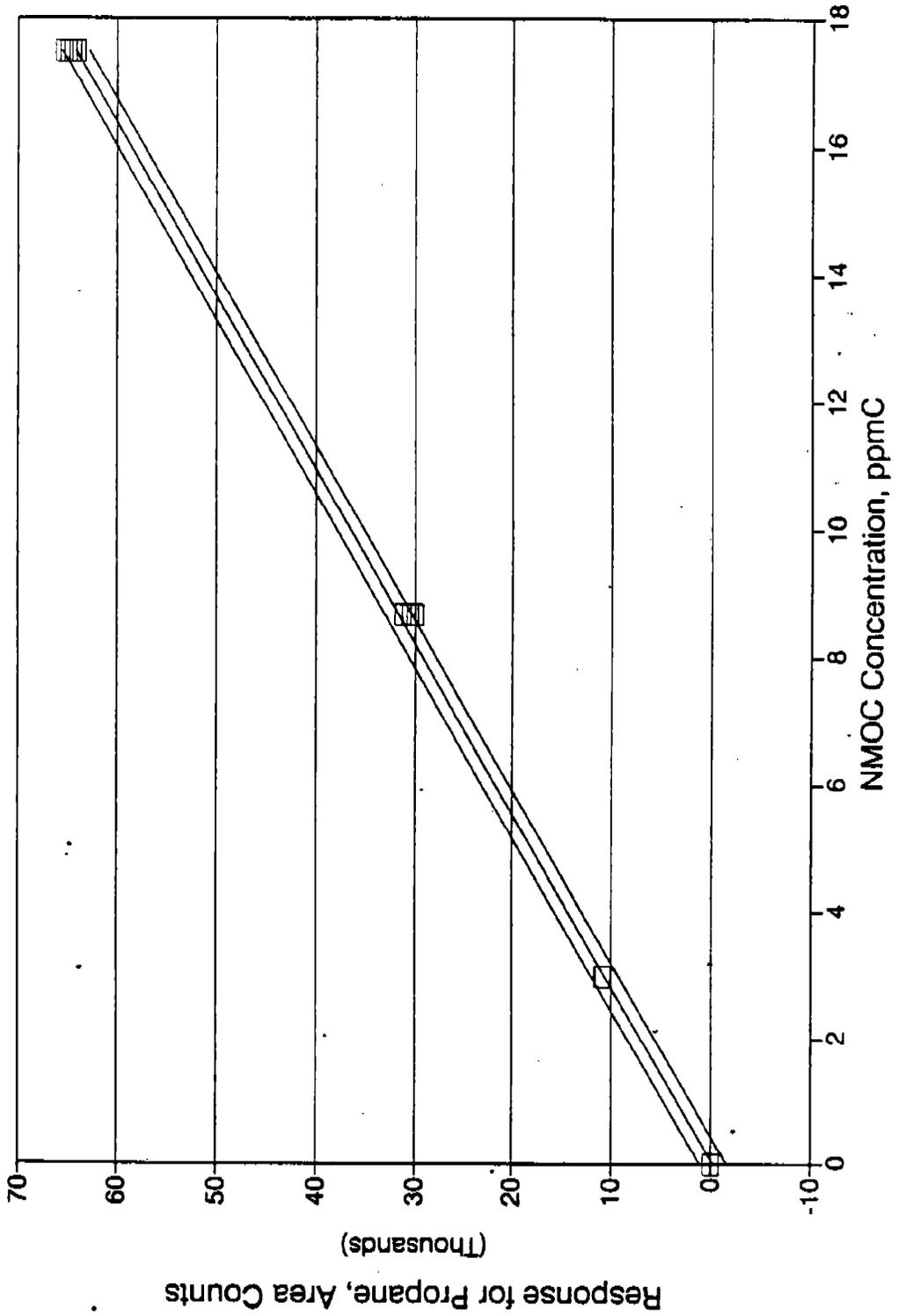


Figure 4-2. NMOC performance results, Channel B.

Four-Point Calibration - Channel C

Linear Regression

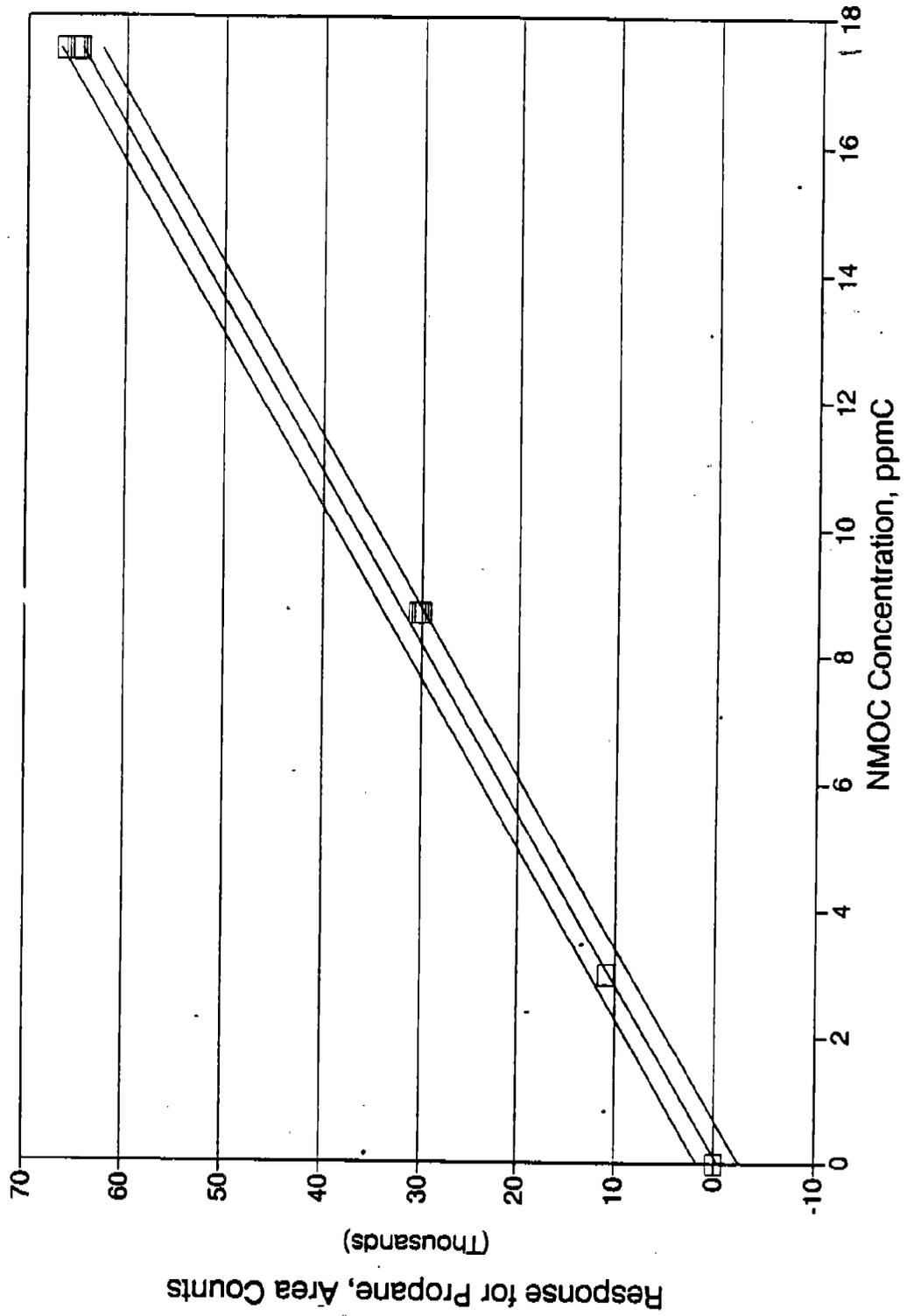


Figure 4-3. NMOC performance results, Channel C.

Four-Point Calibration - Channel D

Linear Regression

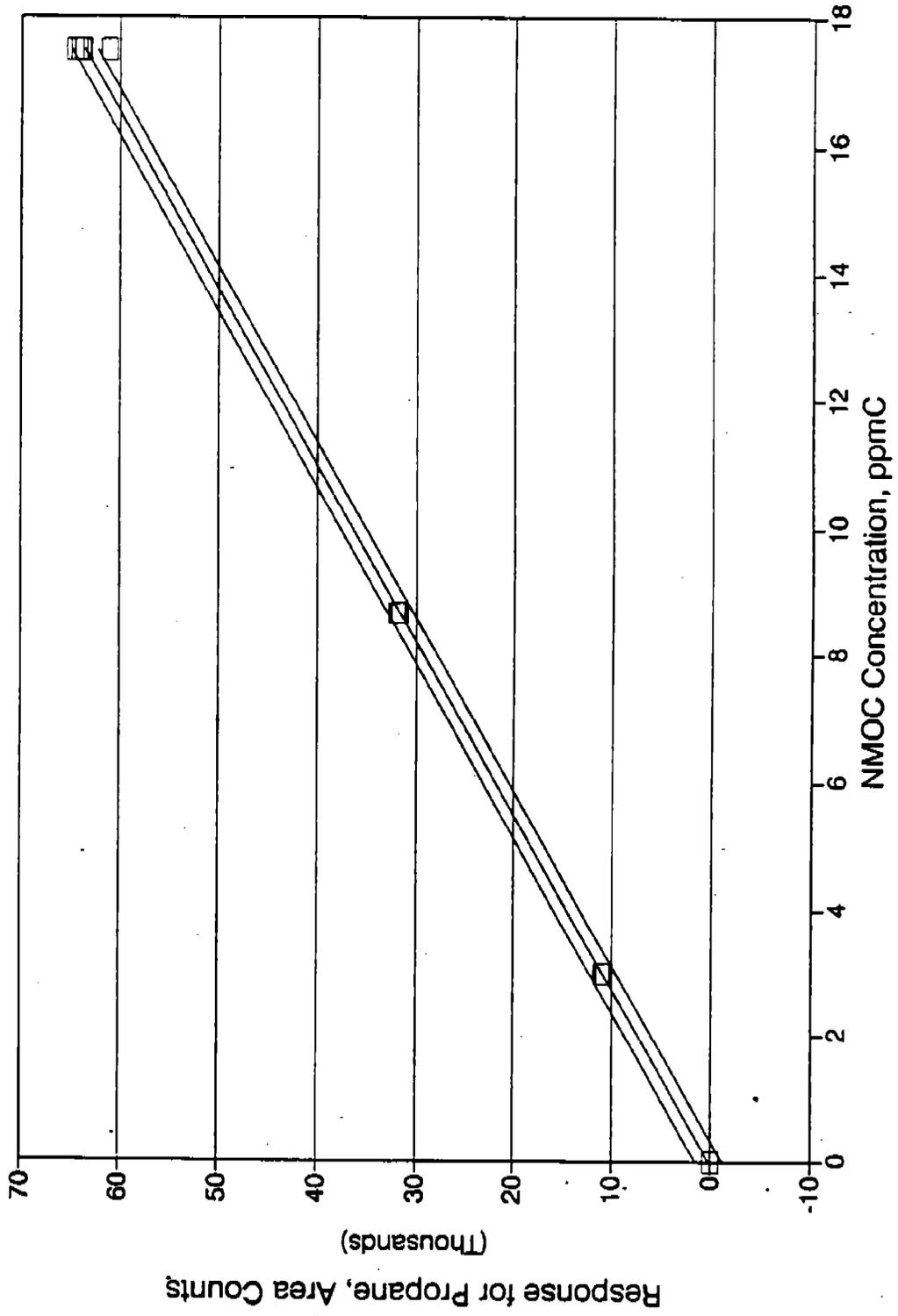


Figure 4-4. NMOC performance results, Channel D.

in the afternoon on randomly selected days after all the ambient air samples had been analyzed. Percent 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 1991 Julian date. Figures 4-13 through 4-16 show the daily percent drift data for Radian Channels A, B, C, and D. Inspection of the percent drift figures shows that the maximum percent drift was 6.81. The average absolute percent drift ranged from 0.835 for Channel B to 1.324 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 propane CRM No. 1666B reference standard as follows:

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

Daily calibration factors ranged from 0.000263 ppmC/area count to 0.000295 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

DAILY CALIBRATION - ZERO

Radian Channel A

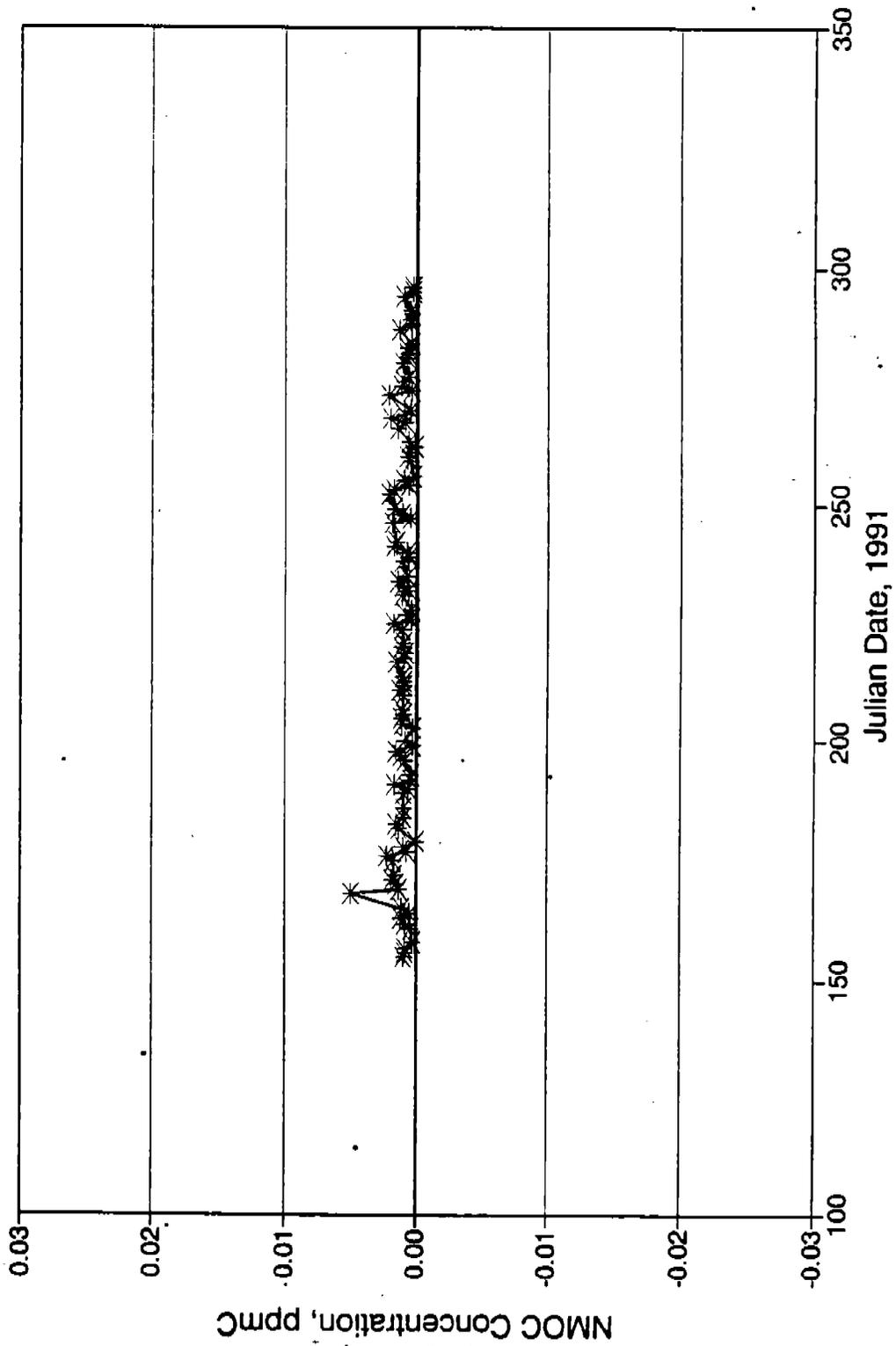


Figure 4-5. Daily calibration zero, Channel A.

DAILY CALIBRATION - ZERO

Russian Channel B

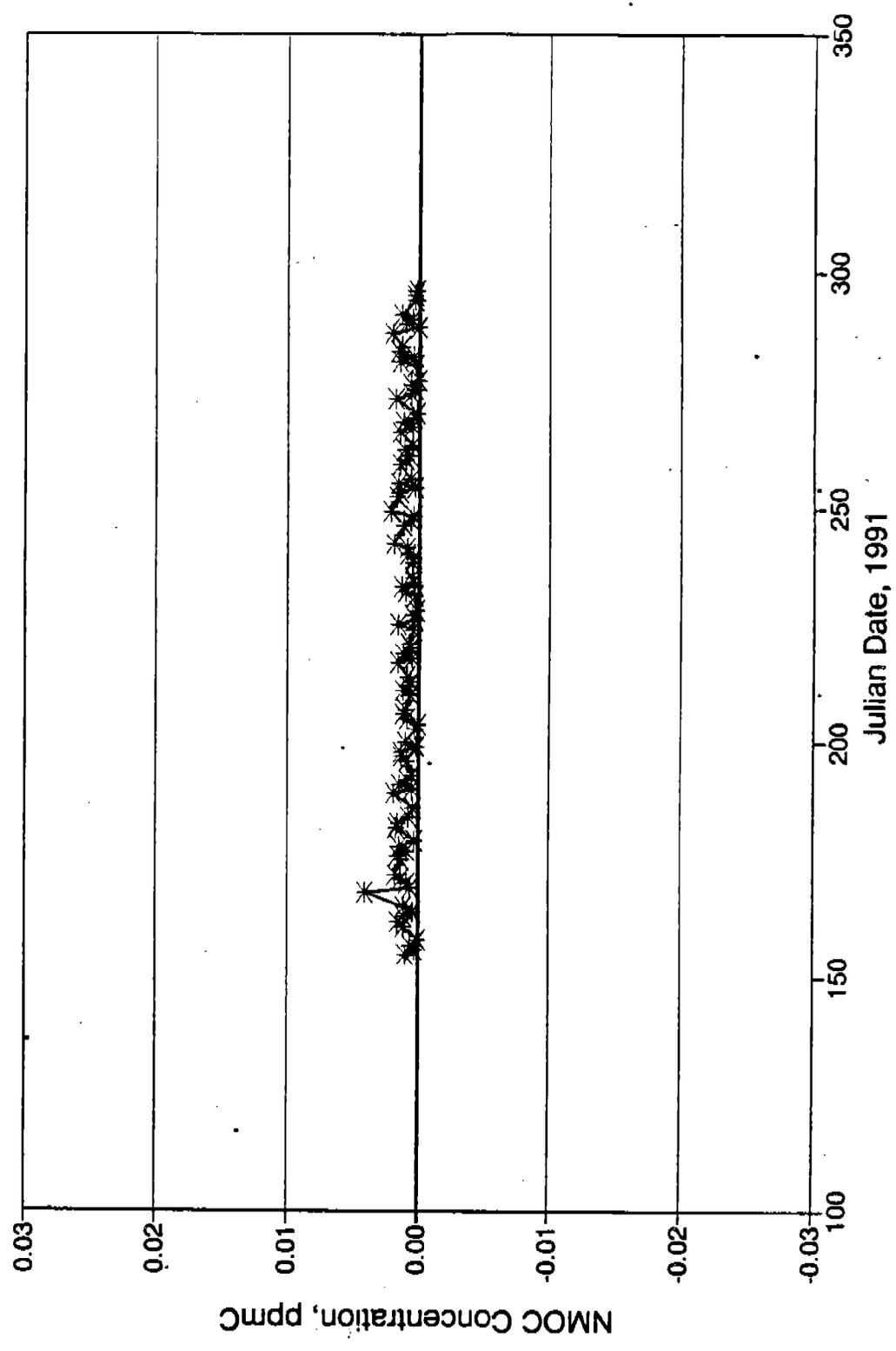


Figure 4-6. Daily calibration zero, Channel B.

DAILY CALIBRATION - ZERO

Radian Channel C.

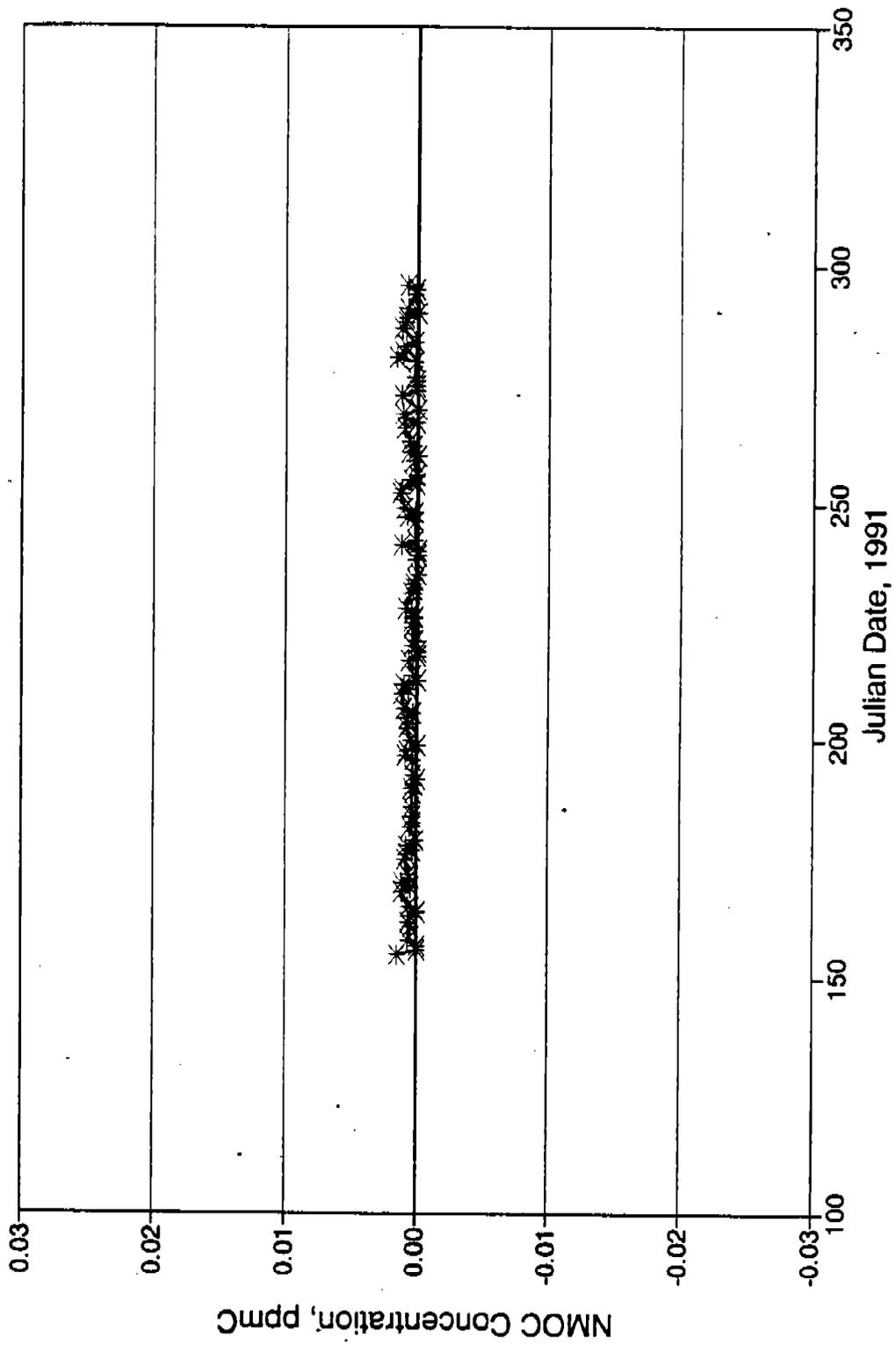


Figure 4-7. Daily calibration zero for Channel C.

DAILY CALIBRATION - ZERO

Radian Channel D

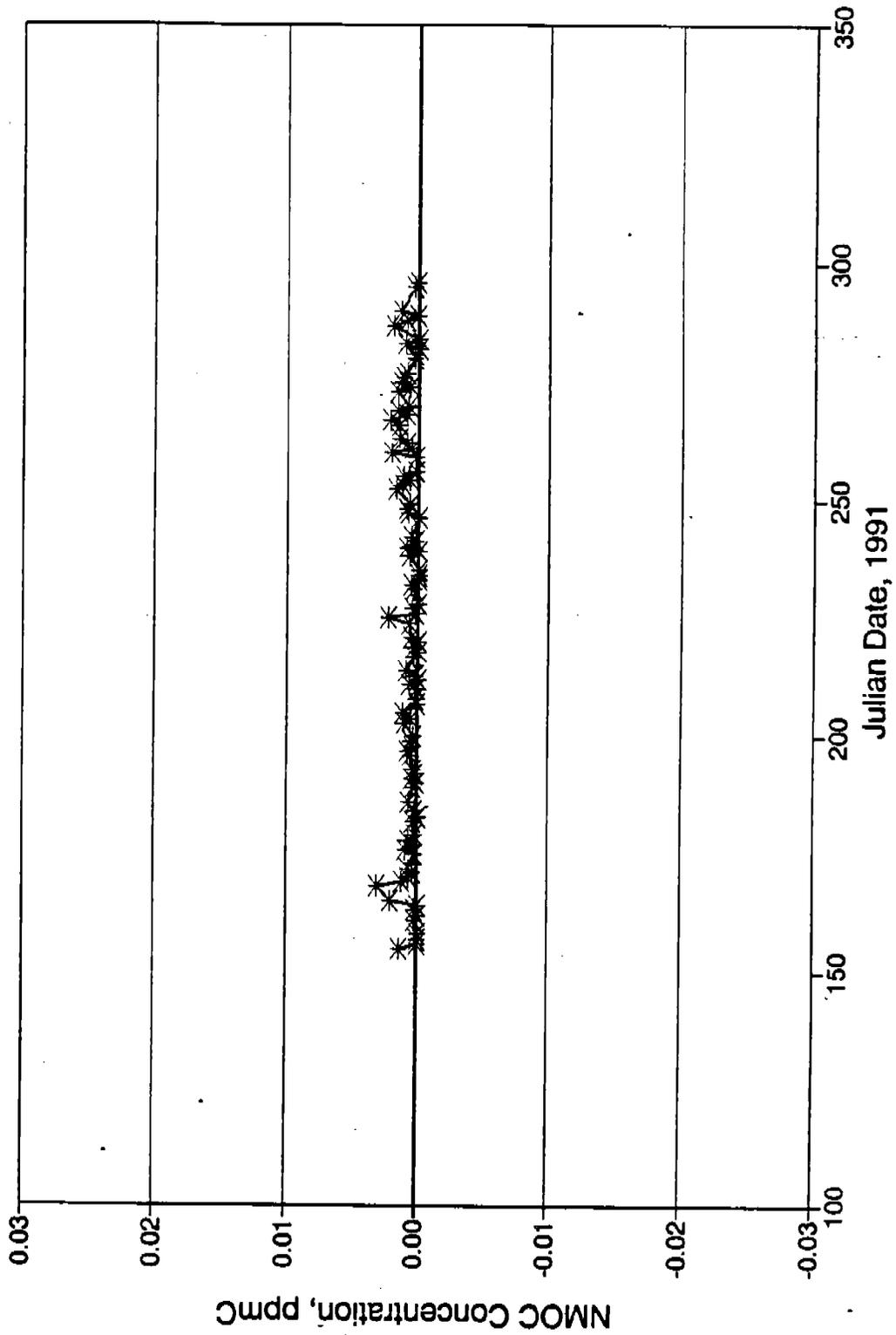


Figure 4-8. Daily calibration zero, Channel D.

DAILY CALIBRATION - SPAN

Radian Channel A

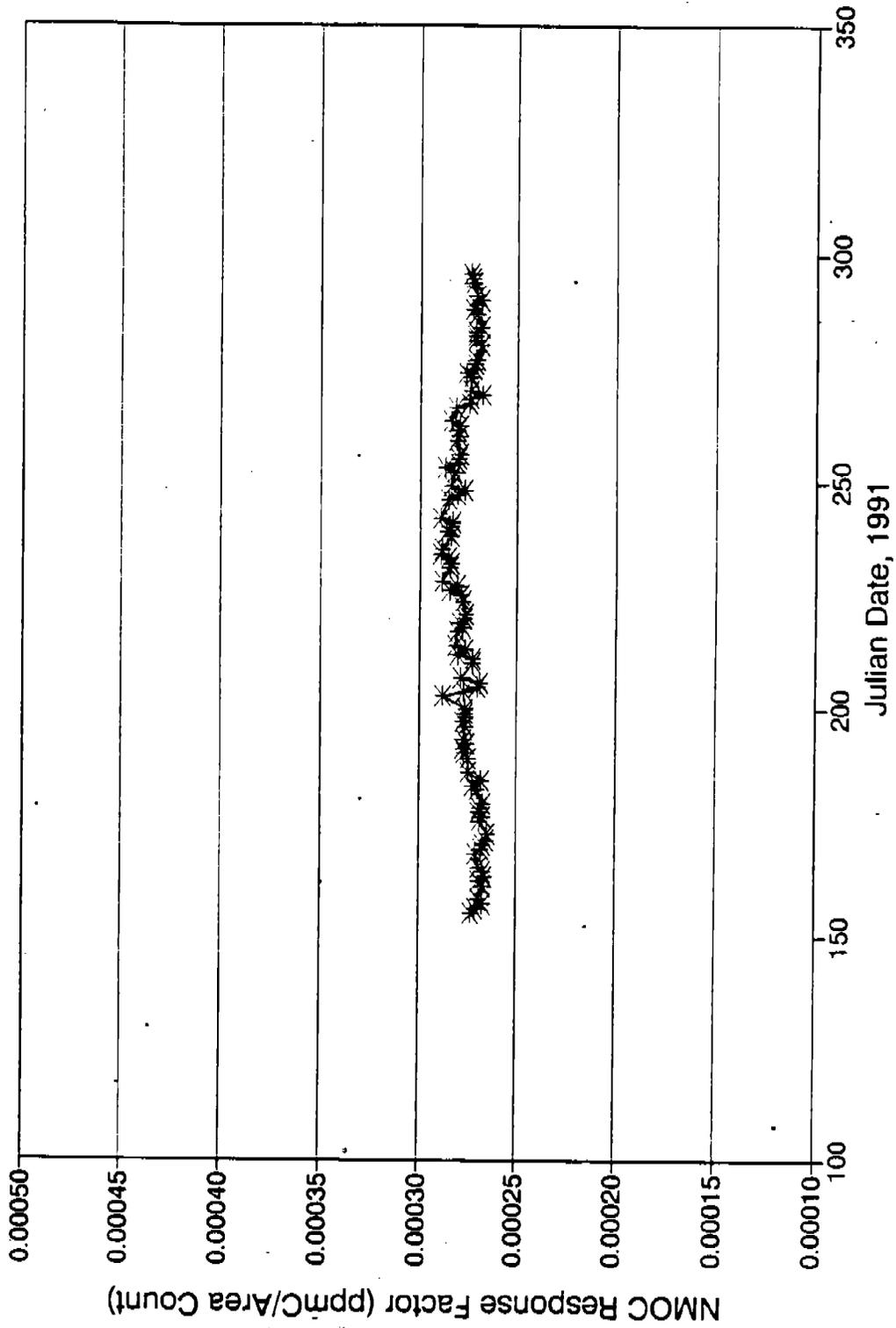


Figure 4-9. Daily calibration span, Channel A.

DAILY CALIBRATION - SPAN

Radian Channel B

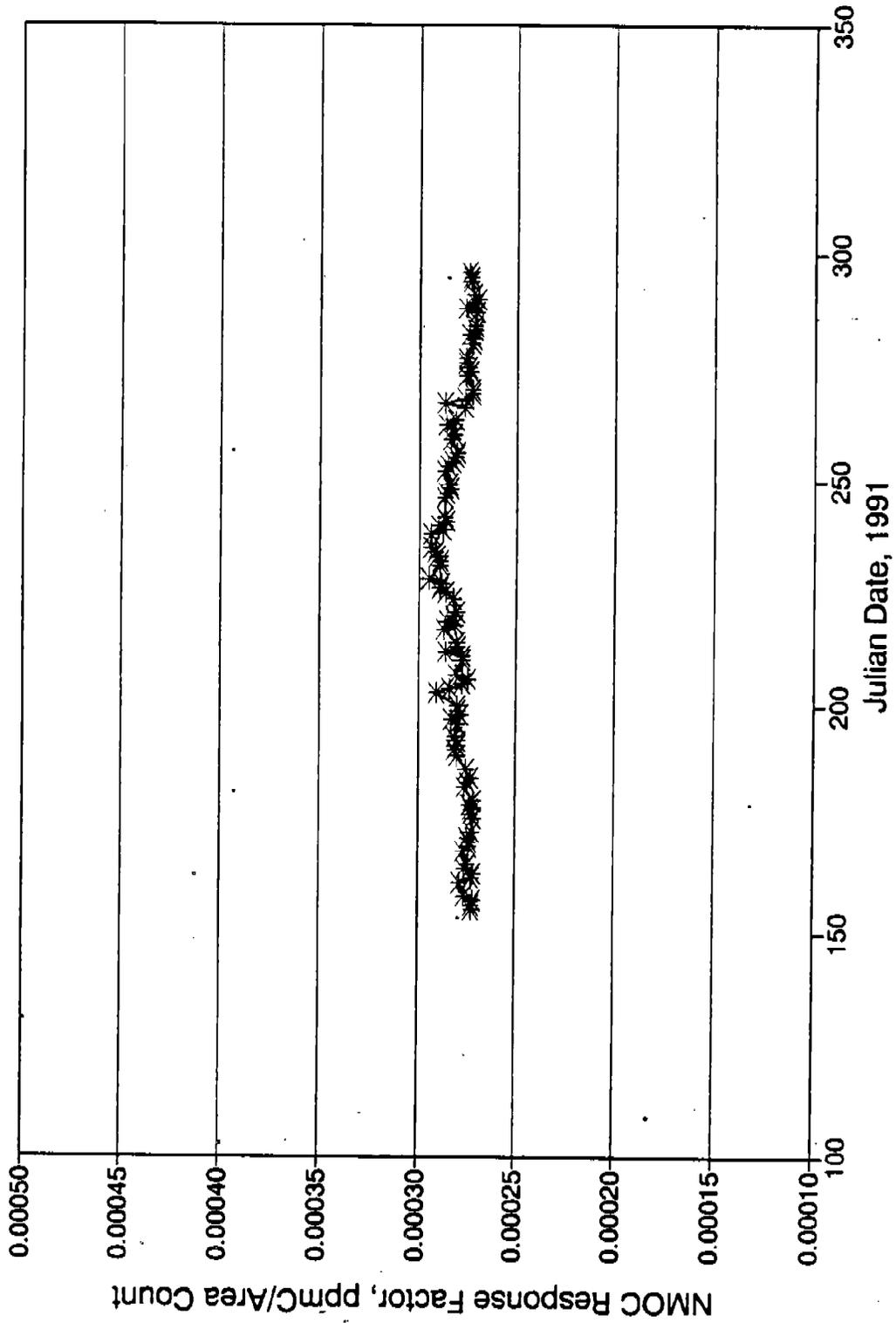


Figure 4-10. Daily calibration span, Channel B.

DAILY CALIBRATION - SPAN

Radian Channel C

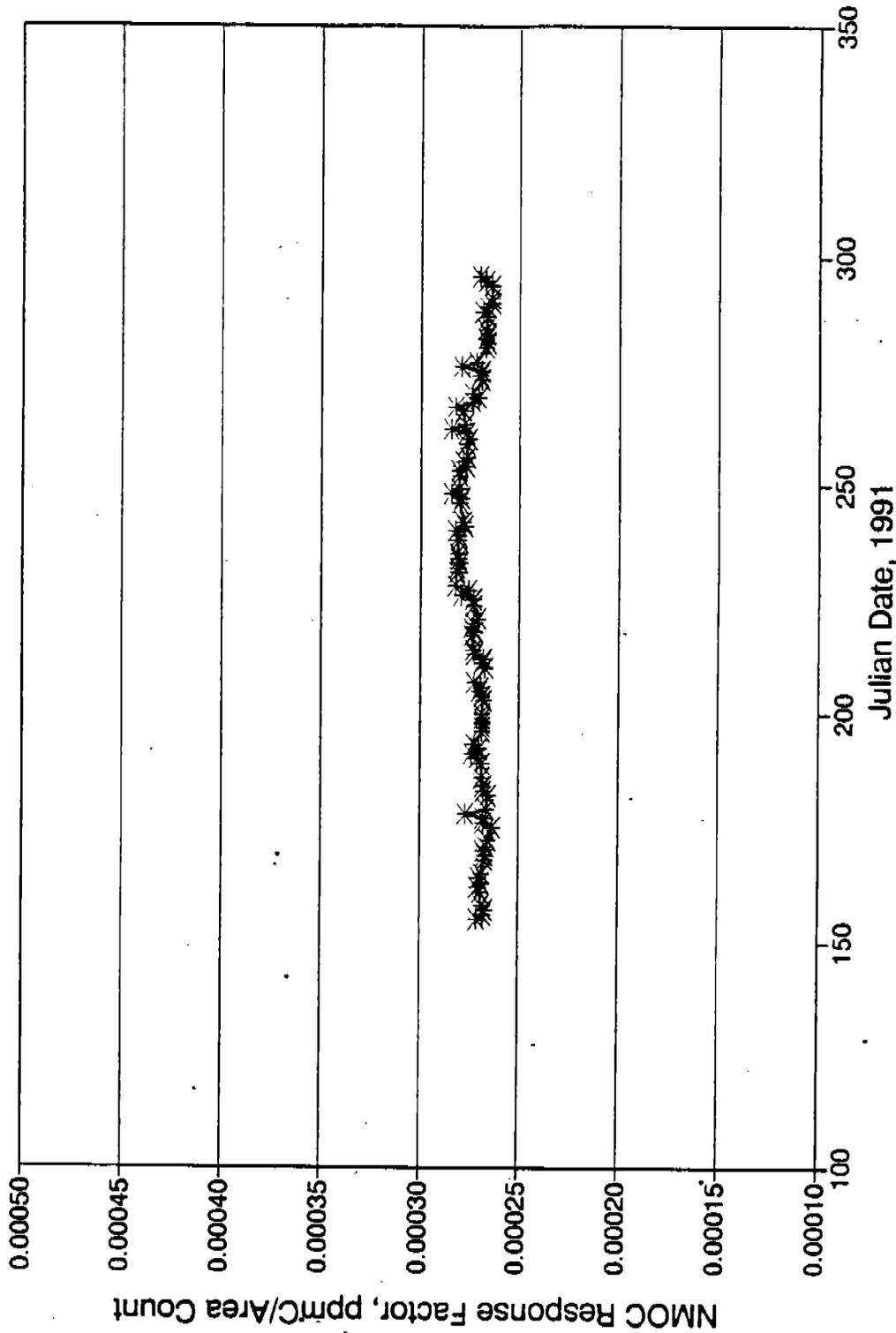


Figure 4-11. Daily calibration span, Channel C.

DAILY CALIBRATION - SPAN

Radian Channel D

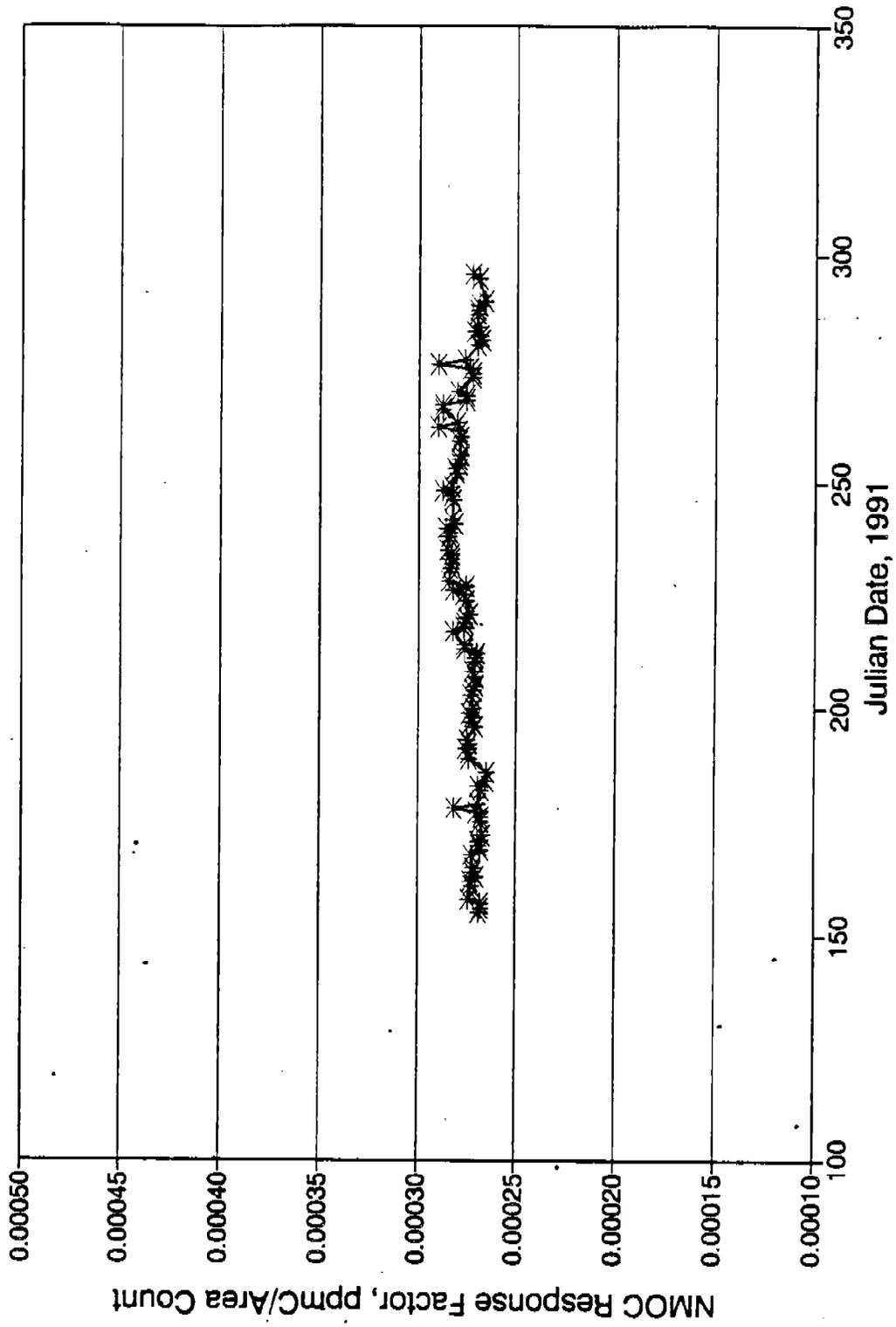


Figure 4-12. Daily calibration span, Channel D.

DAILY CALIBRATION - PERCENT DRIFT

Radian Channel A

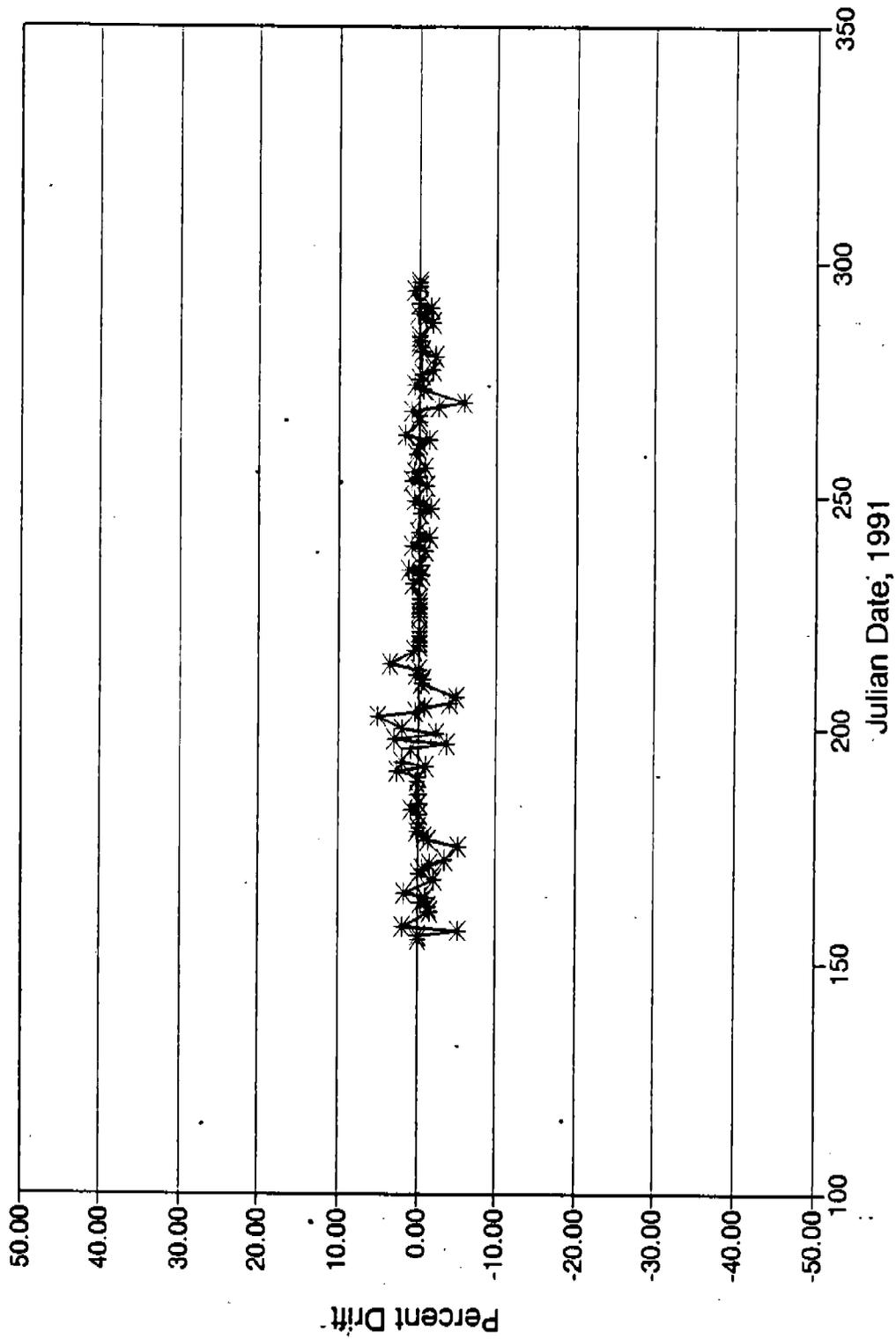


Figure 4-13. Daily calibration percent drift, Channel A.

DAILY CALIBRATION - PERCENT DRIFT

Radian Channel B

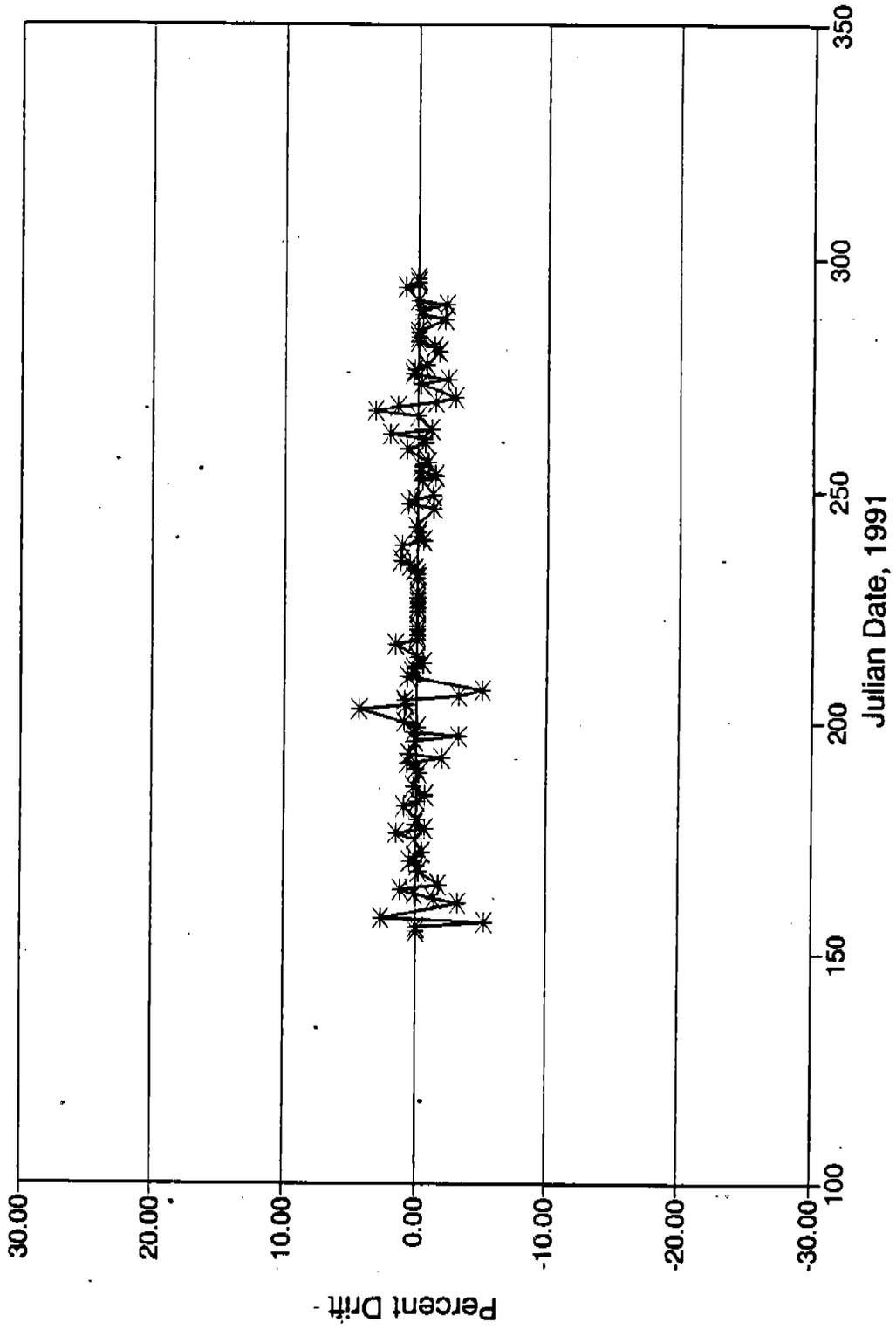


Figure 4-14. Daily calibration percent drift, Channel B.

DAILY CALIBRATION - PERCENT DRIFT

Radian Channel C

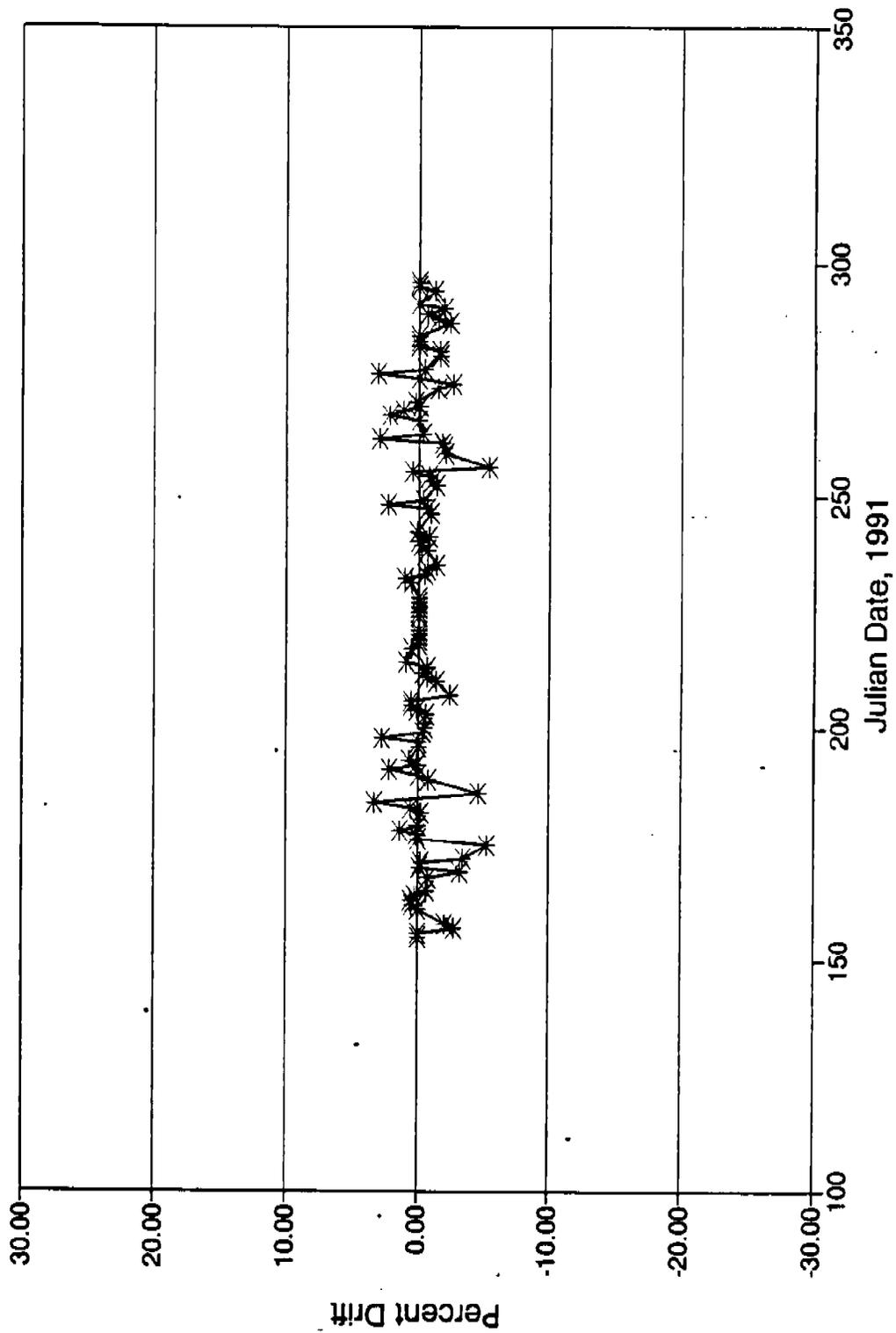


Figure 4-15. Daily calibration percent drift, Channel C.

DAILY CALIBRATION - PERCENT DRIFT

Radian Channel D

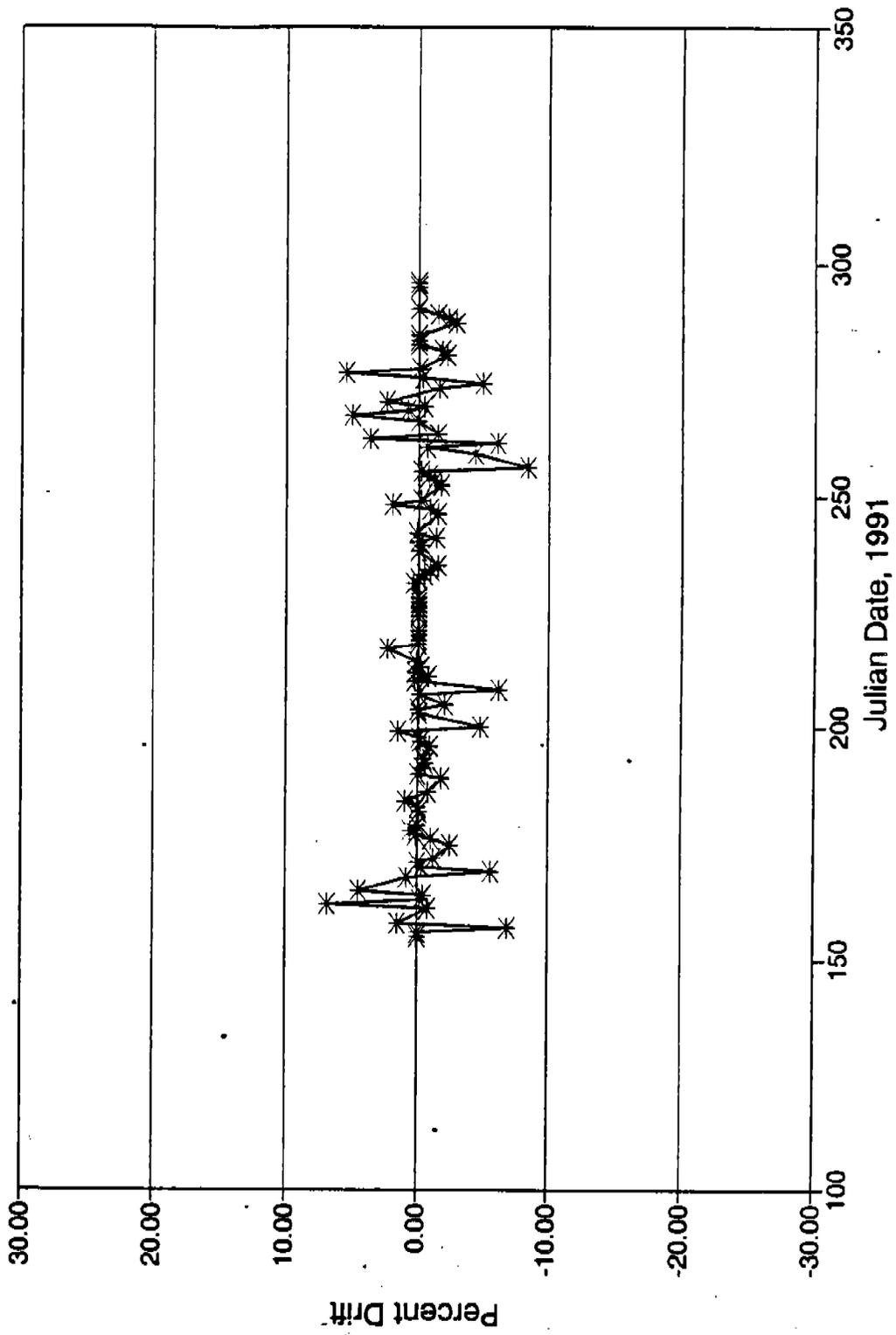


Figure 4-16. Daily calibration percent drift, Channel D.

Table 4-2

Summary NMOC Calibration Factor Drift Results

Radion 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	100	-16.1	-1.0	14.4	-5.865	-0.392	5.014	1.044	1.335
B	100	-14.4	-0.6	12.6	-5.316	-0.235	4.328	0.835	1.112
C	100	-15.1	-1.2	8.8	-5.460	-0.430	3.299	0.975	1.187
D	98	-23.3	-1.5	18.6	-8.378	-0.550	6.814	1.324	1.876
Overall	398	-23.3	-1.1	18.6	-8.378	-0.401	6.814	1.043	1.413

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.

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 1.043% overall. The mean absolute percent calibration drift ranged from 0.835% for Radian Channel B to 1.324% for Radian Channel D.

4.3 IN-HOUSE QC SAMPLES

In-house quality control samples were prepared by Radian personnel. Local ambient sample results are presented and discussed in Section 4.4.2. 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 0.000 ppmC to 3.042 ppmC, but was set to average near the concentration levels that were being analyzed. 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 1991;
- Radian ID Number;
- Calculated NMOC concentration in ppmC;
- Measured NMOC concentration in ppmC;
- Bias (measured NMOC-calculated NMOC); and
- % Bias ($\text{Bias} * 100 / \text{calculated NMOC}$).

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.

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 +3.37%, and ranges from +2.78% for Channel D to +3.91% 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 4.92% for Channel D to 6.18% for Channel B and averaged 5.54 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.

4.4 REPEATED ANALYSES

Replicate (or repeated) analyses results are listed in Table 4-6. Repeated analyses from the contents of a canister are used to estimate analytical precision. The first analysis is performed at the Radian laboratory on the day the canister is received from the sample site. The second analysis from the canister, designated by an R in the sample identification (ID) number (See Table 4-6), was performed at least 24 hours after the first analysis. This procedure was followed to ensure that sufficient time had elapsed between removal of an aliquot for analysis to allow the canister contents to equilibrate with the solid surfaces and to allow any concentration gradients within the canister to disperse.

Sample number; site code; date sampled; sample ID number; measured concentrations for injections 1, 2, and 3; mean NMOC concentration; Radian instrument channel; canister mean; percent differences between replicate analyses and absolute percent differences are given in Table 4-6. The mean

IN-HOUSE PROPANE QC RESULTS

Channel A

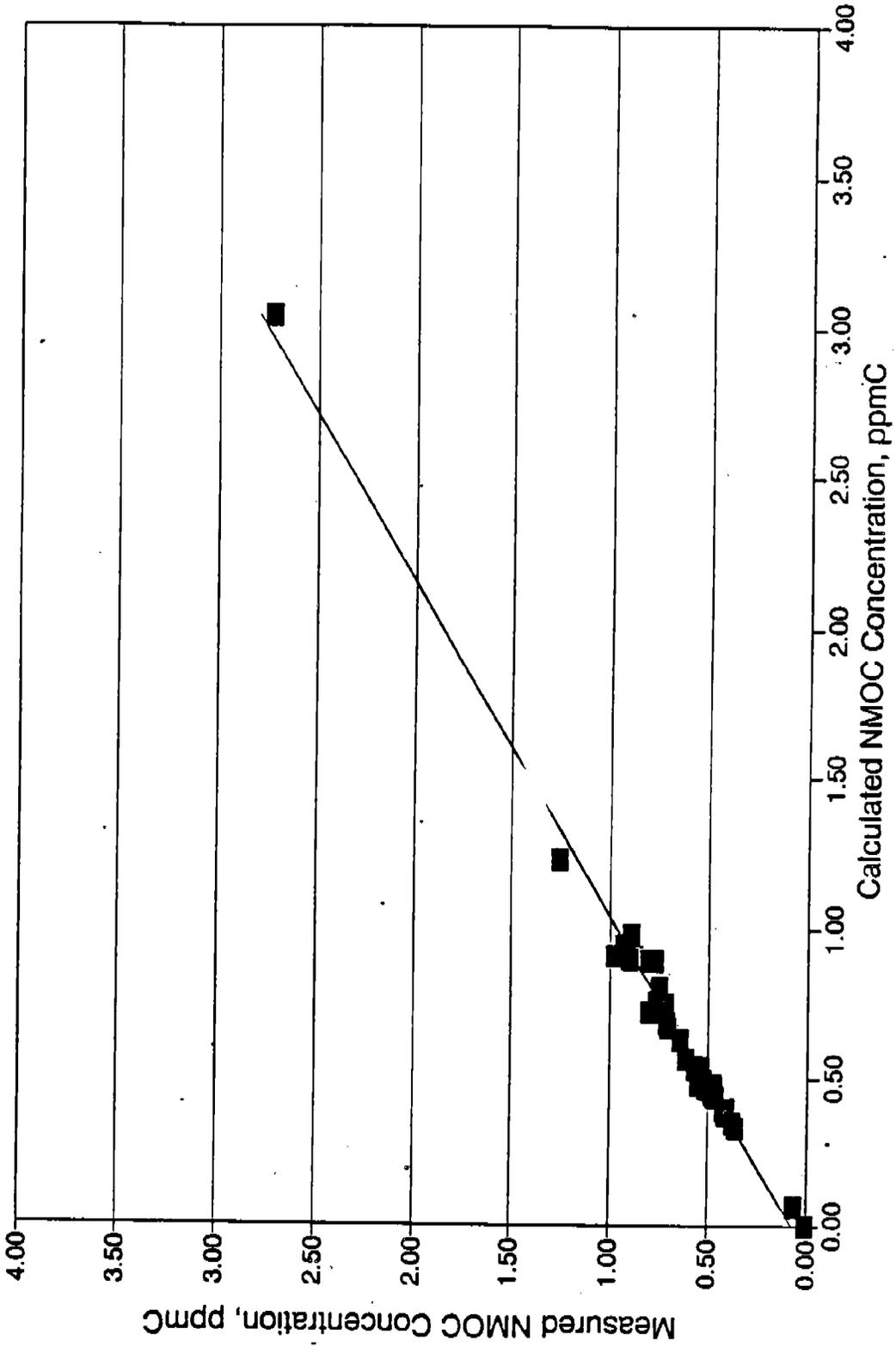


Figure 4-17. In-house quality control results, Channel A.

IN-HOUSE PROPANE QC RESULTS

Channel B

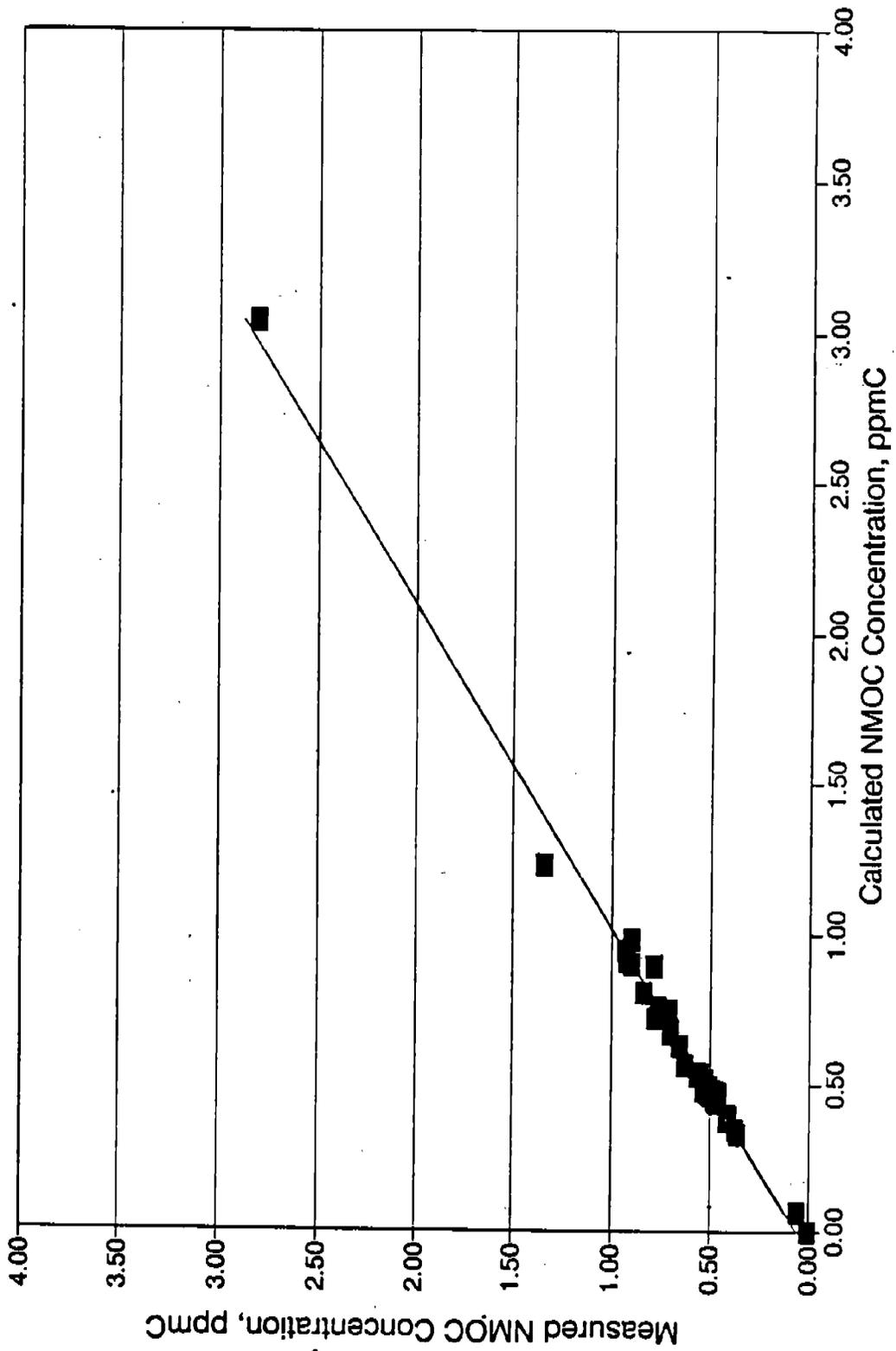


Figure 4-18. In-house quality control results, Channel B.

IN-HOUSE PROPANE QC RESULTS Channel C

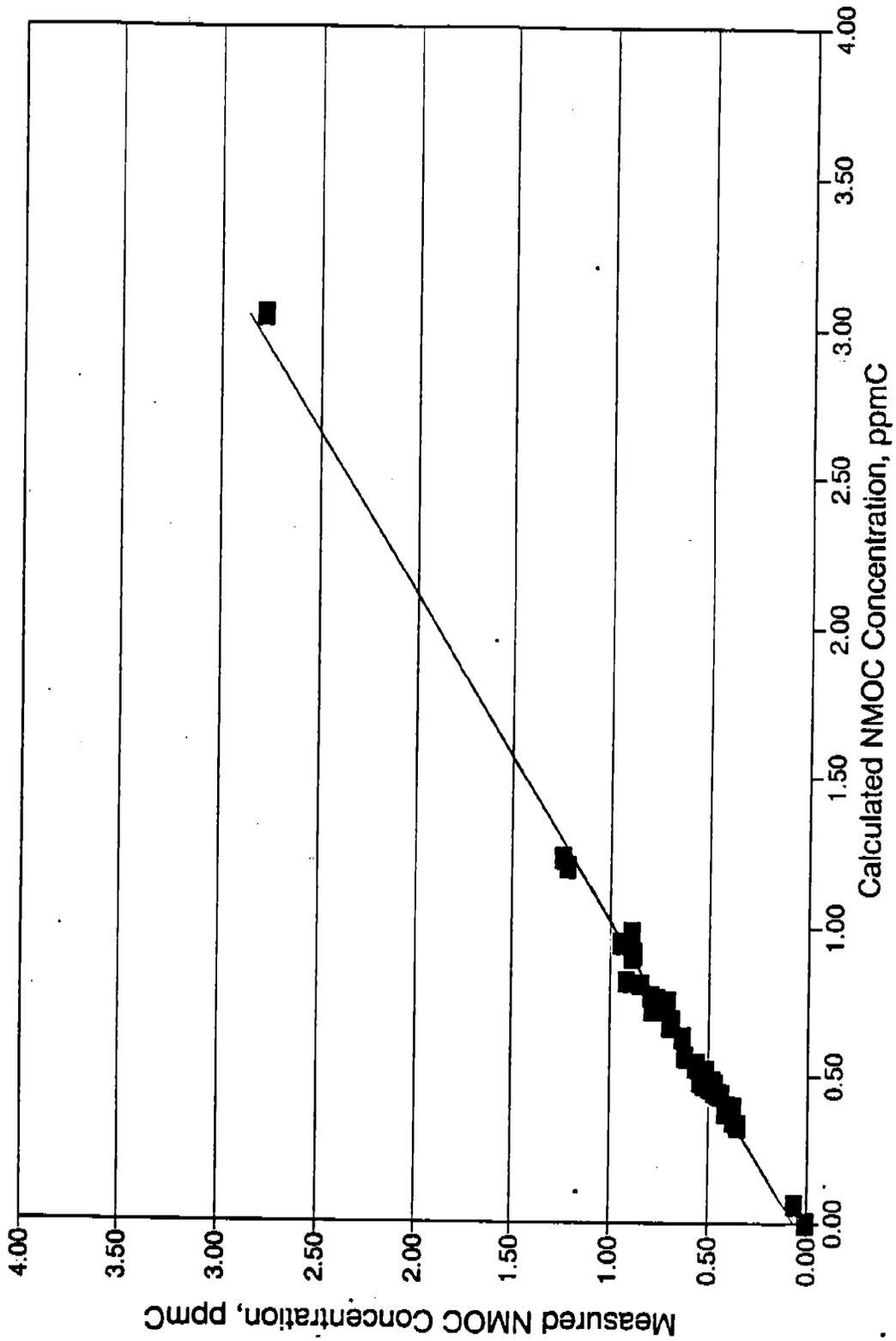


Figure 4-19. In-house quality control results, Channel C.

IN-HOUSE PROPANE QC RESULTS

Channel D

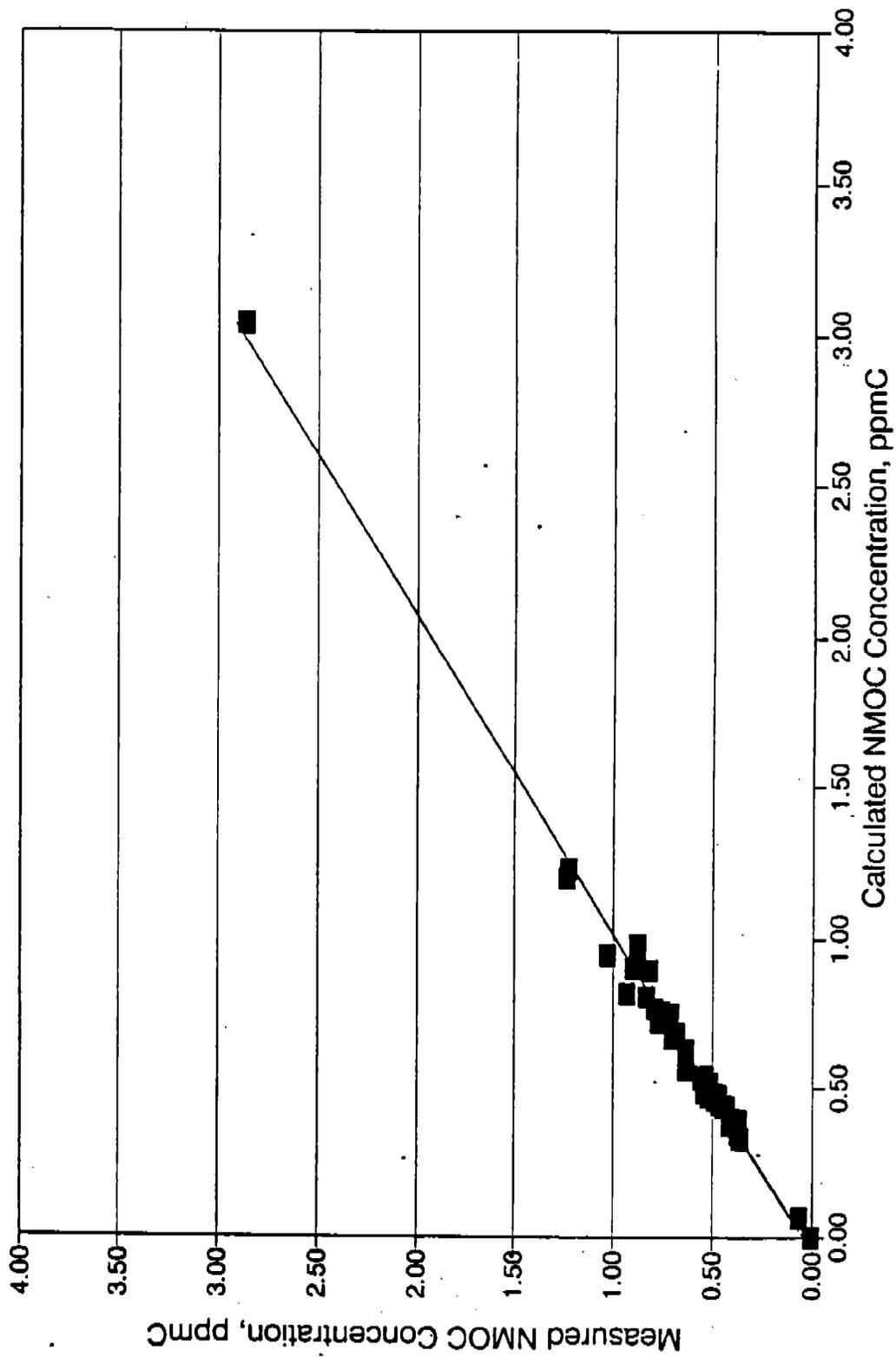


Figure 4-20. In-house quality control results, Channel D.

Table 4-3

Linear Regression Parameters for In-House Quality Control Data

Radian Channel	Cases	Intercept	Slope	Coefficient of Correlation
A	46	0.0728	0.89398	0.994696
B	45	0.0590	0.92559	0.995561
C	46	0.0610	0.92062	0.996163
D	47	0.0454	0.94395	0.995771

Table 4-4

In-House Quality Control Statistics, by Radian Channel

Channel	Statistics	Variables			
		DIFF ^a	PCDIFF ^b	ADIFF ^c	APCDIFF ^d
A	Cases	47	45	47	45
	Minimum	-0.312000	-13.870200	0.001620	0.222222
	Maximum	0.082000	15.856240	0.312000	15.856240
	Mean	0.007629	3.354684	0.038267	6.080063
	Std. Dev.	-0.061617	6.420216	0.048579	3.862838
	Std. Error	0.008988	0.957069	0.007086	0.575838
	Skewness	-3.450080	-0.806570	4.166826	-0.260094
	Kurtosis	15.700210	0.428629	22.162990	-0.525120
B	Cases	46	44	46	44
	Minimum	-0.232000	-14.117600	0.000749	0.444444
	Maximum	0.112000	13.953490	0.232000	14.117650
	Mean	0.014575	3.909148	0.035601	6.181238
	Std. Dev.	0.050497	6.068022	0.038360	3.655332
	Std. Error	0.007445	0.914789	0.005656	0.551062
	Skewness	-2.919320	-1.154560	3.373111	0.312365
	Kurtosis	12.801090	1.485782	15.089960	-0.658300
C	Cases	47	45	47	45
	Minimum	-0.262000	-8.673470	0.000000	0.000000
	Maximum	0.098000	13.090130	0.262000	13.090130
	Mean	0.012224	3.455849	0.030722	5.005915
	Std. Dev.	0.050173	5.328005	0.041300	3.869528
	Std. Error	0.007319	0.794252	0.006024	0.576835
	Skewness	-3.673530	-0.188250	4.073407	0.542715
	Kurtosis	19.604290	-0.144820	21.503520	-0.823260
D	Cases	48	46	48	46
	Minimum	-0.182000	-10.000000	0.000193	0.162866
	Maximum	0.115000	14.093140	0.182000	14.093140
	Mean	0.010639	2.781698	0.030060	4.917520
	Std. Dev.	0.045566	5.830477	0.035624	4.145465
	Std. Error	0.006577	0.859657	0.005142	0.611215
	Skewness	-1.645550	-0.069930	2.222677	0.633769
	Kurtosis	6.776102	-0.185970	6.379028	-0.848870

^aDIFF = Measured NMOC concentration - Calculated NMOC concentration, ppmC.

^bPCDIFF = Absolute value of DIFF.

^cADIFF = DIFF/calculated NMOC concentration x 100.

^dAPCDIFF = Absolute value of PCDIFF.

Table 4-5
Overall In-House Quality Control Statistics

Statistics	DIFF ^a	PCDIFF ^b	ADIFF ^c	APCDIFF ^d
Cases	188	180	188	180
Minimum	-0.312000	-14.117600	0.000000	0.000000
Maximum	0.115000	15.856240	0.312000	15.856240
Mean	0.011246	3.369081	0.033633	5.539163
Standard Deviation	0.051913	5.887588	0.041048	3.901804
Standard Error	0.003786	0.438835	0.002994	0.290823
Skewness	-3.081490	-0.588010	3.671204	0.399326
Kurtosis	14.417300	0.284138	18.486910	-0.832440

^aDIFF = Measured NMOC concentration - Calculated NMOC concentration, ppmC.

^bPCDIFF = Absolute value of DIFF.

^cADIFF = DIFF/calculated NMOC concentration x 100.

^dAPCDIFF = Absolute value of PCDIFF.

Table 4-6
Replicate Analyses for the 1991 NMOC Monitoring Program

Sample No.	Site Code	Date Sampled	Fuller Date	Sample ID	Inj1 NMOC, ppmC	Inj2 NMOC, ppmC	Inj3 NMOC, ppmC	Mean NMOC, ppmC	Rad-Haz Ineq. Channel	Canister Mass, ppmC	Replicates	
											% Diff.	Abs. % Diff.
1	MNY	06/07/91	158	1050	0.654	0.553	0.540	0.582	D	0.586	-1.196	1.196
	MNY	06/07/91	158	1050R	0.668	0.510		0.589				
2	MNY	06/08/91	159	1058	0.473	0.455	0.464	0.364	C	0.414	24.155	24.155
	MNY	06/08/91	159	1058R	0.360	0.367						
3	WSNC	06/12/91	163	1070	0.213	0.215	0.223	0.216	A	0.209	6.699	6.699
	WSNC	06/12/91	163	1070R	0.209	0.173						
4	MNY	06/12/91	163	1089	0.329	0.239	0.316	0.295	D	0.315	-12.401	12.401
	MNY	06/12/91	163	1089R	0.339	0.329						
5	MNY	06/17/91	168	1133	0.641	0.620	0.630	0.677	A	0.654	-7.192	7.192
	MNY	06/17/91	168	1133R	0.689	0.666						
6	PLNJ	06/20/91	171	1182	0.359	0.386	0.372	0.364	D	0.368	2.174	2.174
	PLNJ	06/20/91	171	1182R	0.363	0.366						
7	MNY	06/21/91	172	1186	0.260	0.289	0.274	0.276	C	0.275	-0.727	0.727
	MNY	06/21/91	172	1186R	0.274	0.277						
8	NWNJ	06/21/91	172	1237	0.295	0.251	0.374	0.307	A	0.331	-14.502	14.502
	NWNJ	06/21/91	172	1237R	0.279	0.418						
9	MNY	06/24/91	175	1198	0.398	0.331	0.420	0.420	D	0.420	0.000	0.000
	MNY	06/24/91	175	1198R	0.416	0.423						
10	LINY	06/24/91	175	1218	0.517	0.511	0.514	0.506	B	0.510	1.569	1.569
	LINY	06/24/91	175	1218R	0.506	0.506						
11	PBFL	06/26/91	177	1236	0.645	0.628	0.636	0.611	A	0.624	4.010	4.010
	PBFL	06/26/91	177	1236R	0.643	0.579						
12	NWNJ	06/26/91	177	1243	0.318	0.334	0.326	0.236	D	0.281	32.028	32.028
	NWNJ	06/26/91	177	1243R	0.240	0.232						
13	WSNC	06/27/91	178	1250	0.063	0.088	0.076	0.114	C	0.095	-40.506	40.506
	WSNC	06/27/91	178	1250R	0.128	0.101						
14	WSNC	06/28/91	179	1255	0.339	0.341	0.340	0.351	C	0.346	-3.184	3.184
	WSNC	06/28/91	179	1255R	0.355	0.347						
15	WSNC	06/28/91	179	1256	0.463	0.428	0.446	0.445	D	0.446	0.224	0.224
	WSNC	06/28/91	179	1256R	0.460	0.430						
16	NWNJ	06/28/91	179	1285	0.450	0.472	0.461	0.479	D	0.470	-3.830	3.830
	NWNJ	06/28/91	179	1285R	0.479							
17	NWNJ	06/28/91	179	1286	0.435	0.436	0.436	0.437	C	0.437	-0.229	0.229
	NWNJ	06/28/91	179	1286R	0.433	0.441						
18	F1FL	07/02/91	183	1290	0.519	0.507	0.513	0.530	B	0.522	-3.260	3.260
	F1FL	07/02/91	183	1290R	0.524	0.536						
19	WSNC	07/03/91	184	1308	0.087	0.080	0.083	0.100	D	0.092	-18.341	18.341
	WSNC	07/03/91	184	1308R	0.101	0.100						
20	NWNJ	07/08/91	189	1331	0.447	0.441	0.444	0.269	B	0.357	49.088	49.088
	NWNJ	07/08/91	189	1331R	0.261	0.277						
21	LINY	07/08/91	189	1351	0.336	0.364	0.350	0.349	B	0.350	0.286	0.286
	LINY	07/08/91	189	1351R	0.341	0.357						
22	R1NC	07/09/91	190	1325	0.141	0.150	0.146	0.066	C	0.106	75.992	75.992
	R1NC	07/09/91	190	1325R	0.064	0.067						
23	R1NC	07/09/91	190	1326	0.125	0.113	0.119	0.191	A	0.155	-46.452	46.452
	R1NC	07/09/91	190	1326R	0.186	0.196						
24	F1FL	07/11/91	192	1367	1.078	1.065	1.071	0.989	B	1.030	7.961	7.961
	F1FL	07/11/91	192	1367R	0.992	0.985						
25	F1FL	07/11/91	192	1370	1.832	1.872	1.852	1.853	A	1.853	-0.054	0.054
	F1FL	07/11/91	192	1370R	1.865	1.841						
26	MNY	07/12/91	193	1389	0.521	0.510	0.515	0.382	C	0.449	29.654	29.654
	MNY	07/12/91	193	1389R	0.379	0.385						

Table 4-6
Replicate Analyses for the 1991 NMOC Monitoring Program

Sample No.	Site Code	Date Sampled	Index Date	Sample ID	Inj 1 NMOC, ppmC	Inj 2 NMOC, ppmC	Inj 3 NMOC, ppmC	Mean NMOC, ppmC	Radon Inst. Channel	Counter Mean, ppmC	Replicates	
											% Diff.	Abs. # Diff.
27	MNY	07/12/91	193	1390	0.509	0.503		0.506	B			
	MNY	07/12/91	193	1390R	0.495	0.543		0.519	B	0.512	-2.498	2.498
28	PBFL	07/17/91	198	1444	0.413	0.391		0.402	B			
	PBFL	07/17/91	198	1444R	0.173	0.166		0.170	B	0.286	81.119	81.119
29	PBFL	07/17/91	198	1450	0.387	0.392		0.390	A			
	PBFL	07/17/91	198	1450R	0.216	0.225		0.220	A	0.305	55.738	55.738
30	FIFL	07/22/91	203	1481	0.436	0.437		0.437	C			
	FIFL	07/22/91	203	1481R	0.479	0.478		0.479	C	0.458	-9.170	9.170
31	FIFL	07/22/91	203	1482	0.443	0.429		0.436	B			
	FIFL	07/22/91	203	1482R	0.430	0.420		0.425	B	0.431	2.555	2.555
32	MNY	07/23/91	204	1513	0.518	0.530		0.524	A			
	MNY	07/23/91	204	1513R	0.500	0.521		0.511	A	0.518	2.512	2.512
33	MNY	07/23/91	204	1515	0.471	0.484		0.478	B			
	MNY	07/23/91	204	1515R	0.546	0.549		0.548	B	0.513	-13.645	13.645
34	PBFL	07/25/91	206	1539	0.735	0.700		0.718	C			
	PBFL	07/25/91	206	1539R	0.698	0.709		0.703	C	0.711	2.111	2.111
35	PBFL	07/25/91	206	1540	0.688	0.710		0.699	A			
	PBFL	07/25/91	206	1540R	0.723	0.729		0.726	A	0.713	-3.789	3.789
36	LINY	07/25/91	206	1548	0.319	0.320		0.319	B			
	LINY	07/25/91	206	1548R	0.187	0.202		0.195	B	0.257	48.249	48.249
37	MNY	07/26/91	207	1549	0.873	0.877		0.875	A			
	MNY	07/26/91	207	1549R	0.819	0.838		0.829	A	0.852	5.399	5.399
38	FIFL	07/29/91	210	1560	1.181	1.180		1.180	C			
	FIFL	07/29/91	210	1560R	1.192			1.192	C	1.186	-1.012	1.012
39	WSNC	07/29/91	210	1561	0.085	0.085		0.085	D			
	WSNC	07/29/91	210	1561R	0.109	0.099		0.104	D	0.095	-19.989	19.989
40	PLNJ	07/30/91	211	1602	0.272	0.304		0.288	A			
	PLNJ	07/30/91	211	1602R	0.206	0.200		0.203	A	0.246	34.623	34.623
41	PLNJ	07/30/91	211	1603	0.281	0.293		0.287	B			
	PLNJ	07/30/91	211	1603R	0.151	0.178		0.164	B	0.226	54.545	54.545
42	PBFL	07/31/91	212	1586	0.749	0.720		0.734	A			
	PBFL	07/31/91	212	1586R	0.715	0.742		0.729	A	0.732	0.684	0.684
43	WSNC	07/31/91	212	1589	0.294	0.290		0.292	B			
	WSNC	07/31/91	212	1589R	0.346	0.340		0.343	B	0.318	-16.063	16.063
44	PBFL	08/02/91	214	1618	0.478	0.513		0.496	A			
	PBFL	08/02/91	214	1618R	0.495			0.495	A	0.496	0.202	0.202
45	PBFL	08/02/91	214	1619	0.310	0.284		0.297	B			
	PBFL	08/02/91	214	1619R	0.286			0.286	B	0.292	-3.774	3.774
46	PLNJ	08/02/91	214	1644	0.393	0.385		0.389	D			
	PLNJ	08/02/91	214	1644R	0.331	0.325		0.328	D	0.359	17.015	17.015
47	PBFL	08/05/91	217	1624	0.642	0.613		0.627	D			
	PBFL	08/05/91	217	1624R	0.628	0.617		0.623	D	0.625	0.640	0.640
48	LINY	08/05/91	217	1625	0.112	0.110		0.111	C			
	LINY	08/05/91	217	1625R	0.108	0.110		0.109	C	0.110	1.818	1.818
49	FIFL	08/07/91	219	1668	0.203	0.189		0.196	B			
	FIFL	08/07/91	219	1668R	0.188	0.185		0.186	B	0.191	5.236	5.236
50	NWNJ	08/07/91	219	1685	0.346	0.331		0.338	B			
	NWNJ	08/07/91	219	1685R	0.314	0.312		0.313	B	0.326	7.680	7.680
51	NWNJ	08/07/91	219	1686	0.402	0.369		0.386	A			
	NWNJ	08/07/91	219	1686R	0.307	0.307		0.307	A	0.347	22.799	22.799
52	WSNC	08/09/91	221	1697	0.130	0.119		0.125	C			
	WSNC	08/09/91	221	1697R	0.144	0.129		0.137	C	0.131	-9.160	9.160

Table 4-6
Replicate Analyses for the 1991 NMOC Monitoring Program

Sample No.	Site Code	Date Sampled	Julian Date Sampled	Sample ID Number	Inj1 NMOC, ppmC	Inj2 NMOC, ppmC	Inj3 NMOC, ppmC	Mean NMOC, ppmC	Radon Unit Channel	Container Mean, ppmC	Replicates	
											% Diff.	Abs. % Diff.
53	WSNC	08/09/91	221	1703	0.151	0.153		0.152	D			
	WSNC	08/09/91	221	1703R	0.158	0.158		0.158	D	0.155	-3.871	3.871
54	MNY	08/12/91	224	1710	0.195	0.217		0.206	A			
	MNY	08/12/91	224	1710R	0.307	0.324		0.316	A	0.261	-42.146	42.146
55	WSNC	08/12/91	224	1712	0.178	0.141		0.159	A			
	WSNC	08/12/91	224	1712R	0.191	0.193		0.192	A	0.176	-18.803	18.803
56	LINY	08/13/91	225	1731	0.272	0.279		0.276	C			
	LINY	08/13/91	225	1731R	0.270	0.273		0.272	C	0.274	1.460	1.460
57	LINY	08/13/91	225	1734	0.280	0.280		0.280	D			
	LINY	08/13/91	225	1734R	0.283	0.287		0.285	D	0.283	-1.770	1.770
58	FIFL	08/14/91	226	1741	0.649	0.651		0.650	B			
	FIFL	08/14/91	226	1741R	0.709	0.708		0.708	B	0.679	-8.542	8.542
59	PBFL	08/14/91	226	1750	0.846	0.823		0.834	A			
	PBFL	08/14/91	226	1750R	0.838	0.852		0.845	A	0.840	-1.310	1.310
60	PLNJ	08/15/91	227	1759	0.328	0.328		0.328	D			
	PLNJ	08/15/91	227	1759R	0.382	0.386		0.384	D	0.356	-15.730	15.730
61	PLNJ	08/15/91	227	1760	0.300	0.305		0.302	C			
	PLNJ	08/15/91	227	1760R	0.373	0.372		0.373	C	0.338	-21.037	21.037
62	FIFL	08/16/91	228	1768	0.313	0.315		0.314	A			
	FIFL	08/16/91	228	1768R	0.309	0.323		0.316	A	0.315	-0.635	0.635
63	MNY	08/16/91	228	1771	0.599	0.627		0.613	B			
	MNY	08/16/91	228	1771R	0.677	0.668		0.672	B	0.643	-9.183	9.183
64	PLNJ	08/16/91	228	1807	0.178	0.146		0.161	B			
	PLNJ	08/16/91	228	1807R	0.264	0.257		0.260	B	0.211	-47.031	47.031
65	FIFL	08/19/91	231	1784	0.728	0.749		0.738	D			
	FIFL	08/19/91	231	1784R	0.751	0.750		0.750	D	0.744	-1.613	1.613
66	FIFL	08/19/91	231	1785	0.712	0.740		0.726	C			
	FIFL	08/19/91	231	1785R	0.742	0.729		0.736	C	0.731	-1.368	1.368
67	PLNJ	08/19/91	231	1804	0.232	0.222		0.227	C			
	PLNJ	08/19/91	231	1804R	0.217	0.212		0.214	C	0.221	5.896	5.896
68	PBFL	08/21/91	233	1822	0.605	0.587		0.596	D			
	PBFL	08/21/91	233	1822R	0.582	0.583		0.582	D	0.589	-2.377	2.377
69	FIFL	08/21/91	233	1837	0.711	0.723		0.717	B			
	FIFL	08/21/91	233	1837R	0.696	0.689		0.693	B	0.705	3.404	3.404
70	MNY	08/22/91	234	1836	0.481	0.490		0.485	A			
	MNY	08/22/91	234	1836R	0.416	0.452		0.434	A	0.460	11.099	11.099
71	LINY	08/23/91	235	1846	0.198	0.165		0.181	B			
	LINY	08/23/91	235	1846R	0.171	0.188		0.180	B	0.181	0.554	0.554
72	MNY	08/23/91	235	1852	0.724	0.753		0.739	A			
	MNY	08/23/91	235	1852R	0.739	0.772		0.756	A	0.748	-2.274	2.274
73	PLNJ	08/23/91	235	1892	0.444	0.442		0.443	A			
	PLNJ	08/23/91	235	1892R	0.418	0.422		0.420	A	0.432	5.330	5.330
74	PBFL	08/26/91	238	1861	0.496	0.468		0.482	A			
	PBFL	08/26/91	238	1861R	0.485	0.514		0.499	A	0.491	-3.466	3.466
75	PBFL	08/26/91	238	1862	0.474	0.478		0.476	C			
	PBFL	08/26/91	238	1862R	0.485	0.470		0.478	C	0.477	-0.419	0.419
76	LINY	08/26/91	238	1873	0.397	0.404		0.401	C			
	LINY	08/26/91	238	1873R	0.330	0.325		0.328	C	0.365	20.027	20.027
77	LINY	08/27/91	239	1881	0.610	0.610		0.610	D			
	LINY	08/27/91	239	1881R	0.512	0.508		0.510	D	0.560	17.857	17.857
78	PLNJ	08/28/91	240	1886	0.220	0.231		0.226	B			
	PLNJ	08/28/91	240	1886R	0.227	0.198		0.213	B	0.220	5.923	5.923

Table 4-6
Replicate Analyses for the 1991 NMOC Monitoring Program

Sample No.	Site Code	Date Sampled	Julian Date Sampled	Sample ID Number	Inj1 NMOC, ppmC	Inj2 NMOC, ppmC	Inj3 NMOC, ppmC	Mean NMOC, ppmC	Radon Inst Channel	Concentration Mean, ppmC	Replicates	
											% Diff.	Abs. % Diff.
79	FIFL	08/29/91	241	1912	0.154	0.148		0.151	A			
	FIFL	08/29/91	241	1912R	0.175	0.158		0.167	A	0.159	-10.063	10.063
80	MNY	08/29/91	241	1917	0.369	0.350		0.360	B			
	MNY	08/29/91	241	1917R	0.656	0.664		0.660	B	0.510	-58.824	58.824
81	FIFL	08/30/91	242	1930	2.966	3.002		2.984	A			
	FIFL	08/30/91	242	1930R	3.070	3.092		3.081	A	3.032	-3.192	3.192
82	FIFL	08/30/91	242	1931	3.098	3.119		3.108	B			
	FIFL	08/30/91	242	1931R	3.147	3.171		3.159	B	3.134	-1.628	1.628
83	WSNC	09/04/91	247	1936	1.121	1.115		1.118	A			
	WSNC	09/04/91	247	1936R	1.122	1.121		1.122	A	1.120	-0.357	0.357
84	WSNC	09/04/91	247	1937	1.140	1.114		1.127	B			
	WSNC	09/04/91	247	1937R	1.089	1.107		1.098	B	1.112	2.616	2.616
85	PBFL	09/04/91	247	1951	0.346	0.364		0.355	A			
	PBFL	09/04/91	247	1951R	0.358	0.355		0.356	A	0.356	-0.281	0.281
86	PBFL	09/04/91	247	1952	0.346	0.352		0.349	B			
	PBFL	09/04/91	247	1952R	0.336	0.306		0.321	B	0.335	8.358	8.358
87	LINY	09/05/91	248	1974	0.221	0.186		0.204	D			
	LINY	09/05/91	248	1974R	0.180	0.192		0.186	D	0.195	9.231	9.231
88	LINY	09/05/91	248	1975	0.171	0.179		0.175	C			
	LINY	09/05/91	248	1975R	0.181	0.172		0.176	C	0.176	-0.570	0.570
89	FIFL	09/06/91	249	1989	1.160	1.160		1.160	D			
	FIFL	09/06/91	249	1989R	1.067	1.066		1.067	D	1.113	8.380	8.380
90	WSNC	09/09/91	252	1985	1.040	1.060		1.050	C			
	WSNC	09/09/91	252	1985R	1.020			1.020	C	1.035	2.899	2.899
91	FIFL	09/09/91	252	2006	0.230	0.216		0.223	A			
	FIFL	09/09/91	252	2006R	0.228	0.216		0.222	A	0.223	0.449	0.449
92	LINY	09/09/91	252	2016	0.316	0.300		0.308	A			
	LINY	09/09/91	252	2016R	0.438	0.450		0.444	A	0.376	-36.170	36.170
93	PBFL	09/10/91	253	2010	0.492	0.484		0.488	B			
	PBFL	09/10/91	253	2010R	0.500	0.491		0.495	B	0.492	-1.424	1.424
94	FIFL	09/10/91	253	2018	0.184	0.163		0.174	B			
	FIFL	09/10/91	253	2018R	0.170	0.186		0.178	B	0.176	-2.273	2.273
95	PBFL	09/11/91	254	2027	0.448	0.444		0.446	A			
	PBFL	09/11/91	254	2027R	0.417	0.428		0.423	A	0.435	5.293	5.293
96	FIFL	09/11/91	254	2029	0.358	0.350		0.354	B			
	FIFL	09/11/91	254	2029R	0.353	0.349		0.351	B	0.353	0.851	0.851
97	MNY	09/12/91	255	2041	0.186	0.215		0.201	A			
	MNY	09/12/91	255	2041R	0.210	0.191		0.200	A	0.201	0.499	0.499
98	MNY	09/12/91	255	2042	0.172	0.200		0.186	B			
	MNY	09/12/91	255	2042R	0.208	0.211		0.210	B	0.198	-12.121	12.121
99	FIFL	09/13/91	256	2045	0.688	0.704		0.696	A			
	FIFL	09/13/91	256	2045R	0.691	0.704		0.698	A	0.697	-0.287	0.287
100	FIFL	09/13/91	256	2046	0.746	0.749		0.748	B			
101	LINY	09/16/91	259	2069	0.718	0.723		0.721	B	0.735	3.676	3.676
	LINY	09/16/91	259	2069R	0.355	0.340		0.347	A			
102	LINY	09/16/91	259	2070	0.329	0.353		0.341	A	0.344	1.744	1.744
	LINY	09/16/91	259	2070R	0.162	0.171		0.116	B			
103	LINY	09/17/91	259	2070R	0.367	0.346		0.357	B	0.237	-101.903	101.903
	LINY	09/17/91	260	2088	0.168	0.174		0.171	B			
104	LINY	09/17/91	260	2088R	0.206	0.188		0.197	B	0.184	-14.130	14.130
	FIFL	09/17/91	260	2090	0.158	0.168		0.163	A			
	FIFL	09/17/91	260	2090R	0.180	0.163		0.172	A	0.168	-5.373	5.373

Table 4-6
Replicate Analyses for the 1991 NMOC Monitoring Program

Sample No.	Site Code	Date Sampled	Fullan Base Sampled	Sample ID Number	Inj1	Inj2	Inj3	Mean NMOC ppmC	Radial Inj Change	Canister Mean ppmC	Replicates		
					NMOC ppmC	NMOC ppmC	NMOC ppmC				% Diff.	Abs. % Diff.	
105	LINY	09/18/91	261	2100	0.138	0.136		0.137	B				
	LINY	09/18/91	261	2100R	0.214	0.202		0.208	B	0.173	-41.159	41.159	
106	WSNC	09/18/91	261	2124	0.222	0.204		0.213	B				
	WSNC	09/18/91	261	2124R	0.190	0.202		0.196	B	0.205	8.313	8.313	
107	WSNC	09/19/91	262	2110	0.093	0.093		0.093	C				
	WSNC	09/19/91	262	2110R	0.134	0.137		0.135	C	0.114	-36.738	36.738	
108	WSNC	09/19/91	262	2111	0.135	0.128		0.132	D				
	WSNC	09/19/91	262	2111R	0.126	0.122		0.124	D	0.128	6.250	6.250	
109	RINC	09/19/91	262	2148	0.054	0.058		0.059	D				
	RINC	09/19/91	262	2148R	0.130	0.137		0.133	D	0.096	-77.662	77.662	
110	RINC	09/19/91	262	2149	0.131	0.121		0.126	C				
	RINC	09/19/91	262	2149R	0.144	0.136		0.140	C	0.133	-10.526	10.526	
111	MNY	09/20/91	263	2130	0.197	0.177		0.187	A				
	MNY	09/20/91	263	2130R	0.226	0.239		0.232	A	0.210	-21.480	21.480	
112	MNY	09/24/91	267	2165	0.414	0.430		0.422	A				
	MNY	09/24/91	267	2165R	0.460	0.456		0.458	A	0.440	-8.182	8.182	
113	MNY	09/24/91	267	2166	0.243	0.215		0.229	B				
	MNY	09/24/91	267	2166R	0.472	0.473		0.473	B	0.351	-69.516	69.516	
114	FIFL	09/25/91	268	2170	0.061	0.074		0.068	C				
	FIFL	09/25/91	268	2170R	0.074	0.079		0.077	C	0.072	-13.149	13.149	
115	FIFL	09/25/91	268	2171	0.067	0.078		0.072	D				
	FIFL	09/25/91	268	2171R	0.060	0.045		0.053	D	0.063	31.360	31.360	
116	PLNJ	09/25/91	268	2202	0.312	0.333		0.323	A				
	PLNJ	09/25/91	268	2202R	0.328	0.330		0.329	A	0.326	-1.840	1.840	
117	PLNJ	09/25/91	268	2203	0.258	0.291		0.275	B				
	PLNJ	09/25/91	268	2203R	0.294	0.280		0.287	B	0.281	-4.270	4.270	
118	LINY	09/26/91	269	2218	0.179	0.167		0.173	A				
	LINY	09/26/91	269	2218R	0.180	0.172		0.176	A	0.175	-1.719	1.719	
119	LINY	09/26/91	269	2219	0.164	0.180		0.172	B				
	LINY	09/26/91	269	2219R	0.125	0.120		0.122	B	0.147	34.014	34.014	
120	RINC	09/30/91	273	2236	0.698	0.692		0.695	D				
	RINC	09/30/91	273	2236R	0.739	0.727		0.733	D	0.714	-5.322	5.322	
121	RINC	10/04/91	277	2232	0.444	0.456		0.450	C				
	RINC	10/04/91	277	2232R	0.470	0.472		0.471	C	0.461	-4.560	4.560	
Average											-1.427	14.294	

concentration in Column 9, in parts per million carbon by volume (ppmC), is the arithmetic average of the NMOC concentrations for the two (or three) analyses shown in Columns 6, 7, and 8 and headed "Inj 1, Inj 2, and Inj 3." Column 11, labeled "Canister Mean" is the concentration for each sample number and is the average of the mean concentrations for each analysis.

Percent differences are calculated by the following equation:

$$\% \text{ Diff} = \frac{\bar{X}_2 - \bar{X}_1}{(\bar{X}_1 + \bar{X}_2) / 2} \cdot 100 \quad (4-1)$$

where:

- \bar{X}_1 = The mean NMOC concentration for the first analysis; and
- \bar{X}_2 = The mean NMOC concentration for the second (or repeated) analysis.

A total of 121 analyses are shown in Table 4-6. The percent difference ranged from -101.903 to 81.119 and average -1.427. The small value of the overall average percent difference indicated that there was an insignificant average bias between the second and the first analyses.

The final column in Table 4-6 is absolute percent difference. The overall absolute percent difference was 14.29 for 1991. In 1990, the average absolute percent difference was 7.59, and in 1989 was 8.24. A possible reason for the increase in imprecision for 1991 compared to 1989 and 1990 was that the average NMOC concentrations in 1991 were lower than in 1989 or 1990. Experience has shown that in general the lower the concentration, the higher the percent difference, and especially the absolute percent difference.

In the next section, the results of the analyses of duplicate samples will be discussed. Replicate analyses of several duplicate samples were performed, but the precision results from the duplicate samples were not used in this section.

4.4.1 Local Ambient Samples

Table 4-7 presents the overall statistics for local ambient samples. These data include comparisons among Radian channels. The mean differences

Table 4-7

Overall Statistics for Local Ambient Samples

Statistics	DIFF	PCDIFF	ADIFF	APCDIFF
Cases	24	24	24	24
Minimum	-0.210000	-29.411800	0.005000	0.598444
Maximum	0.080000	24.543080	0.210000	29.411760
Mean	-0.026170	0.149690	0.066667	13.862960
Standard Deviation	0.090603	16.581250	0.065465	8.626910
Standard Error	0.018494	3.384634	0.013363	1.760961
Skewness	-0.963490	-0.406470	1.067793	0.097440
Kurtosis	-0.521020	-1.054040	-0.179580	-1.073860

DIFF = NMOC concentration on Channel Y - NMOC concentration on Channel X, ppmC.

PCDIFF = Absolute value of DIFF.

ADIFF = $\text{DIFF} / ((\text{NMOC concentration on Channel Y} + \text{NMOC concentration on Channel X}) / 2) \times 100$.

APCDIFF = Absolute value of PCDIFF.

and the mean percent differences are both relatively small, which indicates that they are random variables. The overall mean absolute percent difference (APDIFF) is 13.86.

Table 4-8 presents the same information comparing each Radian channel to other Radian channels.

Table 4-9 adds the 95% confidence intervals for the local ambient sample comparisons of the mean values of DIFF (from Table 4-10). Figure 4-21 displays the results of Table 4-9 graphically.

4.5 DUPLICATE SAMPLE RESULTS

Duplicate analysis results are given in Table 4-10. Duplicate samples on which a replicate analysis was performed, e.g., Sample No. 12 with Sample ID Numbers 1285, 1285R, and 1286, and 1286R, may be identified as those from a single site, NWNJ for Sample No. 12, and having a common sampling date. Percent differences (between the canister means) ranged from -60.487 to 57.069 and averaged 0.836. The overall average (0.836) is a small enough number to indicate that there was no systematic bias between samples. The absolute percent difference average 15.768. Absolute percent differences average 7.594 in 1990 and 10.621 in 1989. An average absolute percent difference between duplicate samples of 15.768 experienced in 1991 is not considered to be excessive.

For 27 duplicate samples, replicate analyses were performed. As in the case for replicate analyses discussed in Section 4.4, the second analyses were always performed at least 24 hours after the initial analyses. The results of these analyses were used to separate analytical variability from the variability caused by taking replicate samples from the canisters, and from the variability resulting from the duplicate sampling itself. The total process paths being examined in this analysis may be diagrammed as shown in Figure 4-22. For the NMOC measurements reported here, there were 27 samples, S_i . That is, $i = 1; 2, 3, \dots, 27$. Each sample was drawn into a common manifold and supplied to two canisters, $D_{j(i)}$, through a tee connected to the manifold. For this study, $j = 1, \text{ or } 2$. Two sample aliquots, $A_{k(ij)}$, were taken from each duplicate canister (on successive days), i.e., $k = 1 \text{ or } 2$. Each aliquot was analyzed twice, giving $l = 1 \text{ or } 2$. The analyses of variance

Table 4-8

Statistics for Local Ambient Samples, by Channel Pair

Channel Pair (X-Y)	Statistics	Variables			
		DIFF	ADIFF	PCDIFF	APCDIFF
B-A	Cases	4	4	4	4
	Minimum	-0.142000	0.005000	-18.635200	1.305057
	Maximum	0.008000	0.142000	3.309693	18.635170
	Mean	-0.033000	0.040500	-4.096130	6.403496
	Std. Dev.	0.072906	0.067678	9.973358	8.195457
	Std. Error	0.036453	0.033839	4.986679	4.097728
	Skewness	-1.961450	1.997958	-1.683010	1.940192
	Kurtosis	3.862143	3.993257	2.857485	3.803467
C-A	Cases	4	4	4	4
	Minimum	-0.202000	0.031000	-28.133700	16.020670
	Maximum	0.047000	0.202000	24.543080	28.133700
	Mean	-0.067750	0.106750	-1.699560	21.981430
	Std. Dev.	0.125463	0.081651	25.876010	5.401331
	Std. Error	0.062731	0.040826	12.938000	2.700666
	Skewness	-0.149670	0.344623	-0.008470	0.071998
	Kurtosis	-4.987570	-3.705230	-4.908290	-2.551600
C-B	Cases	4	4	4	4
	Minimum	-0.210000	0.005000	-29.411800	0.598444
	Maximum	0.040000	0.210000	21.276600	29.411760
	Mean	-0.034750	0.072750	2.408427	17.413540
	Std. Dev.	0.118590	0.092827	23.325690	12.145480
	Std. Error	0.059295	0.046414	11.662840	6.072738
	Skewness	-1.832450	1.825027	-1.127510	-1.104660
	Kurtosis	3.358786	3.509672	0.202367	1.955503
D-A	Cases	4	4	4	4
	Minimum	-0.154000	0.022000	-22.190200	9.247757
	Maximum	0.036000	0.154000	18.274110	22.190200
	Mean	-0.040750	0.069750	-0.513190	15.205790
	Std. Dev.	0.088210	0.059230	18.567650	6.067980
	Std. Error	0.044105	0.029615	9.283823	3.033990
	Skewness	-0.749280	1.445893	-0.276020	0.266895
	Kurtosis	-1.653090	1.904490	-3.138560	-3.641800

Table 4-8

Continued

Channel Pair (X-Y)	Statistics	Variables			
		DIFF	ADIFF	PCDIFF	APCDIFF
D-B	Cases	4	4	4	4
	Minimum	-0.162000	0.027000	-23.478300	9.428033
	Maximum	0.075000	0.162000	14.987080	23.478260
	Mean	-0.007750	0.073250	3.600786	15.339930
	Std. Dev.	0.105196	0.063184	18.204490	5.910945
	Std. Error	0.052598	0.031592	9.102245	2.955473
	Skewness	-1.724810	1.357066	-1.903100	1.051621
	Kurtosis	3.274774	1.234090	3.651917	1.847403
D-C	Cases	4	4	4	4
	Minimum	-0.011000	0.009000	-6.340060	4.931507
	Maximum	0.080000	0.080000	10.025060	10.025060
	Mean	0.027000	0.037000	1.197806	6.833590
	Std. Dev.	0.044684	0.033813	8.077402	2.212115
	Std. Error	0.022342	0.016907	4.038701	1.106057
	Skewness	0.423003	0.712368	0.180430	1.539710
	Kurtosis	-3.59224	-2.012250	-4.682680	2.827631

DIFF = NMOC concentration on Channel Y - NMOC concentration on Channel X, ppmC.

PCDIFF = Absolute value of DIFF.

ADIFF = $\text{DIFF} / ((\text{NMOC concentration on Channel Y} + \text{NMOC concentration on Channel X}) / 2) \times 100$.

APCDIFF = Absolute value of PCDIFF.

Table 4-9

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
B-A	-0.03300	0.07291	4	3.182	0.08300	-0.14900
C-A	-0.06775	0.12546	4	3.182	0.13186	-0.26736
C-B	-0.03475	0.11859	4	3.182	0.15411	-0.22361
D-A	-0.04075	0.08821	4	3.182	0.09959	-0.18109
D-B	-0.00775	0.10520	4	3.182	0.15962	-0.17512
D-C	0.02700	0.04468	4	3.182	0.09809	-0.04409

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

Local Ambient Samples

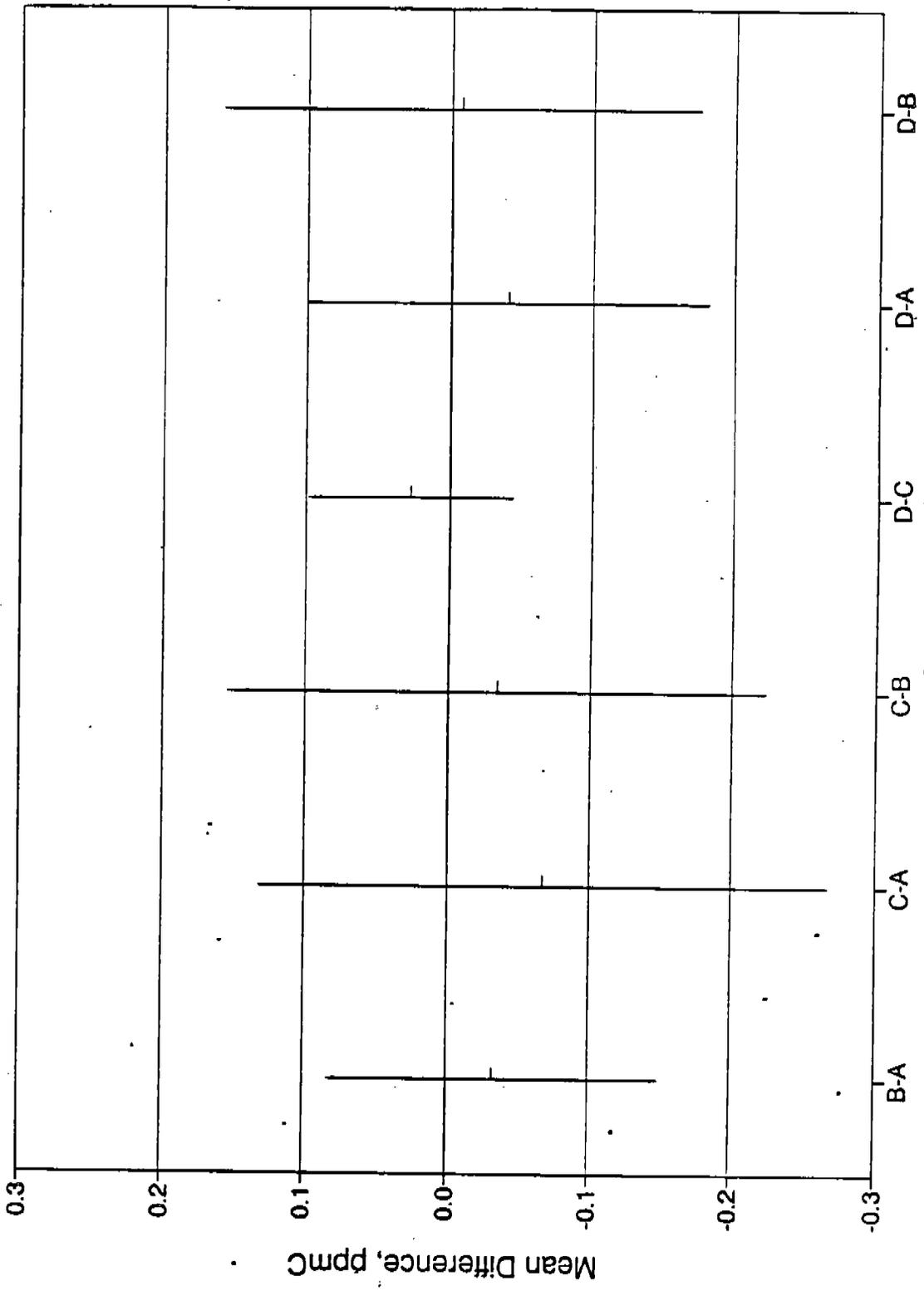


Figure 4-21. 95% Confidence intervals for mean NMOC difference.

Table 4-10
Duplicate Samples for the 1991 NMOC Monitoring Program

Sample No.	Site Code	Date Sampled	Julian Date Sampled	Sample ID Number	Inj1 NMOC, ppmC	Inj2 NMOC, ppmC	Inj3 NMOC, ppmC	Canister NMOC, ppmC	Duplicate	
									% Diff.	Abs. % Diff.
1	LINY	06/12/91	163	1104	0.387	0.384		0.386		
	LINY	06/12/91	163	1105	0.378	0.351		0.365	-5.600	5.600
2	F1FL	06/13/91	164	1106	0.119	0.105		0.112		
	F1FL	06/13/91	164	1107	0.088	0.100		0.094	-17.952	17.952
3	PBFL	06/13/91	164	1101	0.882	0.891		0.887		
	PBFL	06/13/91	164	1102	0.739	0.757		0.748	-16.947	16.947
4	R1NC	06/14/91	165	1111	0.116	0.107		0.112		
	R1NC	06/14/91	165	1113	0.157	0.190	0.168	0.172	42.496	42.496
5	NWNJ	06/18/91	169	1171	0.196	0.200		0.198		
	NWNJ	06/18/91	169	1172	0.213	0.202		0.208	4.686	4.686
6	F1FL	06/21/91	172	1191	0.067	0.074		0.071		
	F1FL	06/21/91	172	1192	0.055	0.053		0.054	-26.400	26.400
7	PLNJ	06/21/91	172	1196	0.349	0.331		0.340		
	PLNJ	06/21/91	172	1197	0.204	0.204		0.204	-50.000	50.000
8	LINY	06/24/91	175	1213	0.520	0.524		0.522		
	LINY	06/24/91	175	1218	0.517	0.511				
	LINY	06/24/91	175	1218R	0.506	0.506		0.510	-2.326	2.326
9	MNY	06/24/91	175	1198	0.398	0.331				
	MNY	06/24/91	175	1198R	0.416	0.423		0.392		
	MNY	06/24/91	175	1199	0.441	0.437		0.439	11.312	11.312
10	WSNC	06/25/91	176	1214	0.107	0.114		0.111		
	WSNC	06/25/91	176	1222	0.101	0.106		0.104	-6.542	6.542
11	R1NC	06/26/91	177	1204	0.092	0.097		0.095		
	R1NC	06/26/91	177	1205	0.074	0.080		0.077	-20.280	20.280
12	NWNJ	06/28/91	179	1285	0.450	0.472				
	NWNJ	06/28/91	179	1285R	0.479			0.467		
	NWNJ	06/28/91	179	1286	0.435	0.436				
	NWNJ	06/28/91	179	1286R	0.433	0.441		0.436	-6.809	6.809
13	WSNC	06/28/91	179	1255	0.339	0.341				
	WSNC	06/28/91	179	1255R	0.355	0.347		0.346		
	WSNC	06/28/91	179	1256	0.463	0.428				
	WSNC	06/28/91	179	1256R	0.460	0.430		0.445	25.229	25.229
14	R1NC	07/09/91	190	1325	0.141	0.150				
	R1NC	07/09/91	190	1325R	0.064	0.067		0.106		
	R1NC	07/09/91	190	1326	0.125	0.113				
	R1NC	07/09/91	190	1326R	0.186	0.196		0.155	37.958	37.958
15	F1FL	07/11/91	192	1367	1.078	1.065				
	F1FL	07/11/91	192	1367R	0.992	0.985		1.030		
	F1FL	07/11/91	192	1370	1.832	1.872				
	F1FL	07/11/91	192	1370R	1.865	1.841		1.853	57.069	57.069
16	PLNJ	07/11/91	192	1386	0.255	0.256		0.256		
	PLNJ	07/11/91	192	1387	0.275	0.292		0.284	10.390	10.390

**Table 4-1
Duplicate Samples for the 1991 NMOC Monitoring Program**

Sample No.	Site Code	Date Sampled	Julian Date Sampled	Sample ID Number	Inj1 NMOC ppmC	Inj2 NMOC ppmC	Inj3 NMOC ppmC	Canister NMOC ppmC	Duplicate	
									% Diff.	Abs. % Diff.
17	LINY	07/12/91	193	1382	0.272	0.302		0.287		
	LINY	07/12/91	193	1383	0.348	0.339		0.344	17.922	17.922
18	MNY	07/12/91	193	1389	0.521	0.510				
	MNY	07/12/91	193	1389R	0.379	0.385		0.449		
	MNY	07/12/91	193	1390	0.509	0.503				
	MNY	07/12/91	193	1390R	0.495	0.543		0.513	13.264	13.264
19	NWNJ	07/15/91	196	1419	0.186	0.177		0.182		
	NWNJ	07/15/91	196	1423	0.272	0.247		0.260	35.374	35.374
20	PBFL	07/17/91	198	1444	0.413	0.391				
	PBFL	07/17/91	198	1444R	0.173	0.166		0.286		
	PBFL	07/17/91	198	1450	0.387	0.392				
	PBFL	07/17/91	198	1450R	0.216	0.225		0.305	6.517	6.517
21	WSNC	07/17/91	198	1440	0.123	0.140		0.132		
	WSNC	07/17/91	198	1449	0.146	0.138		0.142	7.678	7.678
22	FIFL	07/22/91	203	1481	0.436	0.437				
	FIFL	07/22/91	203	1481R	0.479	0.478		0.458		
	FIFL	07/22/91	203	1482	0.443	0.429				
	FIFL	07/22/91	203	1482R	0.430	0.420		0.431	-6.081	6.081
23	LINY	07/23/91	204	1507	0.316	0.287		0.302		
	LINY	07/23/91	204	1511	0.403	0.385		0.394	26.600	26.600
24	MNY	07/23/91	204	1513	0.518	0.530				
	MNY	07/23/91	204	1513R	0.500	0.521		0.517		
	MNY	07/23/91	204	1515	0.471	0.484				
	MNY	07/23/91	204	1515R	0.546	0.549		0.513	-0.923	0.923
25	RINC	07/24/91	205	1517	0.191	0.168		0.180		
	RINC	07/24/91	205	1519	0.317	0.321		0.319	55.968	55.968
26	PBFL	07/25/91	206	1539	0.735	0.700				
	PBFL	07/25/91	206	1539R	0.698	0.709		0.711		
	PBFL	07/25/91	206	1540	0.688	0.710				
	PBFL	07/25/91	206	1540R	0.723	0.729		0.713	0.281	0.281
27	WSNC	07/25/91	206	1541	0.148	0.151		0.150		
	WSNC	07/25/91	206	1542	0.118	0.104		0.111	-29.559	29.559
28	NWNJ	07/26/91	207	1620	0.649	0.650		0.650		
	NWNJ	07/26/91	207	1621	0.680	0.682		0.681	4.735	4.735
29	PLNJ	07/30/91	211	1602	0.272	0.304				
	PLNJ	07/30/91	211	1602R	0.206	0.200		0.246		
	PLNJ	07/30/91	211	1603	0.281	0.293				
	PLNJ	07/30/91	211	1603R	0.151	0.178		0.226	-8.382	8.382
30	PLNJ	07/31/91	212	1605	0.398	0.422		0.410		
	PLNJ	07/31/91	212	1606	0.384	0.390		0.387	-5.772	5.772
31	MNY	08/01/91	213	1599	1.230	1.202		1.216		
	MNY	08/01/91	213	1600	1.226	1.227		1.227	0.860	0.860

Table 4-10
Duplicate Samples for the 1991 NMOC Monitoring Program

Sample No.	Site Code	Date Sampled	Julian Date Sampled	Sample ID Number	Inj1 NMOC ppmC	Inj2 NMOC ppmC	Inj3 NMOC ppmC	Canister NMOC ppmC	Duplicate	
									% Diff.	Abs. % Diff.
32	PLNJ	08/01/91	213	1641	3.678	3.703		3.691		
	PLNJ	08/01/91	213	1642	3.843	3.841		3.842	4.023	4.023
33	PBFL	08/02/91	214	1618	0.478	0.513				
	PBFL	08/02/91	214	1618R	0.495			0.495		
	PBFL	08/02/91	214	1619	0.310	0.284				
	PBFL	08/02/91	214	1619R	0.286			0.293	-51.226	51.226
34	PLNJ	08/02/91	214	1643	0.306	0.320		0.313		
	PLNJ	08/02/91	214	1644	0.393	0.385				
	PLNJ	08/02/91	214	1644R	0.331	0.325		0.359	13.552	13.552
35	RINC	08/06/91	218	1656	0.191	0.181		0.186		
	RINC	08/06/91	218	1657	0.132	0.126		0.129	-36.190	36.190
36	F1FL	08/07/91	219	1668	0.203	0.189				
	F1FL	08/07/91	219	1668R	0.188	0.185		0.191		
	F1FL	08/07/91	219	1672	0.180	0.169		0.175	-9.159	9.159
37	NWNJ	08/07/91	219	1685	0.346	0.331				
	NWNJ	08/07/91	219	1685R	0.314	0.312		0.326		
	NWNJ	08/07/91	219	1686	0.402	0.369				
	NWNJ	08/07/91	219	1686R	0.307	0.307		0.346	6.101	6.101
38	WSNC	08/09/91	221	1697	0.130	0.119				
	WSNC	08/09/91	221	1697R	0.144	0.129		0.131		
	WSNC	08/09/91	221	1703	0.151	0.153				
	WSNC	08/09/91	221	1703R	0.158	0.158		0.155	17.163	17.163
39	LINY	08/13/91	225	1731	0.272	0.279				
	LINY	08/13/91	225	1731R	0.270	0.273		0.274		
	LINY	08/13/91	225	1734	0.280	0.280				
	LINY	08/13/91	225	1734R	0.283	0.287		0.283	3.237	3.237
40	MNY	08/13/91	225	1722	1.387	1.413		1.400		
	MNY	08/13/91	225	1723	1.428	1.457		1.443	2.990	2.990
41	PBFL	08/14/91	226	1747	0.815	0.824		0.820		
	PBFL	08/14/91	226	1750	0.846	0.823				
	PBFL	08/14/91	226	1750R	0.838	0.852		0.840	2.441	2.441
42	WSNC	08/14/91	226	1743	0.501	0.493		0.497		
	WSNC	08/14/91	226	1745	0.464	0.479		0.472	-5.266	5.266
43	PLNJ	08/15/91	227	1759	0.328	0.328				
	PLNJ	08/15/91	227	1759R	0.382	0.386		0.356		
	PLNJ	08/15/91	227	1760	0.300	0.305				
	PLNJ	08/15/91	227	1760R	0.373	0.372		0.338	-5.335	5.335
44	F1FL	08/19/91	231	1784	0.728	0.749				
	F1FL	08/19/91	231	1784R	0.751	0.750		0.745		
	F1FL	08/19/91	231	1785	0.712	0.740				
	F1FL	08/19/91	231	1785R	0.742	0.729		0.731	-1.864	1.864
45	NWNJ	08/19/91	231	1776	0.192	0.175		0.184		
	NWNJ	08/19/91	231	1777	0.238	0.218		0.228	21.628	21.628

Table 4-10
Duplicate Samples for the 1991 NMOC Monitoring Program

Sample No.	Site Code	Date Sampled	Julian Date Sampled	Sample ID Number	Inj1 NMOC, ppmC	Inj2 NMOC, ppmC	Inj3 NMOC, ppmC	Canister NMOC, ppmC	Duplicate	
									% Diff.	Abs. % Diff.
46	PLNJ	08/22/91	234	1849	0.425	0.432		0.429		
	PLNJ	08/22/91	234	1850	0.364	0.354		0.359	-17.651	17.651
47	LINY	08/23/91	235	1846	0.198	0.165				
	LINY	08/23/91	235	1846R	0.171	0.188		0.181		
	LINY	08/23/91	235	1847	0.293	0.302		0.298	48.954	48.954
48	MNY	08/23/91	235	1851	0.740	0.728		0.734		
	MNY	08/23/91	235	1852	0.724	0.753				
	MNY	08/23/91	235	1852R	0.739	0.772		0.747	1.756	1.756
49	PBFL	08/26/91	238	1861	0.496	0.468				
	PBFL	08/26/91	238	1861R	0.485	0.514		0.491		
	PBFL	08/26/91	238	1862	0.474	0.478				
	PBFL	08/26/91	238	1862R	0.485	0.470		0.477	-2.894	2.894
50	WSNC	08/26/91	238	1870	0.064	0.060		0.062		
	WSNC	08/26/91	238	1871	0.072	0.072		0.072	16.119	16.119
51	NWNJ	08/29/91	241	1926	1.180	1.160		1.170		
	NWNJ	08/29/91	241	1927	1.168	1.178		1.173	0.256	0.256
52	F1FL	08/30/91	242	1930	2.966	3.002				
	F1FL	08/30/91	242	1930R	3.070	3.092		3.032		
	F1FL	08/30/91	242	1931	3.098	3.119				
	F1FL	08/30/91	242	1931R	3.147	3.171		3.134	3.289	3.289
53	PLNJ	09/03/91	246	1968	0.154	0.155		0.155		
	PLNJ	09/03/91	246	1969	0.114	0.125		0.120	-25.547	25.547
54	PBFL	09/04/91	247	1951	0.346	0.364				
	PBFL	09/04/91	247	1951R	0.358	0.355		0.356		
	PBFL	09/04/91	247	1952	0.346	0.352				
	PBFL	09/04/91	247	1952R	0.336	0.306		0.335	-6.008	6.008
55	WSNC	09/04/91	247	1936	1.121	1.115				
	WSNC	09/04/91	247	1936R	1.122	1.121		1.120		
	WSNC	09/04/91	247	1937	1.140	1.114				
	WSNC	09/04/91	247	1937R	1.089	1.107		1.112	-0.654	0.654
56	LINY	09/05/91	248	1974	0.221	0.186				
	LINY	09/05/91	248	1974R	0.180	0.192		0.195		
	LINY	09/05/91	248	1975	0.171	0.179				
	LINY	09/05/91	248	1975R	0.181	0.172		0.176	-10.256	10.256
57	MNY	09/05/91	248	1970	0.354	0.358		0.356		
	MNY	09/05/91	248	1971	0.344	0.356		0.350	-1.700	1.700
58	R1NC	09/09/91	252	1979	0.719	0.726		0.723		
	R1NC	09/09/91	252	1980	0.667	0.645		0.656	-9.648	9.648
59	NWNJ	09/11/91	254	2054	0.361	0.363		0.362		
	NWNJ	09/11/91	254	2055	0.331	0.341		0.336	-7.450	7.450

Table 4-10
Duplicate Samples for the 1991 NMOC Monitoring Program

Sample No.	Site Code	Date Sampled	Injection Date	Sample ID Number	Inj 1 NMOC ppmC	Inj 2 NMOC ppmC	Inj 3 NMOC ppmC	Canister NMOC ppmC	Duplicate	
									% Diff.	Abs. % Diff.
60	MNY	09/12/91	255	2041	0.186	0.215				
	MNY	09/12/91	255	2041R	0.210	0.191		0.201		
	MNY	09/12/91	255	2042	0.172	0.200				
	MNY	09/12/91	255	2042R	0.208	0.211		0.198	-1.381	1.381
61	F1FL	09/13/91	256	2045	0.688	0.704				
	F1FL	09/13/91	256	2045R	0.691	0.704		0.697		
	F1FL	09/13/91	256	2046	0.746	0.749				
	F1FL	09/13/91	256	2046R	0.718	0.723		0.734	5.207	5.207
62	PLNJ	09/13/91	256	2072	0.951	0.935		0.943		
	PLNJ	09/13/91	256	2073	0.963	0.978		0.971	2.874	2.874
63	LINY	09/16/91	259	2069	0.355	0.340				
	LINY	09/16/91	259	2069R	0.329	0.353		0.344		
	LINY	09/16/91	259	2070	0.162	0.171				
	LINY	09/16/91	259	2070R	0.367	0.346		0.262	-27.322	27.322
64	MNY	09/16/91	259	2075	0.516	0.510		0.513		
	MNY	09/16/91	259	2076	0.545	0.538		0.542	5.405	5.405
65	PBFL	09/19/91	262	2114	0.955	0.973		0.964		
	PBFL	09/19/91	262	2115	0.968	0.952		0.960	-0.416	0.416
66	R1NC	09/19/91	262	2148	0.054	0.058				
	R1NC	09/19/91	262	2148R	0.130	0.137		0.095		
	R1NC	09/19/91	262	2149	0.131	0.121				
	R1NC	09/19/91	262	2149R	0.144	0.136		0.133	33.641	33.641
67	WSNC	09/19/91	262	2110	0.093	0.093				
	WSNC	09/19/91	262	2110R	0.134	0.137		0.114		
	WSNC	09/19/91	262	2111	0.135	0.128				
	WSNC	09/19/91	262	2111R	0.126	0.122		0.128	11.113	11.113
68	NWNJ	09/23/91	266	2161	0.830	0.828		0.829		
	NWNJ	09/23/91	266	2162	0.449	0.439		0.444	-60.487	60.487
69	MNY	09/24/91	267	2165	0.414	0.430				
	MNY	09/24/91	267	2165R	0.460	0.456		0.440		
	MNY	09/24/91	267	2166	0.243	0.215				
	MNY	09/24/91	267	2166R	0.472	0.473		0.351	-22.574	22.574
70	F1FL	09/25/91	268	2170	0.061	0.074				
	F1FL	09/25/91	268	2170R	0.074	0.079		0.072		
	F1FL	09/25/91	268	2171	0.067	0.078				
	F1FL	09/25/91	268	2171R	0.060	0.045		0.063	-14.121	14.121
71	PLNJ	09/25/91	268	2202	0.312	0.333				
	PLNJ	09/25/91	268	2202R	0.328	0.330		0.326		
	PLNJ	09/25/91	268	2203	0.258	0.291				
	PLNJ	09/25/91	268	2203R	0.294	0.280		0.281	-14.839	14.839

**Table 4-10
Duplicate Samples for the 1991 NMOC Monitoring Program**

Sample No.	Site Code	Date Sampled	Joffin Date Sampled	Sample ID Number	Inj1 NMOC, ppmC	Inj2 NMOC, ppmC	Inj3 NMOC, ppmC	Canister NMOC, ppmC	Duplicate	
									% Diff.	Abs. Diff.
72	LINY	09/26/91	269	2218	0.179	0.167				
	LINY	09/26/91	269	2218R	0.180	0.172		0.175		
	LINY	09/26/91	269	2219	0.164	0.180				
	LINY	09/26/91	269	2219R	0.125	0.120		0.147	-16.939	16.939
73	PLNJ	09/26/91	269	2197	0.152	0.153		0.153		
	PLNJ	09/26/91	269	2198	0.226	0.229		0.228	39.474	39.474
74	PLNJ	09/27/91	270	2220	0.137	0.125		0.131		
	PLNJ	09/27/91	270	2221	0.152	0.158		0.155	16.783	16.783
								Average	0.836	15.768

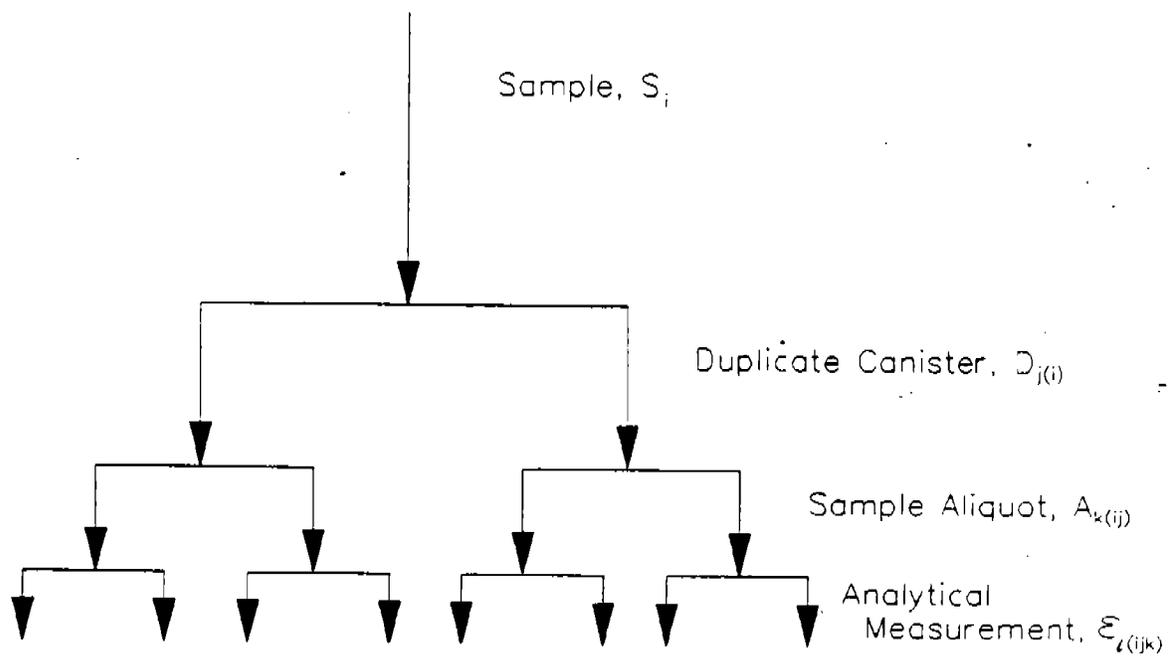


Figure 4-22. Diagram of Replicated Analyses of Duplicate Samples

(ANOVAs) that were performed on these data were nested designs with the following model:

$$Y_{ijkl} = \mu + S_i + D_{j(i)} + A_{k(ij)} + e_{l(ijk)} \quad (4-2)$$

The error term, $e_{l(ijk)}$, was assumed to contain all the analytical error. The variances of all the aliquot compounds were assumed to be equal and the variances of the duplicate pairs $D_{j(i)}$ were also assumed to be equal. Three dependent variable sets, Y_{ijkl} were used in the analysis: (1) the NMOC values in ppmC $(NMOC)_{ijkl}$, and (2) natural logarithms of $(NMOC)_{ijkl}$, and finally (3) rank equivalents of $(NMOC)_{ijkl}$. Table 4-11 gives the results of these analyses which summarize the percents of the total variance which may be attributed to each factor in the model along with the corresponding probability of a greater F statistic. As expected, the between-sample variability accounted for the majority (92 to 96%) of the variance of the dependent variable (either NMOC concentration or a derivative of it). Striking differences in the results appear when examining the results for the other sources of variability: $D_{j(i)}$, $A_{k(ij)}$, or $e_{l(ijk)}$ (analytical variability). Notice the results using $\log(NMOC)_{ijkl}$ or $(Rank)_{ijkl}$ of NMOC are quite similar. This is because the NMOC concentration data are approximately lognormally distributed. The nested ANOVA requires that the dependent variable, Y_{ijkl} , be normally distributed. If the NMOC concentrations are lognormally distributed then the logarithms of the concentrations are normally distributed.

The ANOVA using the ranks of the NMOC concentration does not require any assumption relative to the shape of the data distribution and is probably the most valid of the three analyses. Based on these considerations, it may be concluded that the ANOVA, using the $(NMOC)_{ijkl}$ values as the dependent variable is not valid. For both the analyses using logarithms of NMOC values and using ranks, suggest that there is not significant difference between duplicate canisters, but there is about a 7.9 percent difference because of between-aliquot, or between-replicate, variability. The analytical

Table 4-11

Summary Results for Nested ANOVAs

Source	Dependent Variable, Y_{ijkl}					
	$(NMOC)_{ijkl}$		$\ln(NMOC)_{ijkl}$		$(Rank)_{ijkl}$ of $(NMOC)_{ijkl}$	
	% of Total Variance	Prob. of $> F$	% of Total Variance	Prob. of $> F$	% of Total Variance	Prob. of $> F$
Sample, S_i	95.92	0.0000	93.08	0.0000	91.62	0.0000
Duplicate, $D_{j(i)}$	3.33	0.0000	0.00	0.5221	00.00	0.9210
Aliquot, $A_{k(ij)}$	0.71	0.0000	6.68	0.0000	7.87	0.0000
Residual, $\epsilon_{l(ijk)}$	0.40	--	0.24	--	0.51	--

variability is about 0.5% of the total variability of the NMOC measurements. It is clear that the between-replicate error averages at least 10 times the analytical error.

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. 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 4-12 and 4-13 for both single canister samples and duplicate samples. The pressures reported in Tables 4-14 and 4-13 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 4-12 gives statistics for single and duplicate samples. All sample canisters averaged 15.9 psig, while duplicate samples averaged 16.4 psig. The column entitled "All Samples" includes pressures from both single samples and duplicate samples. Standard deviations were 2.8 and 2.6 psig, respectively.

4.7 CANISTER CLEANUP RESULTS

Prior to the start of the 1991 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 0.0014 ppmC, ranging from 0.000 to 0.019 ppmC. Any canisters that produced more than 0.020 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 0.020 ppmC and cleanup was considered to be satisfactory.

Table 4-12
NMOC Pressure Statistics

Statistics	All Samples	Duplicate Sample Canisters
Number of Cases	687	120
Minimum Pressure, psig	6.0	11.0
Maximum Pressure, psig	34.0	21.5
Mean Pressure, psig	15.9	16.4
Median Pressure, psig	16.0	17.0
Standard Deviation, psig	2.8	2.6
Skewness, psig	0.84	-0.03
Kurtosis, psig	3.14	-1.07

Table 4-13

Pressure Distribution of NMOC Ambient Air Samples

Pressure Range, psig	Single Sample Cases	Duplicate Sample Canister Cases ^b
Blank ^a	10	0
6.0 to 6.9	1	0
7.0 to 7.9	0	0
8.0 to 8.9	3	0
9.0 to 9.9	0	0
10.0 to 10.9	1	0
11.0 to 11.9	0	2
12.0 to 12.9	25	3
13.0 to 13.9	120	18
14.0 to 14.9	87	18
15.0 to 15.9	35	9
16.0 to 16.9	71	5
17.0 to 17.9	88	25
18.0 to 18.9	46	10
19.0 to 19.9	22	19
20.0 to 20.9	35	9
21.0 to 21.9	13	2
22.0 to 22.9	7	0
23.0 to 23.9	0	0
24.0 to 24.9	0	0
25.0 to 25.9	0	0
26.0 to 26.9	1	0
27.0 to 27.9	0	0
28.0 to 28.9	0	0
29.0 to 29.9	0	0
30.0 to 36.0	2	0
Total	567	120

^aBlank indicates no pressure reading given for sample.

^bEquals 60 duplicate samples.

Average percent recoveries, or average percent cleanup, in 1991 averaged 99.747% (99.747% in 1990, 99.742% in 1989, 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 average percent recovery is based on average NMOC concentration and average cleanup concentration. 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 for the NMOC monitoring data were calculated from the results of the analysis of propane audit samples provided by EPA, AREAL. Results are reported in terms of percent bias relative to the EPA concentration spiked.

Two audit sample canister, No. 014 and 185, were analyzed on September 12, 1991; the contents of Audit Canister No. 625 were analyzed on September 25, 1991; and Canister No. 722 on September 25, 1991. The EPA Audit Report is given in Appendix I. Table 4-14 gives the concentrations reported by the EPA Auditor and by the four Radian channels. The theoretical concentration reported in Table 4-14 was calculated using dilution factors estimated when the audit samples were prepared. The column labeled ManTech is the concentration measured by the EPA Audit Laboratory, ManTech. The percent bias results are presented in Table 4-15 and were calculated relative to the ManTech measured values. The Radian bias ranges from +1.914% to +8.858%, and averages 4.0459 for the first three audit canisters. For Canister No. 722, the bias ranges from -16.551 to -14.928. For the same canister; however, ManTech's measured concentration differs from the theoretical value by +12.873 percent. Radian's measured concentrations for Canister No. 722 differ from the theoretical value by from -5.808 to -3.977 percent. Table 4-16 shows the bias of the audit samples from theoretical concentrations.

Based on these findings, the overall bias for the Radian channels for the 1991 NMOC Monitoring Program will be reported at +4.0%, with a range from +1.9 to +8.9 percent.

Table 4-14
External NMOC Audit Samples

Canister No.	Concentration, ppmC					
	Theoretical	Analysis				
		ManTech	Radian A	Radian B	Radian C	Radian D
014	1.248	1.515	1.544	1.551	1.553	1.553
185	1.200	1.500	1.550	1.542	1.539	1.529
625	1.119	1.095	1.095	1.192	1.178	1.161
722	1.911	2.157	2.157	1.835	1.820	1.800

Table 4-15

NMOC External Audits for 1991

Canister No.	Conc., ppmC ManTech	Percent Bias Relative to ManTech Analysis				
		Theoretical	Radian A	Radian B	Radian C	Radian D
014	1.515	-17.624	1.914	2.376	2.508	2.508
185	1.500	-20.000	3.333	2.800	2.600	1.933
625	1.095	2.192	6.484	8.858	7.580	6.027
722	2.157	-11.405	-16.504	-14.928	-15.624	-16.551

Bias = (Chan - ManTech)/ManTech * 100

Table 4-16

Bias of Audit Samples from Theoretical Concentrations

Canister No.	Theoretical Concentration, ppmC	Percent Difference from Theoretical				
		ManTech	Radian A	Radian B	Radian C	Radian D
014	1.248	21.394	23.718	24.279	24.439	24.439
185	1.200	25.000	29.167	28.500	28.250	27.417
625	1.119	-2.145	4.200	6.524	5.273	3.753
722	1.911	12.873	-5.756	-3.977	-4.762	-5.808

Percent Diff = (Chan - Theo) / Theo * 100

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, 10% 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 1028 NMOC concentration measurements were performed by Radian in June through October 1991. This included 687 sample analyses, 121 repeated analyses, 48 in-house QC samples (x 4 analyses each with the exception of one sample for which only three analyses each were performed and one sample where only one analysis was performed), 4 local ambient samples (x 4 analyses each), and 4 audit samples (x 4 analyses each).

Ten percent of the data base was 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.

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 1991 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. Twelve errors were found (and corrected) for an expected error percentage of 0.032.

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;
- 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 QAPP² 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 3.5®, QUATTRO®, and Freelance®. Statistical calculations were performed using SYSTAT® and SAS® 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 1991 study are given in Appendix E.

5.1 OVERALL CHARACTERIZATION

Figure 5-1 gives a stem-and-leaf plot of the 1991 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 0.042 ppmC and is shown as "0 4" on the first row at the top of the plot. The maximum NMOC concentration measured was 3.842 shown as "38 4" in the bottom row of the chart. The plot shows 536 leaves, one for each NMOC site datum in the 1991 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 interquartile 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 samples. Where duplicates were collected, the NMOC determination is the average of the two canister content concentrations. In the case of replicates, each NMOC determination is the average of the original and repeated analysis concentrations.

```

0 4555
0 6666 6777 7777
0 8888 8888 9999 9999 9999 9
1 0000 0000 0111 1111 111
1 2222 2222 2233 3333 3333 3
1 4444 4444 4455 5555 5555 5555 5
1 6666 6666 7777 7777 7777 7777 7
1 H 8888 8888 8888 9999 9999 9999 999
2 0000 0000 0000 0111 1111 11
2 2222 2222 2222 2223 3333 3333 3
2 4444 4444 4455 5555 555
2 6666 6666 6777 7777 7777 77
2 8888 8888 8888 9999 9999
3 M 0000 0011 1111 1111 1111 1111
3 2222 2222 3333 33
3 4444 4444 4445 5555 5555 55
3 6666 6666 6677 7777
3 8888 9999 99
4 0000 1111 111
4 2223 3333 33
4 4444 4444 4555 5555
4 6666 6777 77
4 8888 9999 999
5 0001 1111 1111
5 H 2223 333
5 4445 55
5 6666 667
5 8889 999
6 0001
6 2222 2223 33
6 4444 4555 55
6 6667 7777 7
6 8888 8899
7 0000 1111 11
7 2223 333
7 4444 4455
7 7777
7 8889
8 0011 11
8 2233
8 5
8 6667 7
8 89
9 11
9
9 44
9 6677 7
9 8
10 33
***OUTSIDE VALUES***
10 88
11 1127 78
12 12225 8
13 24
14 04
15 125
17 9
18 5
23 8
30 3
31 3
38 9
38 4

```

NMOC, ppmC	
Cases	687
Minimum	0.042
Maximum	3.842
Mean	0.417
Standard Deviation	0.373
Standard Error	0.014
Skewness	3.974
Kurtosis	26.816
Lower Hinge (H)	0.189
Median (M)	0.318
Upper Hinge (H)	0.538

Figure 5-1. Stem-and-leaf plot of the 1991 NMOC data.

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 3.974 for the 1991 NMOC data suggests a lognormal frequency distribution; that is by the fact that for the logarithm of the NMOC value ($\ln(\text{NMOC})$) (see Figure 5-2), skewness equals 0.04, 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. The numerical values of kurtosis listed in this report are zero centered. That is, 3.0 has been subtracted from the fourth moment to give 0.0 for a distribution shaped similar to a normal distribution.

Figure 5-2 is a stem-and-leaf plot of the 1991 $\ln(\text{NMOC})$ data. The plot shows an approximately symmetrical distribution (skewness = 0.04). The kurtosis equal to -0.094 indicates the $\ln(\text{NMOC})$ distribution to be more 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, 4, 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.

```

-31 8
-30
-29 91
-28 84
-27 88721
-26 97543 2
-25 87832 1
-24 88778 42111 1
-23 99997 66655 44220
-22 88777 66110 0
-21 99998 88532 20
-20 97778 55444 44333 210
-19 99888 75555 54433 2100
-18 99999 88877 76666 44322 211
-17 99887 77784 44444 44433 33222 21110 000
-16 H 99988 87768 54433 33333 32211 10000 00
-15 99998 88778 66665 44422 21111 1100
-14 99999 88777 77785 55544 43322 21100
-13 99998 88778 66655 55444 44333 32220 0000
-12 99999 88887 77778 66666 54433 32222 1111
-11 M 99988 77777 76665 55544 44443 32222 22111 0
-10 99988 87777 77666 66666 55444 43332 22111 11000 000
-9 99988 87778 65443 33322 21100
-8 99998 88778 55444 33322 22111 11100 00
-7 99988 88777 77855 55443 32222 11100 000
-6 H 98888 77777 66665 55432 22211 0
-5 98888 86666 65332 22211 0
-4 99887 77777 77654 44443 33222 11100 000
-3 99999 88888 87778 65555 44443 33322 21110 0
-2 99999 98878 55544 42210 0000
-1 98878 44443 320
-0 88554 33222 1
0 2388
1 00115 879
2 00025 79
3 36
4 114
5 8
6 1
7
8 7
***OUTSIDE VALUES***
11 04
13 04

```

ln (NMOC)	
Cases	687
Minimum	-3.168
Maximum	1.346
Mean	-1.153
Standard Deviation	0.739
Standard Error	0.028
Skewness	0.045
Kurtosis	-0.094
Lower Hinge (H)	-1.666
Median (M)	-1.146
Upper Hinge (H)	-0.620

Figure 5-2. Stem-and-leaf plot of ln(NMOC) data.

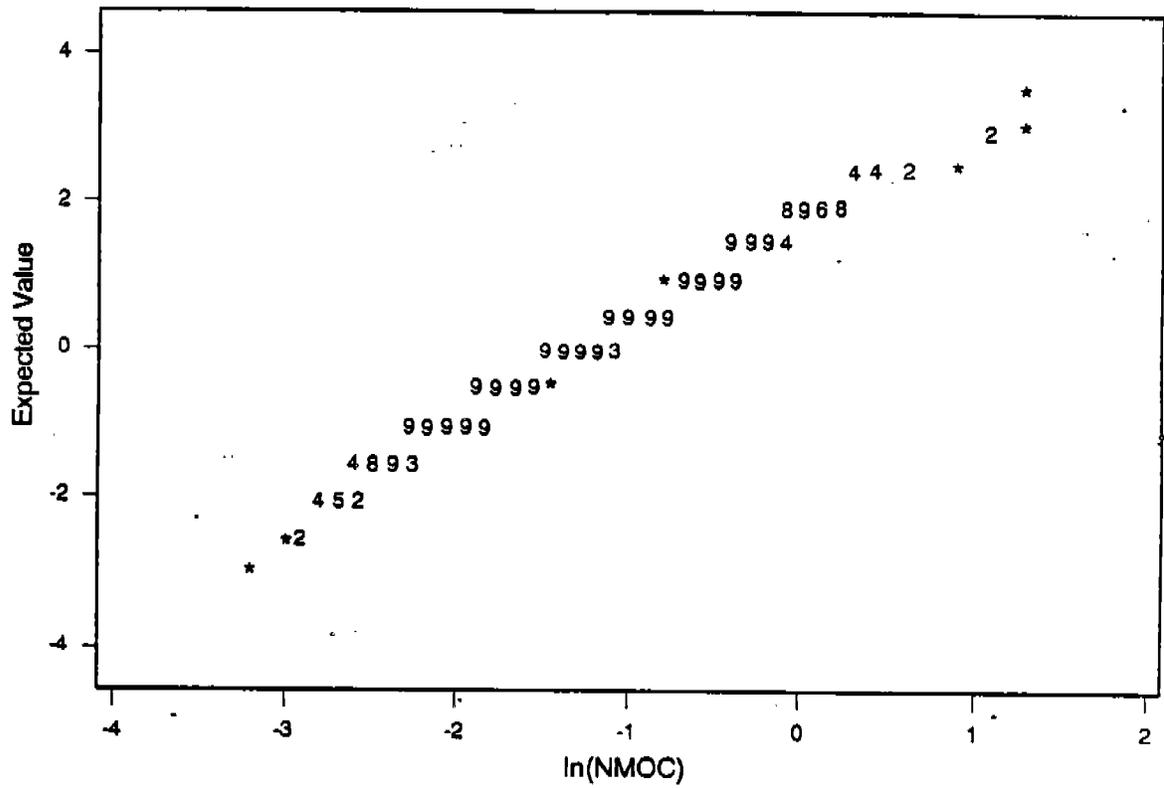


Figure 5-4. Cumulative frequency distribution for 1991 ln(NMOC) data.

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5.2 MONTHLY VARIATIONS, 1984 - 1991

Table 5-1 partitions the NMOC data for the summer of 1991 into groups which correspond to monthly intervals. For the summer of 1991, the monthly means and medians of the NMOC sites for June, July, August, and September parallel one another. That is, the NMOC concentrations mean and median for July 1991 are greater than the mean and median for June 1991. Means and median for August show dramatic increases compared to July 1991. The mean and median for September are less than the mean and median of August 1991. Arithmetic means are used in Table 5-1 in spite of the observations given in Section 5.1 which conclude that the frequency distribution of NMOC concentrations in ambient air are approximately logarithmic normal distributed. Table 5-1 also gives monthly minima, medians, and maxima. These latter three statistics are independent of the probability distribution from which they derive.

Table 5-1

Summary Statistics for 1991 NMOC Sites, by Month

Sample Month 1991	NMOC Concentration, ppmC					Cases
	Minimum	Median	Mean	Maximum	Standard Deviation	
June	0.050	0.283	0.369	1.790	0.281	155
July	0.042	0.300	0.389	1.852	0.304	178
August	0.056	0.358	0.507	3.842	0.538	185
September	0.068	0.326	0.390	1.223	0.266	157
October	0.102	0.540	0.492	0.786	0.292	4

6.0 RECOMMENDATIONS, NMOC MONITORING PROGRAM

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

6.1 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 at one site. In 1988, an additional site was located on top of the World Trade Center in New York, a height of over 1000 feet. It is recommended that further study be performed at these sampling heights 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. It is also recommended that ozone concentrations and NO_x concentrations be monitored at the same locations and altitudes. The information gained from such a study would be useful in validating various atmospheric model predictions.

6.2 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.

6.3 CANISTER CLEANUP STUDIES

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.

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.

Radian has proposed⁷ 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 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.

6.4 FIELD AUDIT

It is recommended that a field audit be designed and conducted at several NMOC sites during the 1991 Monitoring Program. One field audit per month should be performed at an NMOC site during June, July, August, and September 1992. 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. The audit samples should use both dry and humid standards.

6.5 DUPLICATE SAMPLE AND REPLICATE ANALYSIS

During the 1992 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.

6.6 REDESIGN OF NMOC SAMPLING EQUIPMENT

The sampling equipment used to collect NMOC samples was designed in 1984. This equipment is now antiquated and should be replaced. A new design, incorporating current state-of-the-art components, has been presented to U.S. EPA for consideration. The proposed design would reduce the potential for invalid collections in future measurements and provide some flexibility for future programs.

7.0. THREE-HOUR AIR TOXICS DATA SUMMARY

The 1991 NMOC Program included three-hour air toxics samples at two 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 performed 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 10 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. One of the samples from each site was analyzed by gas chromatography/mass spectrometry (GC/MS) for confirmation of compound identification. The GC/MS participated in and was highly successful in our external audits conducted for this program as well as the Urban Air Toxics Monitoring Program (UATMP). The primary method of quantitation for both was chosen to be the FID (or the ECD depending on the compound) because the cost of the analysis by GC/MD was less than the cost by GC/MS, and the FID (or ECD) provided a more sensitive technique for the analysis. In the development of the GC/MD analysis for this program and the UATMP, the GC/MS has been useful in improving the GC/MD ability to identify organic compounds correctly.

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 15 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

Table 7-1
Three-Hour Ambient Air Samples and Analyses

Site Code	No.	Duplicate Pairs	GC/MD Analyses		GC/MS Analyses
			Replicate	Total	
NWNJ	9	1	1	11	1
PLNJ	8	1	1	10	1
Total	17	2	2	21	2

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 1991 3-hour ambient air samples that were speciated. The table shows the number of cases (samples), the percent of cases in which the compound was identified, the minimum, maximum, and mean (arithmetic average) concentrations of the compound in ppbv. In cases where duplicate samples were taken, or replicate analyses were performed, the results of all the analyses were averages for each sample. The mean refers to the daily sample averages, not the averages of all the analyses. The frequency of occurrence of target compounds fall into four prominent percentile categories at concentrations above their method detection limits:

- Those occurring in more than 70% of the samples tested;
- Those occurring in from 40% to 69% of the samples;
- Those occurring in less than 30% of the samples; and
- Those not identified in any of the 3-hour air samples.

These results are summarized in Table 7-3.

Overall concentrations ranged from 0.07 ppbv for p-dichlorobenzene to 169.74 ppbv for acetylene.

7.2 SITE RESULTS

Tables 7-4 and 7-5 gives 3-hour ambient air concentrations by site code for the 38 target air toxics compounds. The overall site means range from 7.39 ppbv for PLNJ to 6.04 for NWNJ. Appendix H tabulates the complete analytical results and includes the NMOC concentrations for each of the 3-hour air toxics samples.

Table 7-2
Compound Identification for all Sites

Compound	Cases ^a		Min ppbv	Max ppbv	Mean ^c ppbv	Mean ^e g/m ³	Mean ^d ppbv	Mean ^f ppbv
	No.	% Freq ^b						
Acetylene	12	70.6	24.37	169.74	88.21	95.49	62.41	62.26
Propylene	1	5.9	8.90	8.90	8.90	15.57	0.57	0.52
Chloromethane	7	41.2	0.37	4.75	1.78	3.73	0.79	0.73
1,3-Butadiene	3	17.6	0.34	3.12	1.36	3.06	0.28	0.24
Methylene chloride	4	23.5	1.47	4.46	3.67	12.97	0.91	0.86
trans-1,2-Dichloroethylene	1	5.9	0.13	0.13	0.13	0.52	0.03	0.01
Chloroprene	3	17.6	2.08	4.48	3.00	11.05	0.55	0.53
1,1,1-Trichloroethane	17	100.0	0.38	4.83	2.02	11.18	2.02	2.02
Benzene	17	100.0	0.34	2.83	1.47	4.77	1.47	1.47
Carbon tetrachloride	17	100.0	0.24	0.30	0.27	1.75	0.27	0.27
Trichloroethylene	12	70.6	0.04	1.27	0.40	2.17	0.28	0.28
1,1,2-Trichloroethane	1	5.9	0.14	0.14	0.14	0.78	0.02	0.01
Toluene	17	100.0	0.87	13.49	5.77	22.09	5.77	5.77
n-Octane	13	76.5	0.10	0.46	0.33	1.55	0.25	0.25
Tetrachloroethylene	14	82.4	0.20	1.30	0.57	3.90	0.47	0.47
Chlorobenzene	1	5.9	0.69	0.69	0.69	3.23	0.05	0.04
Ethylbenzene	17	100.0	0.14	1.33	0.71	3.12	0.71	0.71
m/p-Xylene/Bromform	17	100.0	0.61	6.85	3.36	64.97	3.36	3.36
Styrene	17	100.0	0.25	1.71	0.66	2.84	0.66	0.66
o-Xylene/1,1,2,2-Tetrachloroethane	17	100.0	0.29	3.18	1.49	17.03	1.49	1.49
m-Dichlorobenzene	1	5.9	0.15	0.15	0.15	0.92	0.02	0.01
p-Dichlorobenzene	1	5.9	0.07	0.07	0.07	0.43	0.05	0.00

^aA total of 17 samples were collected and analyzed by GC/MD.

^bThe percent of the total in which the compound was identified.

^cThe arithmetic average concentration of all the compound identification cases.

^dThe arithmetic average concentration of all the sample causes using half the NDL values for compounds not detected.

^eThe arithmetic average concentration of all the sample cases using zero for compounds not detected.

Table 7-3

Frequency of Occurrence of Target Compounds

Range for Frequency Of Occurrence	Target Compounds	
100% to 70%	Acetylene 1,1,1-Trichloroethane Benzene Tetrachloroethylene m/p-Xylene/Bromoform n-Octane	o-Xylene/1,1,2,2-Tetrachloroethane Carbon tetrachloride Toluene Ethylbenzene Styrene Trichloroethylene
69% to 40%	Chloromethane	
39% to >0%	Propylene Methylene Chloride Chloroprene Chlorobenzene p-Dichlorobenzene	1,3-Butadiene trans-1,2-Dichloroethylene 1,1,2-Trichloroethane m-Dichlorobenzene
Zero	Chloroform Bromodichloromethane Vinyl chloride Bromochloromethane cis-1,3-Dichloropropylene Bromoform trans-1,3-Dichloropropylene	Chloroethane Bromomethane 1,1-Dichloroethane 1,2-Dichloroethane Dibromochloromethane o-Dichlorobenzene

Table 7-4
Compound Identifications for NWNJ

Compound	Cases ^a	Min ppbv	Max ppbv	Mean ^b ppbv	Mean ^b g/m ³	Mean ^c ppbv	Mean ^d ppbv
Acetylene	6	24.37	135.69	82.25	89.04	55.00	54.84
Propylene	1	8.90	8.90	8.90	15.57	1.03	0.99
Chloromethane	6	0.37	4.75	1.99	4.18	1.36	1.33
1,3-Butadiene	2	0.34	3.12	1.73	3.89	0.42	0.38
Methylene chloride	1	4.38	4.38	4.38	15.46	0.54	0.49
trans-1,2-Dichloroethylene	1	0.13	0.13	0.13	0.52	0.03	0.01
Chloroprene	2	2.45	4.48	3.57	12.75	0.79	0.77
1,1,1-Trichloroethane	9	1.18	3.59	2.33	12.91	2.33	2.33
Benzene	9	0.78	2.43	1.58	5.12	1.58	1.58
Carbon tetrachloride	9	0.26	0.30	0.28	1.80	0.28	0.28
Trichloroethylene	9	0.10	1.27	0.50	2.71	0.50	0.50
1,1,2-Trichloroethane	1	0.14	0.14	0.14	0.78	0.02	0.02
Toluene	9	2.73	13.49	6.79	26.00	6.79	6.79
n-Octane	8	0.15	0.46	0.36	1.72	0.32	0.32
Tetrachloroethylene	9	0.28	1.30	0.65	4.54	0.66	0.66
Ethylbenzene	9	0.37	1.33	0.89	3.94	0.89	0.89
m/p-Xylene/Bromoform	9	1.58	6.85	4.31	83.25	4.31	4.31
Styrene	9	0.44	1.25	0.72	3.12	0.72	0.72
o-Xylene/1,1,2,2-Tetrachloroethane	9	0.76	3.18	1.94	22.11	1.94	1.94

^aA total of 9 samples were collected and analyzed by GC/MD.

^bThe arithmetic average concentration of all the compound identification cases.

^cthe arithmetic average concentration of all the sample cases using half the MDL values for compounds not detected.

^dThe arithmetic average concentration of all the sample cases using zero.

Table 7-5
Compound Identifications for PLNJ

Compound	Cases ^a	Min ppbv	Max ppbv	Mean ^b ppbv	Mean ^b g/m ³	Mean ^c ppbv	Mean ^d ppbv
Acetylene	6	25.25	169.74	94.16	101.93	70.75	70.62
Chloromethane	1	0.50	0.50	0.50	1.05	0.15	0.06
1,3-Butadiene	1	0.62	0.62	0.62	1.39	0.12	0.08
Methylene chloride	3	0.15	4.46	3.00	10.58	1.16	1.12
Chloroprene	1	2.08	2.08	2.08	7.66	0.29	0.26
1,1,1-Trichloroethane	8	0.38	4.83	1.66	9.23	1.66	1.66
Benzene	8	0.34	2.83	1.35	4.38	1.35	1.35
Carbon tetrachloride	8	0.24	0.28	0.26	1.69	0.26	0.26
Trichloroethylene	3	0.04	0.21	0.10	0.55	0.04	0.04
Toluene	8	0.87	9.85	4.62	17.70	4.62	4.62
n-Octane	5	0.10	0.40	0.27	1.28	0.17	0.17
Tetrachloroethylene	5	0.20	0.61	0.40	2.76	0.26	0.25
Chlorobenzene	1	0.69	0.69	0.69	3.23	0.09	0.09
Ethylbenzene	8	0.14	0.92	0.50	2.19	0.50	0.50
m/p-Xylene/Bromoform	8	0.61	4.46	2.29	44.30	2.29	2.29
Styrene	8	0.25	1.71	0.58	2.52	0.58	0.58
o-Xylene/1,1,2,2-Tetrachloroethane	8	0.29	1.98	0.99	11.31	0.99	0.99
m-Dichlorobenzene	1	0.15	0.15	0.15	0.92	0.03	0.02
p-Dichlorobenzene	1	0.07	0.07	0.07	0.43	0.05	0.01

^aA total of 8 samples were collected and analyzed by GC/MD.

^bThe arithmetic average concentration of all the compound identification cases.

^cThe arithmetic average concentration of all the sample cases using half the MDL values for compounds not detected.

^dThe arithmetic average concentration of all the sample cases using zero.

8.0 THREE-HOUR AIR TOXICS TECHNICAL NOTES

This section describes the equipment used to sample and analyze the 3-hour air toxics samples. Also described are sample handling procedures, sampler certification procedures, standards generation and instrument calibration procedures, compound identification procedures, GC/MS compound identification confirmation, quality assurance/quality control procedures, and data records for the 3-hour air toxics compounds.

8.1 SAMPLING EQUIPMENT AND INTERFACE

The sampling equipment for the 3-hour air toxics samples was the NMOC Monitoring Program sampling equipment described in Section 3.1. The original sample was collected as an integrated ambient air sample from 6:00 a.m. to 9:00 a.m. with a final sample pressure of about 15 psig. As stated above, after NMOC analysis the canister was bled to atmospheric pressure and allowed to stand at least 18 hours before being analyzed by GC/MD.

An interface system was designed and built by Radian Corporation to take a sample from the canister and inject it into the gas chromatograph for analysis.

Figure 8-1 shows the GC/MD system including the Sample Interface System, Analytical System, and Data System. The sample interface takes a 250-mL sample approximately from the canister, draws it through Trap Assembly 1 and condenses all the water and organic compounds, with the exception of methane, in the air sample drawn from the canister. Trap Assembly 1 is a cryogenic, liquid argon trap packed with glass beads. The cryogen is removed, and an electrical heater quickly heats Trap Assembly 1, vaporizing the water and organic compounds condensed from the canister sample.

8.2 THREE-HOUR AIR TOXICS SAMPLING SYSTEMS CERTIFICATION

The sampling systems used to collect 3-hour air toxics samples were certified for use per the specifications described in U.S. EPA Compendium of Methods TO-14.¹²

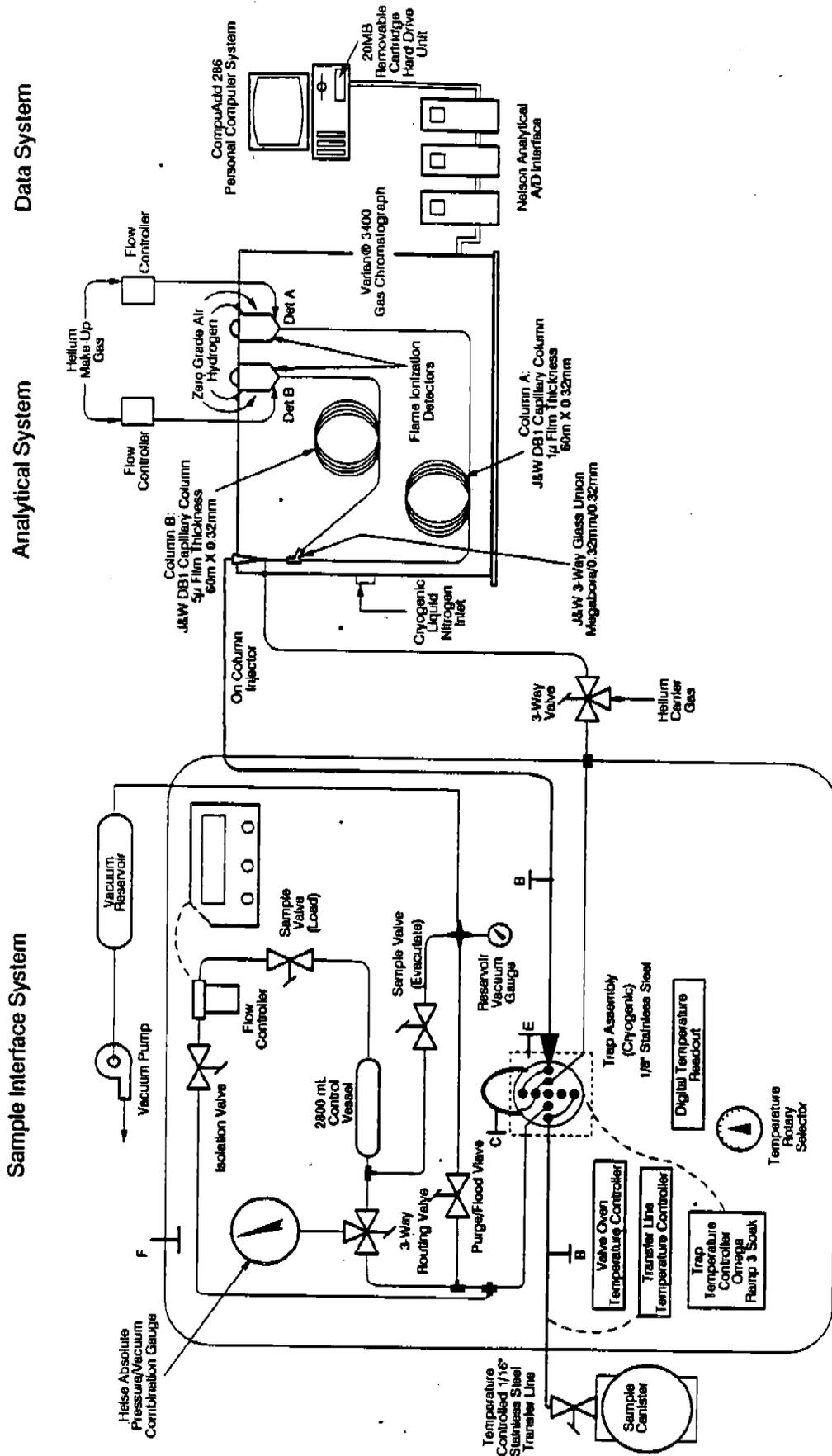


Figure 8-1. Gas Chromatographic Multidetector System

8.2.1 Sampler Certification Blanks - Humidified Zero Air

Zero certification consisted of purging the sampler with cleaned, humidified air, followed by collecting a sample of the cleaned, dried air that had been humidified through the purged NMOC samplers for GC/MD analysis. The purpose of the wet purge was to help remove any adherent contaminants from the sampler. The chromatograms from these certification sample analyses were archived for each sampler. Results presented in Table 8-1 showed a range of 0.007 ppmC to 0.008 ppmC of NMOC, with an average of 0.0075 ppmC. The sampling systems were determined to be very clean and showed no characteristics of additive bias.

8.2.2 Sampler Certification Challenge - Selected Target Compound

Following the NMOC sampler blank certification, a challenge gas containing five selected target compounds was passed through the samplers. The average concentration of the compounds in the challenge gas was 18.5 ppbv/species. Table 8-2 shows the average system percent bias calculated with the analysis of the challenge gas being used as a reference concentration.

System percent bias ranged from 0.8% to 1.2% with an overall average of 1.0 percent. The systems showed acceptable subtractive bias characteristics.

8.3 CALIBRATION

Calibration curves for the UATMP include a 3-point calibration initially, and daily calibration checks at an average 5 ppbv concentration for the target compounds. The origin of the calibration curve will be used as one of the calibration points.

8.3.1 Calibration Standards Generation

Calibration standards are generated with a dynamic flow dilution system. The gases are mixed in a SUMMA®-treated mixing sphere and bled into evacuated canisters. One dilution air stream is routed through a SUMMA®-treated bubbler containing HPLC-grade water to humidify, and the other stream is not humidified. The dilution air streams are then brought together for

Table 8-1

Sampler Certification Zero Results

Canister Number	Canister Blank Date	Blank Sample Conc., ppmC	Sampler System Number	Sampler Zero Collection Date	Sampler Zero Sample, ppmC	Diff., ppmC
676	5/7/91	0.000	12	5/15/91	0.0066	0.0065
649	5/7/91	0.000	19	5/15/91	0.0084	0.0084
Average					0.0075	0.0075

Table 8-2

Sampler Certification Challenge Results

System Number	Percent	
	Average Compound Recovery	Average System Bias
12	100.8	0.8
19	101.2	1.2
Average	101.0	1.0

mixing with the streams for the Scott certified cylinders. Flow rates from all five streams (four from the certified cylinders and one from the dilution cylinder) are gauged and controlled by mass flow controllers. The split air dilution streams are metered by "wet" and "dry" rotameters from the humidified and unhumidified dilution air streams respectively.

The system is evacuated with a vacuum pump while the closed canister is connected. A precision absolute pressure gauge measures the canister pressure before and after filling. The lines leading to the canister and to the mixing sphere are flushed for at least 15 minutes with standard gas before being connected to the canister for filling. A diagram of the apparatus is shown in Figure 8-2.

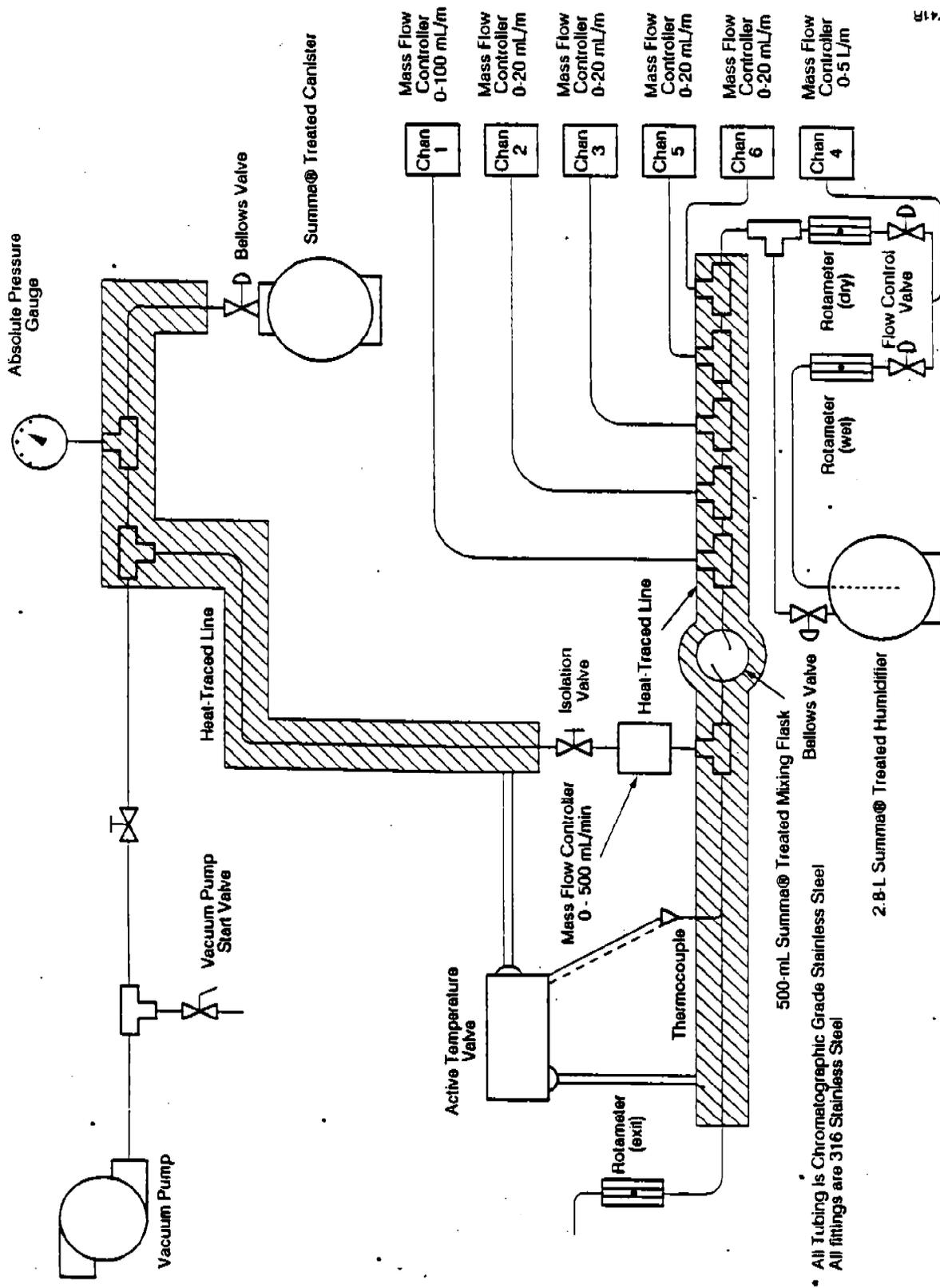
8.3.2 GC/MD Calibration

Initial calibration curve standards are made at 0.5, 1, 5, and 10 ppbv for each of the target compounds. In addition, the point at 0,0 is considered to be a calibration point. A linear regression is done for each of the UATMP compounds and the linear regression coefficient is expected to be 0.995 or better for selected compounds on the detector used for quantitation. The zero air used for canister cleaning and for standards dilution is analyzed at the time of calibration but the results are not used in the calibration curve. Daily calibration is done with in-house standards made from Scott certified gases with average concentration of 5 ppbv.

All the daily calibration data are used to calculate calibration factors for each compound on each detector. Minima, means, maxima, and standard deviations are recorded and tabulated for each detector. The FID calibration factors are used for quantitation for the majority of compounds, except some of the halocarbons. The ECD calibration factors are used in most cases of halogenated compound quantitation because of the greater sensitivity of the ECD at low concentrations.

8.3.3 GC/MS Calibration

When a group of UATMP samples is to be analyzed by GC/MS, calibration is performed in the multiple ion detection mode with a four-point calibration curve at about 1, 5, and 10 ppbv average concentration for each UATMP target



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Figure 8-2. Dynamic Flow Dilution Apparatus

compound. Zero, which is not measured, is included in the correlation. A linear regression is done for each of the UATMP compounds and the linear regression coefficient is expected to be greater than or equal to 0.995. Daily calibration checks at 5 ppbv (beginning and end of day) and daily zero analyses are performed to assure that the analytical system is in control and remains uncontaminated. The daily calibration checks, in terms of percent recovery of the target compounds should be within $\pm 25\%$ of the expected value to be acceptable.

8.4 MONTHLY CALIBRATION

For the 1991 UATMP, there were monthly calibrations of the GC/MD for 38 target compounds. Daily calibration checks were performed and response-factor control charts will be prepared for each compound from the detector used to quantitate the specific target compound. Response factors (RFs) will be used to quantitate target compounds. Eleven compounds were quantitated from the electron capture detector (ECD) results--bromochloromethane, methylene chloride, chloroform, 1,1,1-trichloroethane, carbon tetrachloride, trichloroethylene, bromodichloromethane, 1,1,2-trichloroethane, tetrachloroethylene, dibromochloromethane, bromoform, and 1,1,2,2-tetrachloroethane. All other target compounds were quantitated from the flame ionization detector (FID) results. Ratios of responses of target compounds on ECD/FID, and PID/FID for the daily calibration check will be compared to the same ratios for sample analyses at expected retention times to effect quantitation decisions. Approximately 15 percent of the field samples, already analyzed by GC/MD, were analyzed also by GC/MS for compound identification confirmation.

Monthly calibration were performed using Scott certified standards diluted to the recommended calibration concentrations in the flow dilution apparatus. The calibration standards were stored in 6-L stainless steel canisters used only for standards. For each calibration a number of parameters were derived and used in the course of compound identification and compound quantitation. The monthly calibration procedure is outlined below in a step-by-step manner.

1. Mix calibration standards at approximately 0.5, 1.0, 5.0, and 10.0 ppbv.

2. Determine area counts (a.c.) and RT on the FID and the ECD for each compound and calibration standard.
3. Calculate a regression coefficient, r_1 , and linear regression parameters, intercept, a_1 , and slope, b_1 , for each compound using response data (a.c. vs. ppbv) and a zero-zero (0,0) point as calibration points. These regression calibrations will be performed for each target compound using only the calibration data, i.e., a.c. vs. ppbv, from the detectors which are used to quantitate the compound. If $r_1 \geq 0.995$, the calibration is completed for the given compound.
4. Data using the ECD detector should be checked for saturation of the detector. This is done by performing a second linear regression for the compound using only the results at 0, 0.5, 1.0, and 5.0 ppbv. If $r_2 > r_1$, and if $a_2 < a_1$, the regression intercept ratio, there is evidence that the ECD is saturated at 10 ppbv. In checking for saturation of the ECD, use data only from those compounds quantitated on the ECD. If $r_2 > r_1 \geq 0.995$, the calibration is complete and response factors and moving ranges are calculated from the three calibration points at 0.5, 1.0, and 5.0 ppbv. Calculations involving response factors and moving ranges will be illustrated below. If $r_2 < 0.995$ repeat the calibration point at 0.5 ppbv and recalculate r_2 to see if it attains the acceptance criterion that $r_2 \geq 0.995$. If so, the calibration is complete. If not, prepare new standards and repeat the entire calibration.
5. For the FID, if $r_1 < 0.995$, repeat the calibration point at 0.5 (or 1.0) ppbv and recalculate r_1 using all six calibration points at the following concentrations 0.0, 0.5, 1.0, 5.0, 10.0, and 0.5 (or 1.0) ppbv. If $r_1 < 0.995$, terminate the calibration, clean the calibration standard canisters, and repeat the calibration beginning at Step 1. If $r_1 > 0.995$, the calibration is complete and parameters for the control charts and compound identification programs may be calculated.
6. Determine response factors (RF = ppbv/a.c.) for each calibration data point, with the exception of the 0,0 point, with data from the detector used to quantitate each compound.
7. Calculate the mean response factor, \overline{RF} , the moving range, R, for successive calibration data points, and the average moving range, \overline{R} , with data from the detector used to quantitate the compound. Calculate the upper control limits, UCL, and lower control limits, LCL, for the RF, and the R charts.

8. An example calculation is given below, using calibration data for bromomethane on the FID:

Level	ppbv	a.c.	RF * 10 ⁶	R
1	0	0	--	--
2	0.520	70,262	7.40087	--
3	1.090	149,525	7.28975	0.11112
4	3.560	510,460	6.97410	0.31565
5	5.260	860,772	6.11079	0.86331
Average			6.94388	0.43032

For the regression equation

$$(a.c.) = a + b, (ppbv),$$

$$a_1 = 17504.12;$$

$$b_1 = 160933.80;$$

$$r_1 = 0.99672;$$

$$\text{For Level 3, } R_3 = |7.28975 - 7.40087| = 0.11112; \text{ and}$$

$$\text{For Level 4, } R_4 = |6.97410 - 7.28975| = 0.31565.$$

Note that the values of RF indicate a trend with concentration; therefore, the calibration curve appears to be nonlinear.

9. Calculate control chart parameters. [See "ASTM Manual on Presentation of Data and Control Chart Analysis," ASTM Special Technical Publication 15D, ASTM, Philadelphia, PA 1976, Section 302, p. 99].

$$\text{For RF: } \overline{RF} = 6.944 * 10^{-6}; \text{ and}$$

$$\text{For R: } \overline{R} = 0.4303 * 10^{-6}.$$

For RF: Control Limits: $n = 2$.

$$\overline{RF} \pm E_2 \overline{R} = \overline{RF} \pm 2.660 \overline{R}$$

$$UCL_{RF} = 6.944 * 10^{-6} + 2.660 (0.4303 * 10^{-6})$$

$$LCL_{RF} = 6.944 * 10^{-6} - 2.660 (0.4303 * 10^{-6})$$

$$UCL_{RF} = 8.089 * 10^{-6}$$

$$LCL_{RF} = 5.799 * 10^{-6}$$

For R: Control Limits, $D_4\bar{R}$ and $D_3\bar{R}$

$$UCL_R = D_4\bar{R} = 3.267 (0.4303 * 10^{-6})$$

$$LCL_R = D_3\bar{R} = (0) (0.4303 * 10^{-6})$$

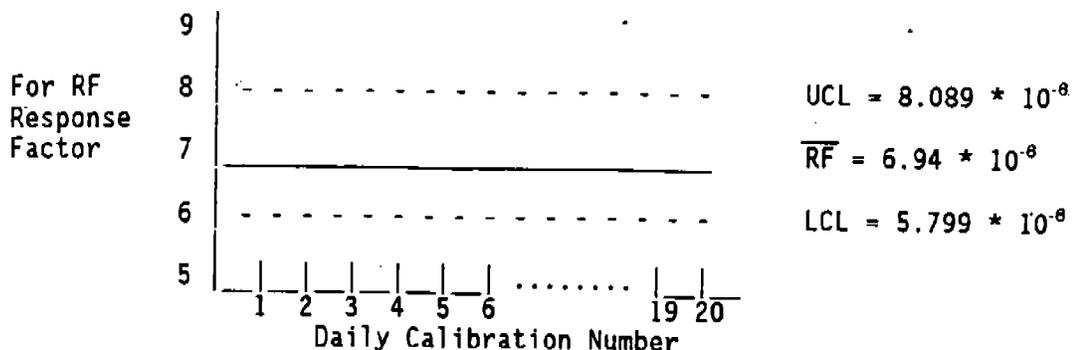
$$UCL_R = 1.406 * 10^{-6}; \text{ and}$$

$$LCL_R = 0.000.$$

The control chart parameters are based on the calibration data and will be used to monitor RF and moving range (R) values for the daily calibration checks in between calibrations. A control chart and its upper and lower limits is required for each compound monitored.

8.5 DAILY CALIBRATION CHECKS AND QUANTITATION

Calibration checks are performed on the GC/MD each day that analyses are performed on field samples. Response factors are calculated for each target compound from the calibration checks. RF for the day is compared and/or plotted on the control chart, see below:



So long as the daily RF is \leq the UCL and \geq LCL, the analytical process is said to be in control. The daily RF for the first calibration check, RF_1 , then averaged in with the four RFs from the monthly calibration. To give an average RF for the day for the given compound and detector for quantitation. The next daily calibration factor, RF_2 , if it is within the control limits for RF, is averaged with RF_1 and the four calibration RFs to give the average RF for the second day for quantitation on the second day. Each successive daily, so long as it falls within the RF control limits, is averaged with the previous RFs for use on the particular day for quantitation. RF's which fall within the control limits, are cumulated until a monthly calibration shows that the average response factor for the month is not equal to the original \overline{RF} for a particular compound.

If a calculated RF value falls outside UCL or LCL, a second daily calibration check is performed that same day. If the second RF for that day also falls outside the control limits, all analysis is terminated, the standard canisters are cleaned, new standards are mixed, and a new five-point calibration (including a 0,0 point) is performed. If the second calibration QC check for the day produces an RF value that falls within the control limits, then the latter value is used to add to the set of RFs used to quantitate samples for the day. The RF that was outside the control limit is still plotted on Figure 1, but discarded and not used in any calculations. If a second daily RF falls outside the control limits between monthly calibrations, all analyses are termination and a new calibration is initiated as described above.

When a regular monthly calibration is scheduled, fresh standards are prepared as described above, and new calibration parameters (r , a , and b),

values of \overline{RF} and \overline{R} are calculated as described above. Student's *t*-tests then performed to determine if the initial population \overline{RF} and the new monthly population \overline{RF} are equal for each compound. If the population means for RF test equal, then the cumulative average response factor may be continued as new RFs are determined each day in the new month. New control chart parameters, \overline{RF} , UCL_{RF} , and LCL_{RF} , are then determined using RF's from the initial calibration and the monthly calibration points. For the daily QC checks, \overline{RF} used to quantitate continues to employ all the RF data from the initial calibration cumulated to the last date. New values for UCL and LCL are used and are then used throughout the new month or until the next full calibration is necessary. If a subsequent monthly calibration fails to test equal to the initial calibration, then the data for the month that failed becomes the new "initial" calibration data set and the cumulative determination of \overline{RF} used for quantitation begins anew.

Moving range values, *R*, are calculated along with each daily calibration. Any moving *R* which falls outside the control limits for *R* indicates when the daily calibration procedure is out of control. When this occurs, there is an indication that the standard operating procedures need to be reviewed for possible revision to reduce variability.

8.6 GAS CHROMATOGRAPH/MASS SPECTROMETER ANALYSIS AND COMPOUND IDENTIFICATION CONFIRMATION

Two of the 3-hour air toxics samples were analyzed by GC/MS for compound identification confirmation following completion of the GC/MD analyses. So that the sensitivity of the GC/MS compared favorably with that of the GC/MD, the GC/MS was operated in the multiple ion detection (MID) mode, and the sample volume was about 500-mL (compared to 250-mL for the GC/MD analyses).

No comparison of the quantitative results for GC/MS and GC/MD was made, because the purpose of the GC/MS analyses was compound identification confirmation only. This comparison is discussed below in Section 8.7.4.

8.7 QA/QC DATA

Precision was estimated from duplicate samples and repeated analysis. Table 8-3 summarizes the duplicate and replicate analyses performed on the 3-hour air toxics samples at NWNJ and PLNJ. Columns headed D1, D2, and R1, were taken from Tables H1 and H2 in Appendix H. D1 and D2 show the results of

the analyses of the samples in duplicate canisters 1 and 2, respectively. R1 shows the results of the second analysis of duplicate canister D1. From the replicate analyses, R1 and D1, the analytical precision may be estimated, and from the duplicate canister analyses the sampling and analytical precisions may be estimated.

In the columns under "Replicate Analyses" XBAR, s, % CV, and Abs % D, represent the average concentrations (in analyses D1 and R1), the standard deviation (between analyses D1 and R1), % CV ($s/XBAR*100$), and absolute percent difference respectively. Note that average concentrations range between less than detection limit (<0.01) to 7.49 ppbv with the exception of acetylene in both NWNJ and PLNJ. These two relatively high concentrations bias the overall average concentration insofar as its ability to characterize the central tendency is concerned. Percent CV for replicates ranges from 0.00 to 37.07 %, and absolute percent difference ranges from 0.00 to 51.59. The pooled % CV is 21.16, while the average absolute percent difference is 9.84. These are excellent results, considering the small number of samples involved, and compare favorably with UATMP replicate analysis results.

Duplicate sample statistics are shown in the last four columns of Table 8-3. XBAR represents the best estimate of the sample mean. It was calculated first by averaging D1 and R1 analyses in the first duplicate canister and then averaging the first average with D2. The duplicate standard deviation was calculated using the average of D1 and R1 and comparing it with D2. The % CV for duplicates was calculated as the quotient of s and XBAR multiplied by 100. Finally the absolute percent deviation was calculated from the difference between the average concentrations of the duplicate canisters, divided by the average concentration in the duplicate canisters, expressed as a percentage. The statistic % CV ranged from 0.00 to 70.71. The pooled % CV was 13.38. Absolute percent difference ranged from 0.00 to 110.13. The very large absolute percent difference for 1,1,1-trichloroethane resulted from an unexpectedly large measured concentration (10.83 ppbv) in D2, compared to analyses of 1.81 ppbv and 1.86 ppbv measured in canister D1 from the same ambient air sample. The average absolute percent difference for duplicates was 11.71, which is an excellent result.

Table 8-3.

1991 NMOC 3-Hour Replicates and Duplicates, ppbv

Site	Compound	D1	D2	R1	Replicate Analyses			
					XBAR	s	% CV	Abs % D
NWNJ	Acetylene	137.82	116.85	124.27	131.045	9.581	7.311	10.932
NWNJ	1, 3-Butadiene	3.90	3.19	2.28	3.090	1.146	37.072	51.592
NWNJ	Methylene chloride	< 0.01	4.38	< 0.01				
NWNJ	1, 1, 1-Trichloroethane	1.59	1.62	0.98	1.285	0.431	33.567	41.997
NWNJ	Benzene	2.33	2.28	2.67	2.500	0.240	9.617	14.226
NWNJ	Carbon tetrachloride	0.27	0.28	0.24	0.255	0.021	8.319	11.215
NWNJ	Trichloroethylene	1.14	1.15	1.10	1.120	0.028	2.525	3.524
NWNJ	Toluene	7.54	7.53	7.44	7.490	0.071	0.944	1.332
NWNJ	n-Octane	0.38	0.38	<0.01	0.380			
NWNJ	Tetrachloroethylene	0.30	0.30	0.25	0.275	0.035	12.856	17.391
NWNJ	Ethylbenzene	1.04	1.03	0.99	1.015	0.035	3.483	4.890
NWNJ	m/p-Xylene/Bromoform	5.06	5.07	5.05	5.055	0.007	0.140	0.198
NWNJ	Styrene	0.52	0.48	0.44	0.480	0.057	11.785	16.667
NWNJ	o-Xylene/1, 1, 2, 2-Tetrachloroethane	2.29	2.22	2.30	2.295	0.007	0.308	0.443
PLNJ	Acetylene	65.45	69.37	<0.01	65.450			
PLNJ	1, 3-Butadiene	<0.01	0.69	0.54	0.540			
PLNJ	Methylene chloride	<0.01	1.47	<0.01				
PLNJ	Chloroprene	2.08	<0.01	<0.01	2.080			
PLNJ	1, 1, 1-Trichloroethane	1.81	10.83	1.86	1.835	0.035	1.927	0.790
PLNJ	Benzene	0.85	0.76	0.81	0.830	0.028	3.408	5.031
PLNJ	Carbon tetrachloride	0.28	0.24	0.26	0.270	0.014	5.238	7.843
PLNJ	Trichloroethylene	<0.01	0.04	0.05	0.050			
PLNJ	Toluene	5.18	3.58	5.12	5.150	0.042	0.824	1.375
PLNJ	n-Octane	0.27	<0.01	0.28	0.275	0.007	2.571	7.273
PLNJ	Tetrachloroethylene	0.38	0.42	0.36	0.370	0.014	3.822	5.063
PLNJ	Ethylbenzene	0.46	0.42	0.46	0.460	0.000	0.000	0.000
PLNJ	m/p-Xylene/Bromoform	2.20	1.90	2.10	2.150	0.071	3.289	4.938
PLNJ	Styrene	0.35	0.44	0.37	0.360	0.014	3.928	5.000
PLNJ	o-Xylene/1, 1, 2, 2-Tetrachloroethane	1.15	0.95	1.20	1.175	0.035	3.009	4.706

Replicates: Average = 8.788
 Median = 1.015
 Cases = 27
 Pooled Standard Deviation = 1.860
 Pooled % CV = 21.162
 Average absolute % Diff = 9.837

Table 8-3.

Continued

Site	Compound	D1	D2	R1	Duplicate Samples			
					XBAR	s	% CV	Abs % D
NWNJ	Acetylene	137.82	116.85	124.27	123.948	5.019	4.049	5.567
NWNJ	1, 3-Butadiene	3.90	3.19	2.28	3.140	0.035	1.126	1.605
NWNJ	Methylene chloride	<0.01	4.38	<0.01				
NWNJ	1, 1, 1-Trichloroethane	1.59	1.62	0.98	1.453	0.118	8.154	12.237
NWNJ	Benzene	2.33	2.28	2.67	2.390	0.078	3.254	4.499
NWNJ	Carbon tetrachloride	0.27	0.28	0.24	0.268	0.009	3.304	4.785
NWNJ	Trichloroethylene	1.14	1.15	1.10	1.135	0.011	0.935	1.330
NWNJ	Toluene	7.54	7.53	7.44	7.510	0.014	0.188	0.267
NWNJ	n-Octane	0.38	0.38	<0.01	0.380	0.000	0.000	0.000
NWNJ	Tetrachloroethylene	0.30	0.30	0.25	0.288	0.009	3.074	3.444
NWNJ	Ethylbenzene	1.04	1.03	0.99	1.023	0.005	0.519	0.736
NWNJ	m/p-Xylene/Bromoform	5.06	5.07	5.05	5.063	0.005	0.105	0.148
NWNJ	Styrene	0.52	0.48	0.44	0.480	0.000	0.000	0.000
NWNJ	o-Xylene/1, 1, 2, 2-Tetrachloroethane	2.29	2.22	2.30	2.258	0.027	1.175	1.647
PLNJ	Acetylene	65.45	69.37	<0.01	67.410	1.386	2.056	2.950
PLNJ	1, 3-Butadiene	<0.01	0.69	0.54	0.615	0.053	8.623	12.987
PLNJ	Methylene chloride	<0.01	1.47	<0.01				
PLNJ	Chloroprene	2.08	<0.01	<0.01				
PLNJ	1, 1, 1-Trichloroethane	1.81	10.83	1.86	6.333	3.180	50.220	110.132
PLNJ	Benzene	0.85	0.76	0.81	0.795	0.025	3.113	4.308
PLNJ	Carbon tetrachloride	0.28	0.24	0.26	0.255	0.011	4.159	5.714
PLNJ	Trichloroethylene	<0.01	0.04	0.05	0.045	0.004	7.857	10.526
PLNJ	Toluene	5.18	3.58	5.12	4.365	0.555	12.717	16.500
PLNJ	n-Octane	0.27	<0.01	0.28	0.138	0.097	70.711	66.667
PLNJ	Tetrachloroethylene	0.38	0.42	0.36	0.395	0.018	4.475	6.536
PLNJ	Ethylbenzene	0.46	0.42	0.46	0.440	0.014	3.214	4.444
PLNJ	m/p-Xylene/Bromoform	2.20	1.90	2.10	2.025	0.088	4.365	5.988
PLNJ	Styrene	0.35	0.44	0.37	0.400	0.028	7.071	10.526
PLNJ	o-Xylene/1, 1, 2, 2-Tetrachloroethane	1.15	0.95	1.20	1.063	0.080	7.487	10.056

Duplicates:	Average	=	8.985
	Median	=	1.043
	Cases	=	26
	Pooled Standard Deviation	=	1.202
	Pooled % CV	=	13.381
	Average absolute % Diff	=	11.715

Quality assurance and quality control in the 3-hour air toxics data included a determination of method detection limits (MDL) for both the GC/MD and the GC/MS analytical methods.

One of the objectives of the UATMP was to make the MDLs as low as possible, recognizing that the lower MDLs may increase the number of false positive or false negative identifications. Other quality measures reported here involved analytical precision results from repeated analyses, and sampling and analysis precision from duplicate samples. Accuracy was assessed for both the GC/MD and GC/MS using external audits supplied by the EPA-QAD.

8.7.1 GC/MD and GC/MS Instrument Detection Limits

MDLs for the GC/MD and GC/MS analytical systems used in this study are given in Table 8-4. MDLs for the GC/MD analytical system are estimated from the minimum area count that reflects approximately three times noise for every compound and are based on a sample approximately 250-mL in volume. The sample volume for the GC/MS system was about 500-mL. The GC/MS was operated in the MID mode, which detected specific ions representative of the 38 air toxics target compounds.

8.7.2 GC/MS Confirmation Results

Based on three GC/MS analyses of the 3-hour air toxics samples, one from each site location, the following results were obtained. The GC/MS analyses confirmed 80.00% of the GC/MD analyses. The results are summarized in Table 8-5, showing 20.00% positive GC/MD-positive GC/MS confirmation, 15.71% positive GC/MD-negative GC/MS confirmation, 4.29% negative GC/MD-positive GC/MS comparisons, and 60.00% negative GC/MD-negative GC/MS comparisons.

8.7.3 External Audits

The external audit for the 3-hour air toxics compounds is conducted bimonthly on the Urban Air Toxics Program and the results will be reported in the 1990 UATMP Final Report. The audit samples that are used are furnished by the Quality Assurance Division of the U.S. EPA.

Table 8-4

Instrument Detection Limits for 3-Hour Air Toxics Compounds

Compound	GC/MS ppbv	GC/MS ^a ppbv
Acetylene	1.00	
Propylene	0.10	0.95
Chloromethane	0.20	0.48
Vinyl chloride	0.20	0.38
1,3-Butadiene	0.10	0.20
Bromomethane	0.20	0.22
Chloroethane	0.10	0.56
Methylene chloride	0.11	0.23
trans-1,2-Dichloroethylene	0.04	0.66
1,1-Dichloroethane	0.04	0.26
Chloroprene	0.06	0.26
Bromochloromethane	0.003	0.23
Chloroform	0.006	0.81
1,1,1-Trichloroethane	0.001	0.72
Carbon tetrachloride	0.001	0.09
1,2-Dichloroethane	0.04	0.21
Benzene	0.04	0.12
Trichloroethylene	0.004	0.15
1,2-Dichloropropane	0.04	0.16
Bromodichloromethane	0.001	0.46
trans-1,3-Dichloropropylene	0.04	0.23
Toluene	0.02	0.52
n-Octane	0.03	1.00
cis-1,3-Dichloropropylene	0.04	0.14
1,1,2-Trichloroethane	0.04	0.96
Tetrachloroethylene	0.07	0.27
Dibromochloromethane	0.001	0.11
Chlorobenzene	0.02	0.22
Ethylbenzene	0.02	0.73
m/p-Xylene/Bromoform	0.04	-
o-Xylene/1,1,2,2-Tetrachloroethane	0.02	-
Styrene	0.02	0.46
m/p-Xylene	-	1.00
o-Xylene	-	0.71
Bromoform	-	0.10
1,1,2,2-Tetrachloroethane	-	0.22
m-Dichlorobenzene	0.02	0.27
p-Dichlorobenzene	0.09	0.11
o-Dichlorobenzene	0.02	0.38

^aGC/MS MDL determined in full scan mode.

^bBelow mass spectrometry range.

Table 8-5

Compound Identification Confirmation

GC/MD versus GC/MS Comparison	Cases	Percentage
Positive GC/MD - Positive GC/MS	14	20.00
Positive GC/MD - Negative GC/MS	11	15.71
Negative GC/MD - Positive GC/MS	3	4.29
Negative GC/MD - Negative GC/MS	42	60.00
Total	70	100.00
Total compound identification confirmation = 20.00% + 60.00% = 80.00%		

8.8 DATA RECORDS

Data records for the 3-hour air toxics samples include:

- NMOC concentration of the sample;
- Copies of the gas chromatographic trace for FID, PID, and ECD;
 - Response data on Bernoulli disk;
 - Retention time for each compound; and
 - Area counts for each detector.

In addition, daily calibration response factors are recorded on magnetic disk along with the retention time and area counts for each compound in the standard.

9.0 RECOMMENDATIONS, THREE-HOUR AIR TOXICS PROGRAM

The following recommendations derive from the 3-hour Air Toxics Monitoring Program. The studies (Sections 9.1 and 9.2) are directed toward areas in which additional information is needed to validate further the air toxics results.

9.1 COMPOUND STABILITY STUDIES

Compound stability in this context refers to whether the apparent concentration of a compound in a sample taken from a canister is changing over time. The apparent change in concentration may result from a chemical reaction of the compound while it is in the canister, or result from a change in the gas phase concentration caused by adsorption of the compound on the interior canister surfaces.

A study needed to investigate this phenomenon would take several canisters--at least three from each initial concentration--ranging in target compound concentration from zero to 20 ppbv. The canisters would be analyzed 24 hours after mixing, 72 hours after mixing, 30 days after mixing, and 60 days after mixing to determine any concentration changes. It is also recommended that the same concentrations be mixed in canisters, but that equilibration times of 7 days and 30 days be assigned before the first samples are drawn from the canisters to determine the effect of equilibration time on the concentration samples withdrawn from the canisters.

9.2 CANISTER CLEANUP STUDIES

The present canister cleanup procedure has not been studied in sufficient detail to determine the amount of carryover for each of the air toxics compounds. Experience has shown that the present cleanup procedure is satisfactory so long as a period less than a week elapses between sampling and analysis.

A study needs to be conducted to determine the effects of:

- Additional pressurization/vacuum cycles on cleanup;
- Heating the canisters during cleanup;
- Vacuum holding time during cleanup; and
- Holding time between cleanup and sampling

on the carryover for each air toxics target compound.

The present canister cleanup procedure is described in Section 3.3.2 and consists of three vacuum/pressurization cycles with cleaned, dried air that has been humidified. These cycles are followed by a final vacuum step to 5 mm Hg vacuum. Preliminary measurements¹¹ have indicated that after this cleaning procedure has been completed, there may be sufficient organic compounds still adsorbed on the canister interior surfaces to be desorbed and measured in the 0.05 to 0.50 ppbv range, especially for holding times of 7 days, 14 days, and 28 days.

9.3 THREE-HOUR TOXICS SAMPLING SYSTEMS

Recommendation modifications to the sampling equipment are referred to in Section 6 for the NMOC sampler, which also takes 3-hour air samples.

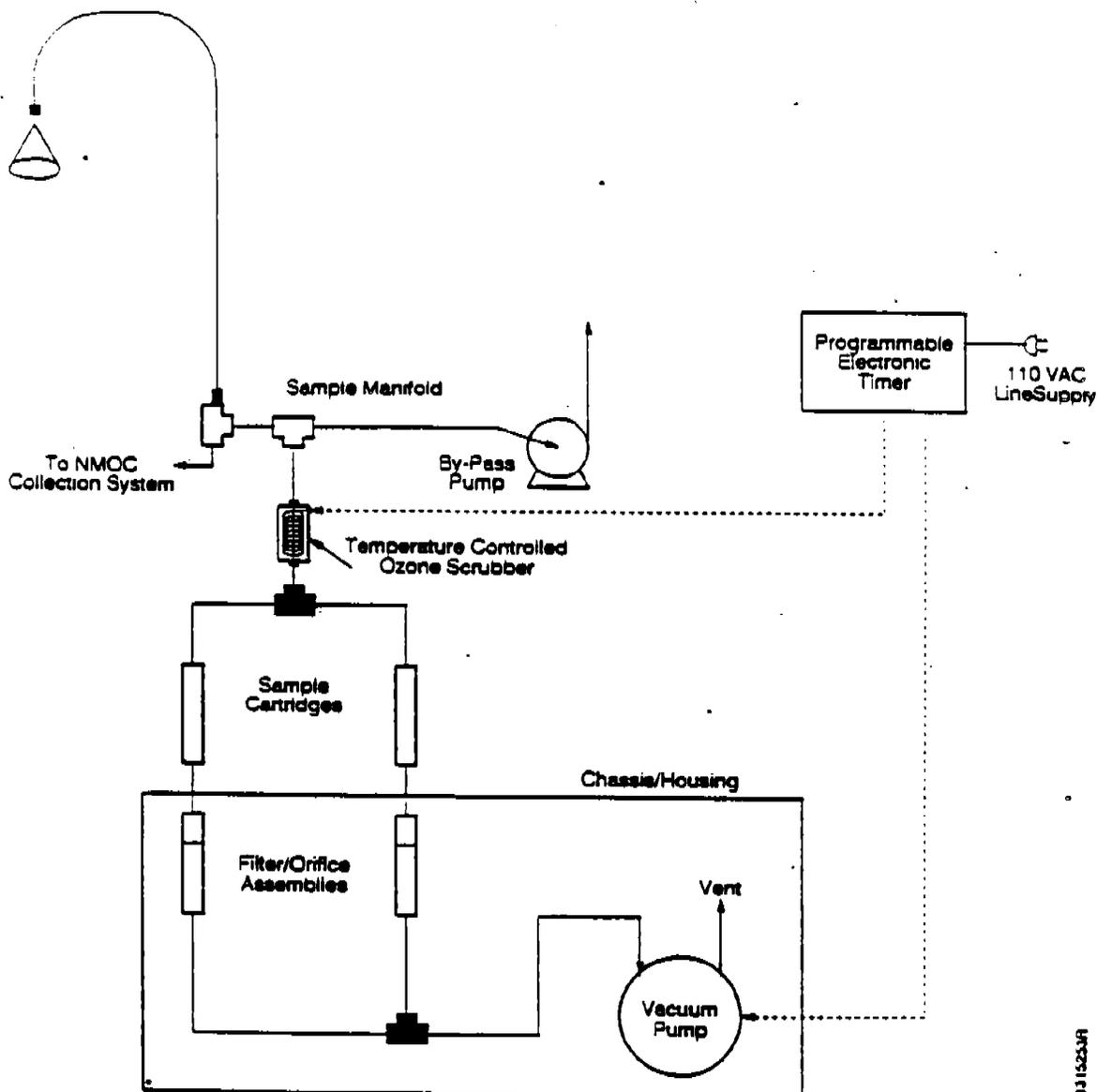
10.0 CARBONYL SAMPLING, ANALYSIS, AND QUALITY ASSURANCE PROCEDURES

Sampling and analysis procedures for the carbonyl samples, along with the quality assurance procedures used to quantify data quality are described in this section. The site operator's task involved sample collection, recognizing problems with sampling equipment and procedures, and notifying Radian personnel at Research Triangle Park so that appropriate corrective action might be taken.

10.1 SAMPLING EQUIPMENT AND PROCEDURES

A schematic diagram of a typical carbonyl sampler is shown in Figure 10-1. The 3-hour carbonyl sample subsystem collected a discrete sample using the control system of the NMOC canister system. Ambient air was drawn through the carbonyl collection cartridges from a glass manifold. The ambient air was then passed through a short section of chromatographic-grade stainless steel tubing into an ozone scrubber column or denuder, before entering the carbonyl collection cartridges. The ozone scrubber consisted of a 36-inch length of 1/4-inch o.d. copper tubing that had been exposed internally to a saturated solution of potassium iodide (KI). The copper tube was coiled to a diameter of approximately two inches. The entrance and exit of the coil was outfitted with a 1/4-inch brass bulkhead union and housed in an aluminum chassis box. A Glas-Col® cord heater, rated at 80 watts, was wrapped around the outside spiral of the copper coil. All space remaining inside the aluminum chassis was packed with fiber glass insulation. The ozone scrubber was actively controlled to about 66°C during sample collection. The carbonyl collection cartridges were mounted in parallel, so that the carbonyl samples were collected in duplicate during each sample collection episode. The carbonyl cartridges used, commercially available (Waters Co.) silica gel Sep-Pak® cartridges, were coated with 2,4-dinitrophenol hydrazine (DNPH). The cartridges were prepared in batches by the Radian PPK laboratory and stored under refrigeration until shipped to the field.

The carbonyl collection cartridges were installed in the sample line one day prior to scheduled sample collection. A 3-hour sample collection period, 6:00 a.m. to 9:00 a.m., was utilized for both the canister and cartridge samples. In addition to the carbonyl collection cartridges



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Figure 10-1. 3-Hour Carbonyl Sampling Subsystem

installed in the sample line, a third cartridge was sent to the field as a trip blank or spare cartridge.

The flow rate through each sample cartridge was measured before and after each collection period by the site operator. The flow rate was measured with a calibrated rotameter and recorded on a preformatted data sheet. The volume of ambient air sampled through each cartridge was calculated in the laboratory based on the field-recorded flow rate measurements.

10.2 ANALYTICAL PROCEDURES

Sample preparation and analysis was performed at the Radian PPK laboratory. Carbonyl compounds analytical preparation procedures are as follows:

1. Remove the carbonyl cartridge from its shipping vial.
2. Attach the carbonyl cartridges to the end of a 10-mL polypropylene syringe.
3. Add four (4) milliliters of acetonitrile to the syringe and catch the drainage in a graduated centrifuge tube.
4. After the syringe has finished draining, add acetonitrile to the graduated centrifuge tube until the total volume is four (4) milliliters, and mix the solution.
5. Transfer the solution in the graduated centrifuge tube to a 4-mL sample vial fitted with a Teflon®-line self-sealing septum.
6. Store the solution in a refrigerator until analysis.

T0-11 high pressure liquid chromatography (HPLC) column and elution solvents used for analysis were modified to decrease analysis time, as shown in the following gradient elution:

<u>Time (Min.)</u>	<u>% Water</u>	<u>% Acetonitrile</u>	<u>% Methanol</u>
0	40	20	40
25	25	5	70
40	15	5	80
48	15	5	80
53	40	20	40
63	40	20	40

Detector signals from a multiwavelength detector were collected for 60 minutes at 360 nanometers (nm).

The separation is done using a 25 cm x 4.6 mm C18 analytical column with a 5-micron particle size. Typically 25-microliter samples are injected with an automatic sample injector. The preceding gradient elution is carried out at a flow rate of 0.8 mL/min.

The relevant chromatographic peaks determined by acceptable retention times, were integrated and the concentrations calculated using response factors obtained from multipoint calibration curves. An average sample volume of 140-L was used to calculate the detection limits.

Carbonyl compounds reported are as follows:

- Formaldehyde;
- Acetaldehyde;
- Acrolein;
- Propionaldehyde;
- Crotonaldehyde;
- Butyraldehyde;
- Isobutyraldehyde;
- Benzaldehyde;
- Isovaleraldehyde;
- Valeraldehyde;
- Tolualdehyde;
- Hexanaldehyde;
- Dimethylbenzaldehyde; and
- Acetone.

All sample results were reported in parts per billion by volume (ppbv). The field blank results were also reported in ppbv, assuming an average 140-L sample volume. All Radian reported analyses were identified by a unique tube number which was recorded on the preformatted field data sheets.

10.3 QUALITY ASSURANCE PROCEDURES

Quality assurance procedures relative to calibration data for all of the analytes are discussed below. Daily quality control procedures are also discussed. Sampling and analysis precision was determined from the analysis of duplicate field samples and replicate laboratory analyses. Sample custody records were maintained throughout the program. Figure 10-2 shows the multipage field data and custody sheet used for the carbonyl cartridges.

10.4 CALIBRATION PROCEDURES

The calibration procedures used for this study followed Radian standard operating procedures.

10.4.1 Daily Quality Control Procedures

Daily calibration checks were used to assure that the analytical procedures were in control. Approximately 40 tubes were analyzed for carbonyl compounds. Daily QC checks were performed after every seven samples on each day that samples were analyzed.

10.4.2 Duplicate Samples

Duplicate field cartridges were installed in parallel in the sample probe for each sampling episode, as shown in Figure 10-1. One set of field duplicates from each site was prepared and analyzed in replicate to determine both the sampling precision and the analytical accuracy.

10.4.3 Trip Blanks

For each pair of carbonyl compounds samples, a trip-blank cartridge was included in the field site shipment. The trip blank consisted of an unused DNPH-cartridge with caps, identical with the sample cartridges. Each cartridge had a unique serial number for identification purposes. The trip blank cartridge accompanied the duplicate sample cartridges on the trip to and from the site, and was not exposed to air at any time during the shipment or sampling periods. One trip-blank cartridge from each site was analyzed for carbonyl compounds at the same time the sample cartridges for that site were analyzed. The purpose of the trip blank was to assess the potential for field trip contamination. Because no contamination was found, the field sample results were not blank corrected.



NMOC MONITORING PROGRAM
Aldehyde Data Sheet

City _____ Sample Date _____

SAROAD No. _____ A05 Sampler No. _____

Cartridge Port A (red) Port B (green) (blank)

Tube No. _____

Lot No. _____

Rotameter No. _____

	Port A	Port B	
Rotameter Reading ¹			(before)
Rotameter Reading ¹			(after)
Sampling Volume ³			(liters)

	LPM	
	Port A	Port B
Flow Rate ²		
Before		
After		
Average		

Sampling Time/Duration _____ (hours) _____ (min)

Average Ambient Temperature _____ (C° or F°)

Average Barometric Pressure _____ (mm Hg)

Site Operator _____

Comments/Remarks _____

¹ Rotameter reading center of black ball.
² Calculated from calibration curve by the laboratory.
³ Calculated by laboratory.

Sample Control Copy

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Figure 10-2. Field Data and Custody Form

10.4.4 Detection Limits

Detection limits are given in Table 10-1 for the target carbonyl compounds of this study. The detection limits were determined by performing seven replicate analyses of the lowest calibration standard and following the method listed in the Federal Register, CFR Title 40, Part 136.1.

10.5 RESULTS

The analytical results for the sample analyses, replicate analyses, duplicate analyses and quality control standards are discussed below.

10.5.1 Sample Results

Analytical results of ambient air samples and trip blanks for carbonyl compounds at Long Island, NY, (LINY); Manhattan, NY, (MNY); Plainfield, NJ, (PLNJ); and Newark, NJ, (NWNJ) are given in Tables 10-2 through 10-5. The tables give the sampling date, the Radian sample ID, the sample volume in liters and the carbonyl concentrations in ppbv. The quality control standards analyzed during the program indicate that the analyses remained in control throughout the program. The concentrations of carbonyl compounds in the trip-blanks are calculated assuming the same 140-L sample volume as regular samples. Each of the trip blanks contained low concentrations of formaldehyde ranging from 0.8 to 2.2 ppbv, acetaldehyde ranging from 0.6 to 3.2 ppbv, and acetone ranging from 0.3 to 3.3 ppbv. Table 10-6 presents the dates of sampling, extraction and analysis for the samples as well as the laboratory data file name used in tracking of the samples. Table 10-7 gives the average carbonyl concentrations for each of the four sites.

10.5.2 Precision

Precision was measured as the average standard deviation of the paired duplicate samples. The results for the duplicate analyses are given in Table 10-8. The duplicate analyses were performed on 10% of the samples from each site. Sampling error for all duplicate pairs ranged from -17.4% to 136.6%, averaging 40.5% overall, with a standard deviation of the percent differences equal to 0.64 ppbv as listed in Table 10-10.

10.5.3 Accuracy

Accuracy was measured as the average standard deviation of the replicate analyses performed on the paired duplicate samples. The results for the replicate analyses are given in Table 10-9. The replicate analyses were

Table 10-1
Aldehyde Detection Limits

Analyte	Detection Limit (ppbv) (B)
Formaldehyde	0.16
Acetaldehyde	0.27
Acrolein	0.12
Acetone	0.30
Propionaldehyde	0.34
Crotonaldehyde	0.26
Butyr/Isobutyraldehyde	0.18
Benzaldehyde	0.13
Isovaleraldehyde	0.21
Valeraldehyde	0.21
Tolualdehydes	0.12
Hexanaldehyde	0.42
2,5-Dimethylbenzaldehyde	0.40

B - Detection limit is based upon an average 140 L sample

Table 10-2

Carbonyl Results for Long Island, New York (LINY)

Sampling Date	08/05/91	08/16/91	08/16/91
Sample ID	LINY-LOT-25 G 40	LINY-LOT-25 R 53	LINY-LOT-25 R 53 REP
Sample Volume (L)	126.8	119.9	119.9
Concentrations (ppbv)			
Formaldehyde	5.6	ND	ND
Acetaldehyde	ND	ND	ND
Acrolein	ND	ND	ND
Acetone	ND	ND	ND
Propionaldehyde	ND	0.3 @	0.4
Crotonaldehyde	ND	ND	ND
Butyr/Isobutyraldehyde	1.4	ND	ND
Benzaldehyde	ND	ND	ND
Isovaleraldehyde	ND	ND	ND
Valeraldehyde	ND	ND	ND
Tolualdehydes	ND	ND	ND
Hexanaldehyde	ND	ND	ND
2,5-Dimethylbenzaldehyde	ND	ND	ND

Sampling Date	08/13/91	08/16/91	08/16/91
Sample ID	LINY LOT-25 R 54	LINY LOT-25 G 60	LINY LOT-25 G 60 REP
Sample Volume (L)	121.8	135.6	135.6
Concentrations (ppbv)			
Formaldehyde	5.6	5.7	5.5
Acetaldehyde	1.1	0.8	0.8
Acrolein	ND	0.4	0.2
Acetone	ND	ND	ND
Propionaldehyde	0.3 @	ND	ND
Crotonaldehyde	ND	ND	ND
Butyr/Isobutyraldehyde	ND	ND	ND
Benzaldehyde	ND	ND	ND
Isovaleraldehyde	ND	ND	ND
Valeraldehyde	ND	ND	ND
Tolualdehydes	ND	ND	ND
Hexanaldehyde	ND	ND	ND
2,5-Dimethylbenzaldehyde	ND	ND	8.0

Table 10-2

Continued

Sampling Date	08/08/91	09/06/91	NA
Sample ID	LINY LOT-25 G 72	LINY LOT-25 R 106	LINY LOT-25 112 BLANK
Sample Volume (L)	124.8	125.8	140.0 C
Concentrations (ppbv)			
Formaldehyde	5.0	ND	0.8
Acetaldehyde	1.2	ND	0.6
Acrolein	ND	ND	ND
Acetone	ND	ND	0.3
Propionaldehyde	ND	ND	ND
Crotonaldehyde	ND	ND	ND
Butyr/Isobutyraldehyde	ND	ND	ND
Benzaldehyde	ND	ND	ND
Isovaleraldehyde	ND	ND	ND
Valeraldehyde	ND	ND	ND
Tolualdehydes	ND	ND	ND
Hexanaldehyde	ND	ND	ND
2,5-Dimethylbenzaldehyde	ND	ND	ND

Sampling Date	09/02/91	09/11/91	08/29/91
Sample ID	LINY LOT-27 R 24	LINY LOT-27 G 26	LINY LOT-27 R 40
Sample Volume (L)	123.8	138.6	127.7
Concentrations (ppbv)			
Formaldehyde	7.7	6.6	6.3
Acetaldehyde	6.9	3.9	1.2
Acrolein	ND	ND	ND
Acetone	18.0	0.5	ND
Propionaldehyde	ND	ND	0.4
Crotonaldehyde	ND	0.5	ND
Butyr/Isobutyraldehyde	ND	1.4	1.4
Benzaldehyde	ND	ND	ND
Isovaleraldehyde	ND	ND	ND
Valeraldehyde	ND	ND	ND
Tolualdehydes	ND	ND	ND
Hexanaldehyde	ND	ND	ND
2,5-Dimethylbenzaldehyde	ND	ND	ND

Table 10-2

Continued

Sampling Date	08/21/91	08/26/91
Sample ID	LINY LOT-27 R 43	LINY LOT-27 G 61
Sample Volume (L)	124.8	136.6
Concentrations (ppbv)		
Formaldehyde	3.9	15.2
Acetaldehyde	2.7	2.8
Acrolein	ND	ND
Acetone	2.0	ND
Propionaldehyde	ND	0.5
Crotonaldehyde	ND	ND
Butyr/Isobutyraldehyde	ND	ND
Benzaldehyde	ND	ND
Isovaleraldehyde	ND	ND
Valeraldehyde	ND	ND
Tolualdehydes	ND	ND
Hexanaldehyde	ND	ND
2,5-Dimethylbenzaldehyde	ND	ND

ND - Not detected in sample

@ - Estimated value is below detection limit

C - Blank concentrations are based on average 140 L sample volume

Table 10-3

Carbonyl Results for Manhattan, New York (MNY)

Sampling Date	08/13/91	NA	08/16/91
Sample ID	MNY LOT-25 G 45	MNY LOT-25 R 49	MNY LOT-25 R 63
Sample Volume (L)	180.8	184.7	172.9
Concentrations (ppbv)			
Formaldehyde	4.5	4.8	7.2
Acetaldehyde	1.2	2.9	4.3
Acrolein	ND	ND	ND
Acetone	ND	3.2	0.9
Propionaldehyde	0.2 @	ND	1.0
Crotonaldehyde	ND	ND	ND
Butyr/Isobutyraldehyde	ND	ND	ND
Benzaldehyde	ND	ND	ND
Isovaleraldehyde	ND	ND	ND
Valeraldehyde	ND	ND	ND
Tolualdehydes	ND	ND	ND
Hexanaldehyde	ND	ND	ND
2,5-Dimethylbenzaldehyde	ND	ND	ND

Sampling Date	08/16/91	08/08/91	08/16/91
Sample ID	MNY LOT-25 R 63 REP	MNY LOT-25 R 69	MNY LOT-25 G 81
Sample Volume (L)	172.9	180.8	180.8
Concentrations (ppbv)			
Formaldehyde	7.3	8.0	6.2
Acetaldehyde	4.4	4.5	6.1
Acrolein	ND	ND	ND
Acetone	0.8	5.2	4.6
Propionaldehyde	0.7	ND	1.1
Crotonaldehyde	ND	ND	ND
Butyr/Isobutyraldehyde	ND	ND	ND
Benzaldehyde	ND	ND	ND
Isovaleraldehyde	ND	ND	ND
Valeraldehyde	ND	ND	ND
Tolualdehydes	ND	ND	ND
Hexanaldehyde	ND	ND	ND
2,5-Dimethylbenzaldehyde	ND	ND	ND

Table 10-3

Continued

Sampling Date	08/16/91	NA	09/06/91
Sample ID	MNY LOT-25 G 81 REP	MNY LOT-25 105 BLANK	MNY LOT-25 R 108
Sample Volume (L)	180.8	140.0 C	176.9
Concentrations (ppbv)			
Formaldehyde	6.3	2.1	1.9
Acetaldehyde	6.5	1.8	ND
Acrolein	ND	ND	ND
Acetone	4.8	0.7	ND
Propionaldehyde	1.8	0.4	ND
Crotonaldehyde	ND	ND	ND
Butyr/Isobutyraldehyde	ND	ND	ND
Benzaldehyde	ND	ND	ND
Isovaleraldehyde	ND	ND*	ND
Valeraldehyde	ND	ND	ND
Tolualdehydes	ND	ND	ND
Hexanaldehyde	ND	ND	ND
2,5-Dimethylbenzaldehyde	ND	ND	ND

Sampling Date	08/29/91	09/20/91	08/22/91
Sample ID	MNY LOT-27 R 3	MNY LOT-27 G 18	MNY LOT-27 G 31
Sample Volume (L)	174.9	180.8	174.9
Concentrations (ppbv)			
Formaldehyde	7.2	2.9	5.0
Acetaldehyde	2.4	1.2	2.9
Acrolein	ND	ND	ND
Acetone	ND	ND	4.9
Propionaldehyde	0.4	0.3 @	ND
Crotonaldehyde	ND	ND	ND
Butyr/Isobutyraldehyde	ND	ND	ND
Benzaldehyde	ND	ND	ND
Isovaleraldehyde	ND	ND	ND
Valeraldehyde	ND	ND	ND
Tolualdehydes	ND	ND	ND
Hexanaldehyde	ND	ND	ND
2,5-Dimethylbenzaldehyde	ND	ND	ND

Table 10-3

Continued

Sampling Date	09/03/91	08/27/91
Sample ID	MNY LOT-27 G 52	MNY LOT-27 R 55
Sample Volume (L)	176.9	180.8
Concentrations (ppbv)		
Formaldehyde	7.5	4.1
Acetaldehyde	2.8	2.4
Acrolein	ND	ND
Acetone	6.6	ND
Propionaldehyde	ND	ND
Crotonaldehyde	ND	ND
Butyr/Isobutyraldehyde	ND	ND
Benzaldehyde	ND	ND
Isovaleraldehyde	ND	ND
Valeraldehyde	ND	ND
Tolualdehydes	ND	ND
Hexanaldehyde	ND	ND
2,5-Dimethylbenzaldehyde	ND	ND

ND - Not detected in sample

@ - Estimated value is below detection limit

C - Blank concentrations are based on average 140 L sample volume

Table 10-4

Carbonyl Results for Plainfield, New Jersey (PLNJ)

Sampling Date	07/02/91	07/10/91	08/05/91
Sample ID	PLNJ LOT-1 G 15	PLNJ LOT-1 R 20	PLNJ LOT-22 R 622
Sample Volume (L)	128.7	143.5	107.1
Concentrations (ppbv)			
Formaldehyde	7.1	12.1	7.1
Acetaldehyde	4.5	7.4	2.6
Acrolein	ND	ND	ND
Acetone	12.0	9.9	3.1
Propionaldehyde	0.9	0.7	3.3
Crotonaldehyde	ND	ND	ND
Butyr/Isobutyraldehyde	1.7	2.1	1.5
Benzaldehyde	ND	ND	ND
Isovaleraldehyde	ND	ND	ND
Valeraldehyde	ND	ND	ND
Tolualdehydes	ND	ND	ND
Hexanaldehyde	ND	ND	ND
2,5-Dimethylbenzaldehyde	ND	ND	ND

Sampling Date	NA	08/29/91	08/29/91
Sample ID	PLNJ LOT-25 BLANK 66	PLNJ LOT-25 R 70	PLNJ LOT-25 R 70 REP
Sample Volume (L)	140.0 C	131.7	131.7
Concentrations (ppbv)			
Formaldehyde	1.7	1.3	1.3
Acetaldehyde	3.2	ND	ND
Acrolein	ND	ND	ND
Acetone	1.7	ND	ND
Propionaldehyde	ND	0.3 @	0.3 @
Crotonaldehyde	ND	ND	ND
Butyr/Isobutyraldehyde	ND	ND	ND
Benzaldehyde	ND	ND	ND
Isovaleraldehyde	ND	ND	ND
Valeraldehyde	ND	ND	ND
Tolualdehydes	ND	ND	ND
Hexanaldehyde	ND	ND	ND
2,5-Dimethylbenzaldehyde	ND	ND	ND

Table 10-4

Continued

Sampling Date	08/29/91	08/29/91	08/13/91
Sample ID	PLNJ LOT-25 G 109	PLNJ LOT-25 G 109 REP	PLNJ LOT-25 G 41 RUN #2
Sample Volume (L)	121.8	121.8	132.7
Concentrations (ppbv)			
Formaldehyde	3.3	3.0	4.0
Acetaldehyde	1.7	1.6	4.6
Acrolein	ND	ND	ND
Acetone	ND	ND	2.9
Propionaldehyde	0.4	0.3 @	ND
Crotonaldehyde	ND	ND	ND
Butyr/Isobutyraldehyde	ND	ND	ND
Benzaldehyde	ND	ND	ND
Isovaleraldehyde	ND	ND	ND
Valeraldehyde	ND	ND	ND
Tolualdehydes	ND	ND	ND
Hexanaldehyde	ND	ND	ND
2,5-Dimethylbenzaldehyde	ND	ND	ND

Sampling Date	NA	NA	08/21/91
Sample ID	PLNJ LOT-27 R 19 RUN #2	PLNJ LOT-27 G 27 RUN #2	PLNJ LOT-27 R 42 RUN #2
Sample Volume (L)	128.9 A	128.9 A	141.5
Concentrations (ppbv)			
Formaldehyde	0.8	0.9	3.3
Acetaldehyde	1.0	0.6	2.4
Acrolein	ND	ND	ND
Acetone	1.8	2.0	6.0
Propionaldehyde	ND	ND	ND
Crotonaldehyde	ND	ND	ND
Butyr/Isobutyraldehyde	ND	ND	ND
Benzaldehyde	ND	ND	ND
Isovaleraldehyde	ND	ND	ND
Valeraldehyde	ND	ND	ND
Tolualdehydes	ND	ND	ND
Hexanaldehyde	ND	ND	ND
2,5-Dimethylbenzaldehyde	ND	ND	ND

Table 10-4

Continued

Sampling Date	NA
Sample ID	PLNJ LOT-27 G 60 RUN #2
Sample Volume (L)	128.9 A
Concentrations (ppbv)	
Formaldehyde	1.0
Acetaldehyde	ND
Acrolein	ND
Acetone	ND
Propionaldehyde	ND
Crotonaldehyde	ND
Butyr/Isobutyraldehyde	ND
Benzaldehyde	ND
Isovaleraldehyde	ND
Valeraldehyde	ND
Tolualdehydes	ND
Hexanaldehyde	ND
2,5-Dimethylbenzaldehyde	ND

ND - Not detected in sample

@ - Estimated value is below detection limit

A - Estimated values due to lack of sufficient information on Chain of Custody

C - Blank concentrations are based on average 140 L sample volume

Table 10-5
 Carbonyl Results for Newark, New Jersey (NWNJ)

Sampling Date	NA	07/02/91	07/02/91
Sample ID	NWNJ LOT-1 BLANK 8 RUN #2	NWNJ LOT-1 G 16 RUN #3	NWNJ LOT-1 G 16 REP RUN #3
Sample Volume (L)	140.0 C	148.4	148.4
Concentrations (ppbv)			
Formaldehyde	2.2	2.2	2.4
Acetaldehyde	0.9	2.7	2.7
Acrolein	ND	ND	ND
Acetone	3.3	ND	ND
Propionaldehyde	ND	ND	ND
Crotonaldehyde	ND	ND	ND
Butyr/Isobutyraldehyde	ND	ND	ND
Benzaldehyde	ND	ND	ND
Isovaleraldehyde	ND	ND	ND
Valeraldehyde	ND	ND	ND
Tolualdehydes	ND	ND	ND
Hexanaldehyde	ND	ND	ND
2,5-Dimethylbenzaldehyde	ND	ND	ND

Sampling Date	07/02/91	07/02/91	07/18/91
Sample ID	NWNJ LOT-1 R 23 RUN #2	NWNJ LOT-1 R 23 REP RUN #2	NWNJ LOT-1 G 19 RUN #2
Sample Volume (L)	148.4	148.4	147.4
Concentrations (ppbv)			
Formaldehyde	3.5	4.4	6.8
Acetaldehyde	1.8	2.7	ND
Acrolein	ND	ND	ND
Acetone	ND	ND	ND
Propionaldehyde	ND	ND	ND
Crotonaldehyde	ND	ND	ND
Butyr/Isobutyraldehyde	ND	ND	ND
Benzaldehyde	ND	ND	ND
Isovaleraldehyde	ND	ND	ND
Valeraldehyde	ND	ND	ND
Tolualdehydes	ND	ND	ND
Hexanaldehyde	ND	ND	ND
2,5-Dimethylbenzaldehyde	ND	ND	ND

Table 10-5

Continued

Sampling Date	07/10/91	06/25/91	07/29/91
Sample ID	NWNJ LOT-1 G 21 RUN #2	NWNJ LOT-1 R 30 RUN #2	NWNJ LOT-16 R 339 RUN #2
Sample Volume (L)	149.4	143.5	144.4
Concentrations (ppbv)			
Formaldehyde	6.5	6.8	4.8
Acetaldehyde	7.8	0.9	0.9
Acrolein	ND	ND	ND
Acetone	20.7	ND	ND
Propionaldehyde	1.3	ND	ND
Crotonaldehyde	ND	ND	ND
Butyr/Isobutyraldehyde	ND	ND	ND
Benzaldehyde	ND	ND	ND
Isovaleraldehyde	ND	ND	ND
Valeraldehyde	ND	ND	ND
Tolualdehydes	ND	ND	ND
Hexanaldehyde	ND	ND	ND
2,5-Dimethylbenzaldehyde	ND	ND	ND

Sampling Date	08/13/91	09/06/91	08/05/91
Sample ID	NWNJ LOT-25 R 64 RUN #2	NWNJ LOT-25 G 78 RUN #2	NWNJ LOT-25 G 96 RUN #2
Sample Volume (L)	145.4	147.4	139.5
Concentrations (ppbv)			
Formaldehyde	7.7	ND	2.5
Acetaldehyde	4.3	ND	ND
Acrolein	ND	ND	ND
Acetone	ND	ND	ND
Propionaldehyde	0.6	ND	ND
Crotonaldehyde	ND	ND	ND
Butyr/Isobutyraldehyde	ND	ND	ND
Benzaldehyde	ND	ND	ND
Isovaleraldehyde	ND	ND	ND
Valeraldehyde	ND	ND	ND
Tolualdehydes	ND	ND	ND
Hexanaldehyde	ND	ND	ND
2,5-Dimethylbenzaldehyde	ND	ND	ND

Table 10-5

Continued

Sampling Date	08/23/91	08/29/91
Sample ID	NWNJ LOT-25 R 16 RUN #2	NWNJ LOT-25 G 31 RUN #2
Sample Volume (L)	143.5	143.5
Concentrations (ppbv)		
Formaldehyde	4.1	6.1
Acetaldehyde	0.8	0.7
Acrolein	ND	ND
Acetone	ND	ND
Propionaldehyde	ND	ND
Crotonaldehyde	ND	ND
Butyr/Isobutyraldehyde	ND	ND
Benzaldehyde	ND	ND
Isovaleraldehyde	ND	ND
Valeraldehyde	ND	ND
Tolualdehydes	ND	ND
Hexanaldehyde	ND	ND
2,5-Dimethylbenzaldehyde	ND	ND

ND - Not detected in sample

@ - Estimated value is below detection limit

C - Blank concentrations are based on average 140 L sample volume

Table 10-6

Sampling Information Table

Long Island, New York (LINY)

Sample ID	Data File ID	Date Sampled	Date Extracted	Date Analyzed
LINY-LOT-25 G 40	RC127916	08/05/91	10/05/91	10/05/91
LINY-LOT-25 R 53	RC127917	08/16/91	10/05/91	10/05/91
LINY-LOT-25 R 53 REP	RC127918	08/16/91	10/05/91	10/05/91
LINY LOT-25 R 54	RC127919	08/13/91	10/05/91	10/05/91
LINY LOT-25 G 60	RC127920	08/16/91	10/05/91	10/05/91
LINY LOT-25 G 60 REP	RC127921	08/16/91	10/05/91	10/05/91
LINY LOT-25 G 72	RC127923	08/08/91	10/05/91	10/05/91
LINY LOT-25 R 106	RC127925	09/06/91	10/05/91	10/05/91
LINY LOT-25 112 BLANK	RC127926	NA	10/05/91	10/05/91
LINY LOT-27 R 24	RC127927	09/02/91	10/05/91	10/05/91
LINY LOT-27 G 26	RC127928	09/11/91	10/05/91	10/05/91
LINY LOT-27 R 40	RC127929	08/29/91	10/05/91	10/05/91
LINY LOT-27 R 43	RC127930	08/21/91	10/05/91	10/05/91
LINY LOT-27 G 61	RC127931	08/26/91	10/05/91	10/05/91

Manhattan, New York (MNY)

Sample ID	Data File ID	Date Sampled	Date Extracted	Date Analyzed
MNY LOT-25 G 45	RC127934	08/13/91	10/05/91	10/05/91
MNY LOT-25 R 49	RC127935	NA	10/05/91	10/05/91
MNY LOT-25 R 63	RC127936	08/16/91	10/05/91	10/05/91
MNY LOT-25 R 63 REP	RC127937	08/16/91	10/05/91	10/05/91
MNY LOT-25 R 69	RC127938	08/08/91	10/05/91	10/05/91
MNY LOT-25 G 81	RC127939	08/16/91	10/05/91	10/05/91
MNY LOT-25 G 81 REP	RC127940	08/16/91	10/05/91	10/05/91
MNY LOT-25 105 BLANK	RC127941	NA	10/05/91	10/05/91
MNY LOT-25 R 108	RC127942	09/06/91	10/05/91	10/05/91
MNY LOT-27 R 3	RC127945	08/29/91	10/05/91	10/05/91
MNY LOT-27 G 18	RC127946	09/20/91	10/05/91	10/05/91
MNY LOT-27 G 37	RC127947	08/22/91	10/05/91	10/05/91
MNY LOT-27 G 52	RC127948	09/03/91	10/05/91	10/05/91
MNY LOT-27 R 55	RC127949	08/27/91	10/05/91	10/05/91

Table 10-6

Continued

Plainfield, New Jersey (PLNJ)

Sample ID	Data File ID	Date Sampled	Date Extracted	Date Analyzed
PLNJ LOT-1 G 15	RC12844	07/02/91	10/07/91	10/11/91
PLNJ LOT-1 R 20	RC12845	07/10/91	10/07/91	10/11/91
PLNJ LOT-22 R 622	RC12846	08/05/91	10/07/91	10/11/91
PLNJ LOT-25 BLANK 66	RC12847	NA	10/07/91	10/11/91
PLNJ LOT-25 R 70	RC12848	08/29/91	10/07/91	10/11/91
PLNJ LOT-25 R 70 REP	RC12849	08/29/91	10/07/91	10/11/91
PLNJ LOT-25 G 109	RC128410	08/29/91	10/07/91	10/11/91
PLNJ LOT-25 G 109 REP	RC128411	08/29/91	10/07/91	10/11/91
PLNJ LOT-25 G 41 RUN #2	RC131112	08/13/91	10/07/91	10/11/91
PLNJ LOT-27 R 19 RUN #2	RC131113	NA	10/07/91	10/11/91
PLNJ LOT-27 G 27 RUN #2	RC131114	NA	10/07/91	10/11/91
PLNJ LOT-27 R 42 RUN #2	RC131115	08/21/91	10/07/91	10/11/91
PLNJ LOT-27 G 60 RUN #2	RC131116	NA	10/07/91	10/11/91

Newark, New Jersey (NWNJ)

Sample ID	Data File ID	Date Sampled	Date Extracted	Date Analyzed
NWNJ LOT-1 BLANK 8 RUN #2	RC131117	NA	10/07/91	10/11/91
NWNJ LOT-1 G 16 RUN #2	RC131119	07/02/91	10/07/91	10/11/91
NWNJ LOT-1 G 16 REP RUN #2	RC131120	07/02/91	10/07/91	10/11/91
NWNJ LOT-1 R 23 RUN #2	RC131121	07/02/91	10/07/91	10/11/91
NWNJ LOT-1 R 23 REP RUN #2	RC131122	07/02/91	10/07/91	10/11/91
NWNJ LOT-1 G 19 RUN #2	RC131123	07/18/91	10/07/91	10/11/91
NWNJ LOT-1 G 21 RUN #2	RC131124	07/10/91	10/07/91	10/11/91
NWNJ LOT-1 R 30 RUN #2	RC131125	06/25/91	10/07/91	10/11/91
NWNJ LOT-16 R 339 RUN #2	RC131126	07/29/91	10/07/91	10/11/91
NWNJ LOT-25 R 64 RUN #2	RC131128	08/13/91	10/07/91	10/11/91
NWNJ LOT-25 R 16 RUN #2	RC131131	08/23/91	10/07/91	10/11/91
NWNJ LOT-25 G 31 RUN #2	RC131132	08/29/91	10/07/91	10/11/91
NWNJ LOT-1 G 16 RUN #3	RC13147	07/02/91	10/07/91	10/14/91
NWNJ LOT-1 G 16 REP RUN #3	RC131410	07/02/91	10/07/91	10/14/91

Table 10-7

Average Concentration Summary

	LINY	MNY	PLNJ	NWNJ
Average Concentrations (ppbv)				
Formaldehyde	6.2	5.4	3.6	4.6
Acetaldehyde	2.2	3.3	2.9	2.4
Acrolein	0.3	NA	NA	NA
Acctone	5.2	3.5	4.9	12.0
Propionaldehyde	0.4	0.7	0.9	1.0
Crotonaldehyde	0.5	NA	NA	NA
Butyr/Isobutyraldehyde	1.4	NA	1.8	NA
Benzaldehyde	NA	NA	NA	NA
Isovaleraldehyde	NA	NA	NA	NA
Valeraldehyde	NA	NA	NA	NA
Tolualdehydes	NA	NA	NA	NA
Hexanaldehyde	NA	NA	NA	NA
2,5-Dimethylbenzaldehyde	NA	NA	NA	NA

Table 10-8
Carbonyl Duplicate Analysis
Long Island, New York (LINY)

Sampling Date	08/16/91	08/16/91	Percent Difference (%)	Standard Deviation (ppbv)
Sample ID	LINY-LOT-25 R 53	LINY LOT-25 G 6		
Sample Volume (L)	119.9	135.6		
Average Concentrations (ppbv)				
Formaldehyde	ND	5.6	NA	NA
Acetaldehyde	ND	0.8	NA	NA
Acrolein	ND	0.3	NA	NA
Acetone	ND	ND	NA	NA
Propionaldehyde	0.4	ND	NA	NA
Crotonaldehyde	ND	ND	NA	NA
Butyr/Isobutyraldehyde	ND	ND	NA	NA
Benzaldehyde	ND	ND	NA	NA
Isovaleraldehyde	ND	ND	NA	NA
Valeraldehyde	ND	ND	NA	NA
Tolualdehydes	ND	ND	NA	NA
Hexanaldehyde	ND	ND	NA	NA
2,5-Dimethylbenzaldehyde	ND	ND	NA	NA
		Average	NA	NA

Manhattan, New York (MNY)

Sampling Date	08/16/91	08/16/91	Percent Difference (%)	Standard Deviation (ppbv)
Sample ID	MNY LOT-25 R 63	MNY LOT-25 G 8		
Sample Volume (L)	172.9	180.8		
Average Concentrations (ppbv)				
Formaldehyde	7.2	6.3	-14.6%	0.49
Acetaldehyde	4.4	6.3	36.1%	0.97
Acrolein	ND	ND	NA	NA
Acetone	0.9	4.7	136.6%	1.89
Propionaldehyde	0.9	1.5	51.3%	0.30
Crotonaldehyde	ND	ND	NA	NA
Butyr/Isobutyraldehyde	ND	ND	NA	NA
Benzaldehyde	ND	ND	NA	NA
Isovaleraldehyde	ND	ND	NA	NA
Valeraldehyde	ND	ND	NA	NA
Tolualdehydes	ND	ND	NA	NA
Hexanaldehyde	ND	ND	NA	NA
2,5-Dimethylbenzaldehyde	ND	ND	NA	NA
		Average	52.4%	0.91

Table 10-8

Continued

Plainfield, New Jersey (PLNJ)

Sampling Date	08/29/91	08/29/91		Standard
Sample ID	PLNJ LOT-25 R 70	PLNJ LOT-25 G 1	Percent	Deviation
Sample Volume (L)	131.7	121.8	Difference (%)	(ppbv)
Average Concentrations (ppbv)				
Formaldehyde	1.3	3.2	81.3%	0.92
Acetaldehyde	ND	1.6	NA	NA
Acrolein	ND	ND	NA	NA
Acetone	ND	ND	NA	NA
Propionaldehyde	0.3	0.3	22.2%	0.03
Crotonaldehyde	ND	ND	NA	NA
Butyr/Isobutyraldehyde	ND	ND	NA	NA
Benzaldehyde	ND	ND	NA	NA
Isovaleraldehyde	ND	ND	NA	NA
Valeraldehyde	ND	ND	NA	NA
Tolualdehydes	ND	ND	NA	NA
Hexanaldehyde	ND	ND	NA	NA
2,5-Dimethylbenzaldehyde	ND	ND	NA	NA
		Average	51.7%	0.47

Newark, New Jersey (NWNJ)

Sampling Date	07/02/91	07/02/91		Standard
Sample ID	NWNJ LOT-1 G 16 RUN #	NWNJ LOT-1 R 2	Percent	Deviation
Sample Volume (L)	148.4	148.4	Difference (%)	(ppbv)
Average Concentrations (ppbv)				
Formaldehyde	2.3	4.0	52.3%	0.82
Acetaldehyde	2.7	2.3	-17.4%	0.22
Acrolein	ND	ND	NA	NA
Acetone	ND	ND	NA	NA
Propionaldehyde	ND	ND	NA	NA
Crotonaldehyde	ND	ND	NA	NA
Butyr/Isobutyraldehyde	ND	ND	NA	NA
Benzaldehyde	ND	ND	NA	NA
Isovaleraldehyde	ND	ND	NA	NA
Valeraldehyde	ND	ND	NA	NA
Tolualdehydes	ND	ND	NA	NA
Hexanaldehyde	ND	ND	NA	NA
2,5-Dimethylbenzaldehyde	ND	ND	NA	NA
		Average	17.4%	0.52

Table 10-9
Carbonyl Replicate Analysis

Long Island, New York (LINY)

Sampling Date	08/16/91	08/16/91		Standard
Sample ID	LINY-LOT-25 R 53	LINY-LOT-25 R 53 REP	Percent	Deviation
Sample Volume (L)	119.9	119.9	Difference (%)	(ppbv)
Concentrations (ppbv)				
Formaldehyde	ND	ND	NA	NA
Acetaldehyde	ND	ND	NA	NA
Acrolein	ND	ND	NA	NA
Acetone	ND	ND	NA	NA
Propionaldehyde	0.3	0.4	18.0%	0.03
Crotonaldehyde	ND	ND	NA	NA
Butyr/Isobutyraldehyde	ND	ND	NA	NA
Benzaldehyde	ND	ND	NA	NA
Isovaleraldehyde	ND	ND	NA	NA
Valeraldehyde	ND	ND	NA	NA
Tolualdehydes	ND	ND	NA	NA
Hexanaldehyde	ND	ND	NA	NA
2,5-Dimethylbenzaldehyde	ND	ND	NA	NA
Average			18.0%	0.03

Sampling Date	08/16/91	08/16/91		Standard
Sample ID	LINY LOT-25 G 60	LINY LOT-25 G 60 REP	Percent	Deviation
Sample Volume (L)	135.6	135.6	Difference (%)	(ppbv)
Concentrations (ppbv)				
Formaldehyde	5.7	5.5	-3.7%	0.10
Acetaldehyde	0.8	0.8	-3.0%	0.01
Acrolein	0.4	0.2	-51.9%	0.07
Acetone	ND	ND	NA	NA
Propionaldehyde	ND	ND	NA	NA
Crotonaldehyde	ND	ND	NA	NA
Butyr/Isobutyraldehyde	ND	ND	NA	NA
Benzaldehyde	ND	ND	NA	NA
Isovaleraldehyde	ND	ND	NA	NA
Valeraldehyde	ND	ND	NA	NA
Tolualdehydes	ND	ND	NA	NA
Hexanaldehyde	ND	ND	NA	NA
2,5-Dimethylbenzaldehyde	ND	ND	NA	NA
Average			-19.5%	0.06

Table 10-9

Continued

Manhattan, New York (MNY)

Sampling Date	08/16/91	08/16/91		Standard
Sample ID	MNY LOT-25 R 63	MNY LOT-25 R 63 REP	Percent	Deviation
Sample Volume (L)	172.9	172.9	Difference (%)	(ppbv)
Concentrations (ppbv)				
Formaldehyde	7.2	7.3	0.4%	0.01
Acetaldehyde	4.3	4.4	1.8%	0.04
Acrolein	ND	ND	NA	NA
Acetone	0.9	0.8	-8.8%	0.04
Propionaldehyde	1.0	0.7	-28.7%	0.12
Crotonaldehyde	ND	ND	NA	NA
Butyr/Isobutyraldehyde	ND	ND	NA	NA
Benzaldehyde	ND	ND	NA	NA
Isovaleraldehyde	ND	ND	NA	NA
Valeraldehyde	ND	ND	NA	NA
Tolualdehydes	ND	ND	NA	NA
Hexanaldehyde	ND	ND	NA	NA
2,5-Dimethylbenzaldehyde	ND	ND	NA	NA
Average			-8.8%	0.05

Sampling Date	08/16/91	08/16/91		Standard
Sample ID	MNY LOT-25 G 81	MNY LOT-25 G 81 REP	Percent	Deviation
Sample Volume (L)	180.8	180.8	Difference (%)	(ppbv)
Concentrations (ppbv)				
Formaldehyde	6.2	6.3	1.5%	0.05
Acetaldehyde	6.1	6.5	6.4%	0.20
Acrolein	ND	ND	NA	NA
Acetone	4.6	4.8	4.7%	0.11
Propionaldehyde	1.1	1.8	43.4%	0.32
Crotonaldehyde	ND	ND	NA	NA
Butyr/Isobutyraldehyde	ND	ND	NA	NA
Benzaldehyde	ND	ND	NA	NA
Isovaleraldehyde	ND	ND	NA	NA
Valeraldehyde	ND	ND	NA	NA
Tolualdehydes	ND	ND	NA	NA
Hexanaldehyde	ND	ND	NA	NA
2,5-Dimethylbenzaldehyde	ND	ND	NA	NA
Average			14.0%	0.17

Table 10-9

Continued

Plainfield, New Jersey (PLNJ)

Sampling Date Sample ID Sample Volume (L)	08/29/91 PLNJ LOT-25 R 70 131.7	08/29/91 PLNJ LOT-25 R 70 REP 131.7	Percent Difference (%)	Standard Deviation (ppbv)
Concentrations (ppbv)				
Formaldehyde	1.3	1.3	-0.1%	0.00
Acetaldehyde	ND	ND	NA	NA
Acrolein	ND	ND	NA	NA
Acetone	ND	ND	NA	NA
Propionaldehyde	0.3	0.3	9.4%	0.01
Crotonaldehyde	ND	ND	NA	NA
Butyr/Isobutyraldehyde	ND	ND	NA	NA
Benzaldehyde	ND	ND	NA	NA
Isovaleraldehyde	ND	ND	NA	NA
Valeraldehyde	ND	ND	NA	NA
Tolualdehydes	ND	ND	NA	NA
Hexanaldehyde	ND	ND	NA	NA
2,5-Dimethylbenzaldehyde	ND	ND	NA	NA
Average			4.7%	0.01

Sampling Date Sample ID Sample Volume (L)	08/29/91 PLNJ LOT-25 G 109 121.8	08/29/91 PLNJ LOT-25 G 109 REP 121.8	Percent Difference (%)	Standard Deviation (ppbv)
Concentrations (ppbv)				
Formaldehyde	3.3	3.0	-7.5%	0.12
Acetaldehyde	1.7	1.6	-5.3%	0.04
Acrolein	ND	ND	NA	NA
Acetone	ND	ND	NA	NA
Propionaldehyde	0.4	0.3	-23.2%	0.04
Crotonaldehyde	ND	ND	NA	NA
Butyr/Isobutyraldehyde	ND	ND	NA	NA
Benzaldehyde	ND	ND	NA	NA
Isovaleraldehyde	ND	ND	NA	NA
Valeraldehyde	ND	ND	NA	NA
Tolualdehydes	ND	ND	NA	NA
Hexanaldehyde	ND	ND	NA	NA
2,5-Dimethylbenzaldehyde	ND	ND	NA	NA
Average			-12.0%	0.07

Table 10-9

Continued

Newark, New Jersey (NWNJ)

Sampling Date Sample ID Sample Volume (L)	07/02/91 NWNJ LOT-1 G 16 RUN #3 148.4	07/02/91 NWNJ LOT-1 G 16 REP RUN #3 148.4	Percent Difference (%)	Standard Deviation (ppbv)
Concentrations (ppbv)				
Formaldehyde	2.2	2.4	6.8%	0.08
Acetaldehyde	2.7	2.7	1.2%	0.02
Acrolein	ND	ND	NA	NA
Acetone	ND	ND	NA	NA
Propionaldehyde	ND	ND	NA	NA
Crotonaldehyde	ND	ND	NA	NA
Butyr/Isobutyraldehyde	ND	ND	NA	NA
Benzaldehyde	ND	ND	NA	NA
Isovaleraldehyde	ND	ND	NA	NA
Valeraldehyde	ND	ND	NA	NA
Tolualdehydes	ND	ND	NA	NA
Hexanaldehyde	ND	ND	NA	NA
2,5-Dimethylbenzaldehyde	ND	ND	NA	NA
Average			4.0%	0.05

Sampling Date Sample ID Sample Volume (L)	07/02/91 NWNJ LOT-1 R 23 RUN #2 148.4	07/02/91 NWNJ LOT-1 R 23 REP RUN #2 148.4	Percent Difference (%)	Standard Deviation (ppbv)
Concentrations (ppbv)				
Formaldehyde	3.5	4.4	22.1%	0.44
Acetaldehyde	1.8	2.7	42.7%	0.48
Acrolein	ND	ND	NA	NA
Acetone	ND	ND	NA	NA
Propionaldehyde	ND	ND	NA	NA
Crotonaldehyde	ND	ND	NA	NA
Butyr/Isobutyraldehyde	ND	ND	NA	NA
Benzaldehyde	ND	ND	NA	NA
Isovaleraldehyde	ND	ND	NA	NA
Valeraldehyde	ND	ND	NA	NA
Tolualdehydes	ND	ND	NA	NA
Hexanaldehyde	ND	ND	NA	NA
2,5-Dimethylbenzaldehyde	ND	ND	NA	NA
Average			32.4%	0.46

Table 10-10
Carbonyl Analysis Summary Table

	Replicate Analyses	Duplicate Analyses
Average % Difference	4.1%	40.5%
Average STD	0.11	0.64
Max % difference	43.4%	136.6%
Min % difference	-51.9%	-17.4%

performed on 10% of the samples from each site. Analytical error for all replicate pairs ranged from -51.9% to 43.4%, averaging 4.1% overall, with a standard deviation of the percent differences equal to 0.11 ppbv as listed in Table 10-10.

10.5.4 Quality Control Standards

As a quality control (QC) procedure on the analytical results for all of the quantitated analytes, a solution containing the target carbonyl compounds at a known concentration was generated. Throughout the period of time that analyses were performed, QC samples were analyzed between every seven sample analyses on the dates that samples were analyzed. Table 10-11 gives the percent recoveries for the quality control standards that were analyzed during this program. Shown in Table 10-12 are the average percent recovery, maximum percent recovery, minimum percent recovery and the relative standard deviation for each carbonyl compound. These results show that the analyses remained in control.

10.6 RECOMMENDATIONS

Previous studies showed that the ozone scrubber was needed to accurately measure the carbonyl concentrations in ambient air. One recommendation is to continue using the carbonyl scrubber when sampling for carbonyl compounds. An additional recommendation is to determine the life of the effectiveness of the KI denuder. Some preliminary studies performed by the U.S. EPA indicated that the effective life was approximately 6000 sample-hours. These results need to be checked and more definitively defined with field studies that extend over several years. It is also recommended that a log be kept on the cumulative total sample time a denuder is in use.

Table 10-11
Carbonyl Quality Control Recoveries

Sample ID Data File ID	QC CHECK RC127914	QC CHECK RC127924	QC CHECK RC127932	QC CHECK RC127943	QC CHECK RC12842	QC CHECK RC128412
Formaldehyde	97.5%	96.1%	93.6%	94.7%	98.2%	98.4%
Acetaldehyde	104.1%	98.6%	98.8%	97.9%	104.1%	105.0%
Acrolein	65.2%	74.5%	74.4%	74.0%	93.8%	95.1%
Acetone	83.6%	80.2%	79.6%	79.1%	88.7%	89.7%
Propionaldehyde	130.7%	132.2%	129.5%	118.0%	111.0%	111.7%
Crotonaldehyde	92.0%	87.0%	87.7%	85.2%	105.0%	102.0%
Butyr/Isobutyraldehyde	105.6%	101.7%	101.7%	101.5%	108.7%	101.0%
Benzaldehyde	53.7%	49.8%	50.7%	49.4%	100.3%	105.0%
Isovaleraldehyde	72.5%	70.6%	71.1%	69.0%	84.2%	95.0%
Valeraldehyde	97.0%	90.1%	92.6%	91.3%	78.6%	88.1%
Tolualdehydes	97.6%	92.5%	92.8%	93.1%	107.4%	107.5%
Hexanaldehyde	125.2%	118.9%	118.8%	120.5%	100.9%	92.9%
2,5-Dimethylbenzaldehyde	103.7%	94.5%	90.0%	98.0%	102.0%	100.8%

Sample ID Data File ID	QC CHECK RC131112	QC CHECK RC131111	QC CHECK RC131118	QC CHECK RC131127	QC CHECK RC131133	QC CHECK RC131146	QC CHECK RC131411
Formaldehyde	72.1%	93.5%	81.2%	81.4%	79.3%	102.2%	119.6%
Acetaldehyde	75.8%	99.2%	83.7%	85.6%	83.2%	109.0%	123.6%
Acrolein	64.1%	83.6%	69.7%	71.7%	70.0%	91.6%	102.1%
Acetone	68.8%	90.5%	75.4%	77.6%	75.2%	98.8%	110.3%
Propionaldehyde	75.5%	98.7%	83.4%	84.2%	81.6%	110.1%	127.8%
Crotonaldehyde	74.6%	98.7%	82.7%	83.4%	81.8%	104.2%	116.6%
Butyr/Isobutyraldehyde	78.1%	100.9%	85.4%	87.4%	84.7%	110.0%	124.2%
Benzaldehyde	77.6%	98.2%	78.0%	83.5%	81.9%	111.4%	126.1%
Isovaleraldehyde	78.9%	99.1%	80.0%	82.6%	85.4%	108.8%	123.3%
Valeraldehyde	77.2%	100.1%	81.8%	86.0%	87.2%	108.7%	120.7%
Tolualdehydes	72.4%	96.6%	80.4%	83.2%	80.5%	83.2%	120.9%
Hexanaldehyde	73.7%	98.9%	82.9%	84.9%	81.3%	109.5%	121.7%
2,5-Dimethylbenzaldehyde	75.3%	101.3%	83.0%	86.7%	82.8%	107.9%	123.8%

Table 10-12
QC Standard Statistical Summary

	Average Percent Recovery	Maximum Percent Recovery	Minimum Percent Recovery	Relative Standard Deviation
Formaldehyde	92.9%	119.6%	72.1%	12.6%
Acetaldehyde	97.6%	123.6%	75.8%	12.6%
Acrolein	79.2%	102.1%	64.1%	15.2%
Acetone	84.4%	110.3%	68.8%	12.7%
Propionaldehyde	107.3%	132.2%	75.5%	18.4%
Crotonaldehyde	92.4%	116.6%	74.6%	12.5%
Butyr/Isobutyraldehyde	99.3%	124.2%	78.1%	12.1%
Benzaldehyde	82.0%	126.1%	49.4%	30.0%
Isovaleraldehyde	86.2%	123.3%	69.0%	18.2%
Valeraldehyde	92.3%	120.7%	77.2%	12.7%
Tolualdehydes	92.9%	120.9%	72.4%	13.9%
Hexanaldehyde	102.3%	125.2%	73.7%	16.9%
2,5-Dimethylbenzaldehyde	96.1%	123.8%	75.3%	12.8%

11.0 SPECIATED NONMETHANE ORGANIC COMPOUND PROGRAM

This section describes the speciated nonmethane organic compound monitoring program operated under EPA's NMOC program during 1991. Five sites, RINC (Raleigh, NC), PLNJ (Plainfield, NJ), PBFL (West Palm Beach, FL), NWNJ (Newark, NJ), and FIFL (Fort Lauderdale, FL), carried out a reduced monitoring program with 10 samples collected during the monitoring season from June through September 1991. Five other sites, BMTX (Beaumont, TX), BRLA (Baton Rouge, LA), ELTX (El Paso, TX), HITX (Houston, TX), and JUMX (Juarez, CH, Mexico), collected integrated ambient air samples from 6:00 a.m. to 9:00 a.m. (local civil time), Monday through Friday, from June 3, 1991, through September 27, 1991.

11.1 INTRODUCTION

The speciated nonmethane organic compound method follows general guidelines in the EPA's "Research Protocol Method for Analysis of C₂ - C₁₂ Hydrocarbons in Ambient Air by Gas Chromatography with Cryogenic Concentration" and is given in the Appendix J. The method uses cryogenic preconcentration followed by gas chromatography with an FID.

11.2 SAMPLING EQUIPMENT AND PROCEDURE

The sampling equipment and sampling procedures used to collect samples for the Speciated Nonmethane Organic Compound (SNMOC) Monitoring Program is the same as those used for the NMOC monitoring program. Section 3.1 describes the equipment in detail, and also gives the sampling procedure. Integrated ambient air samples were collected in cleaned, evacuated, 6-L stainless steel canisters using a diaphragm pump. Three-hour samples were collected and the final canister pressure was about 15 psig.

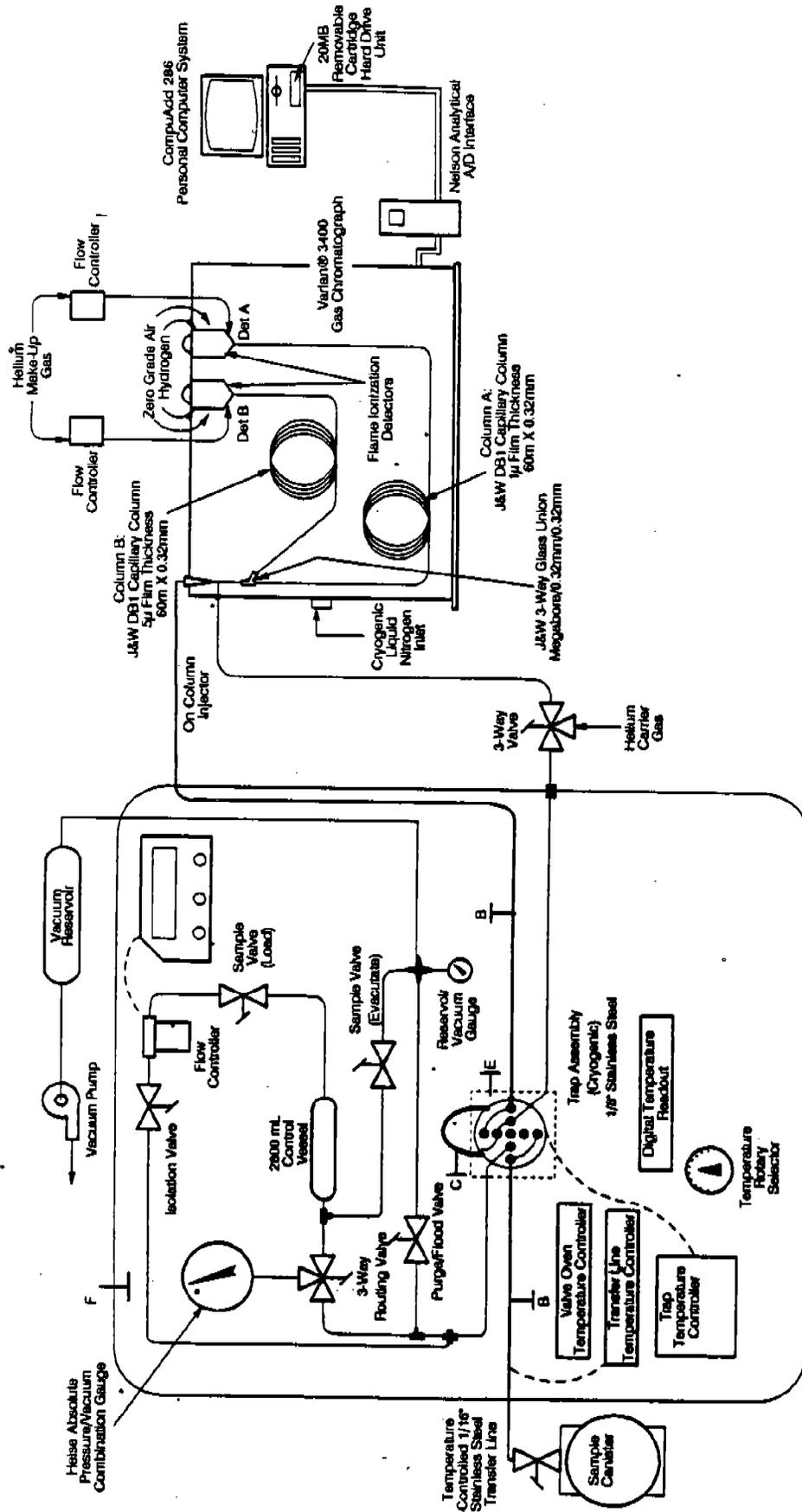
11.3 SPECIATED NMOC ANALYTICAL SYSTEM

The analytical system for speciated NMOC, shown in Figure 11-1, consists of a Radian Sample Interface System and gas chromatograph (GC). When the six-port gas valve is in the sample load mode (see Figure 11-2), the sample interface serves to preconcentrate cryogenically a measurable sample volume. In the sample inject mode (see Figure 11-3), the cryogenically

Sample Interface System

Analytical System

Data System



5116032R

Figure 11-1. Speciated NMOC System

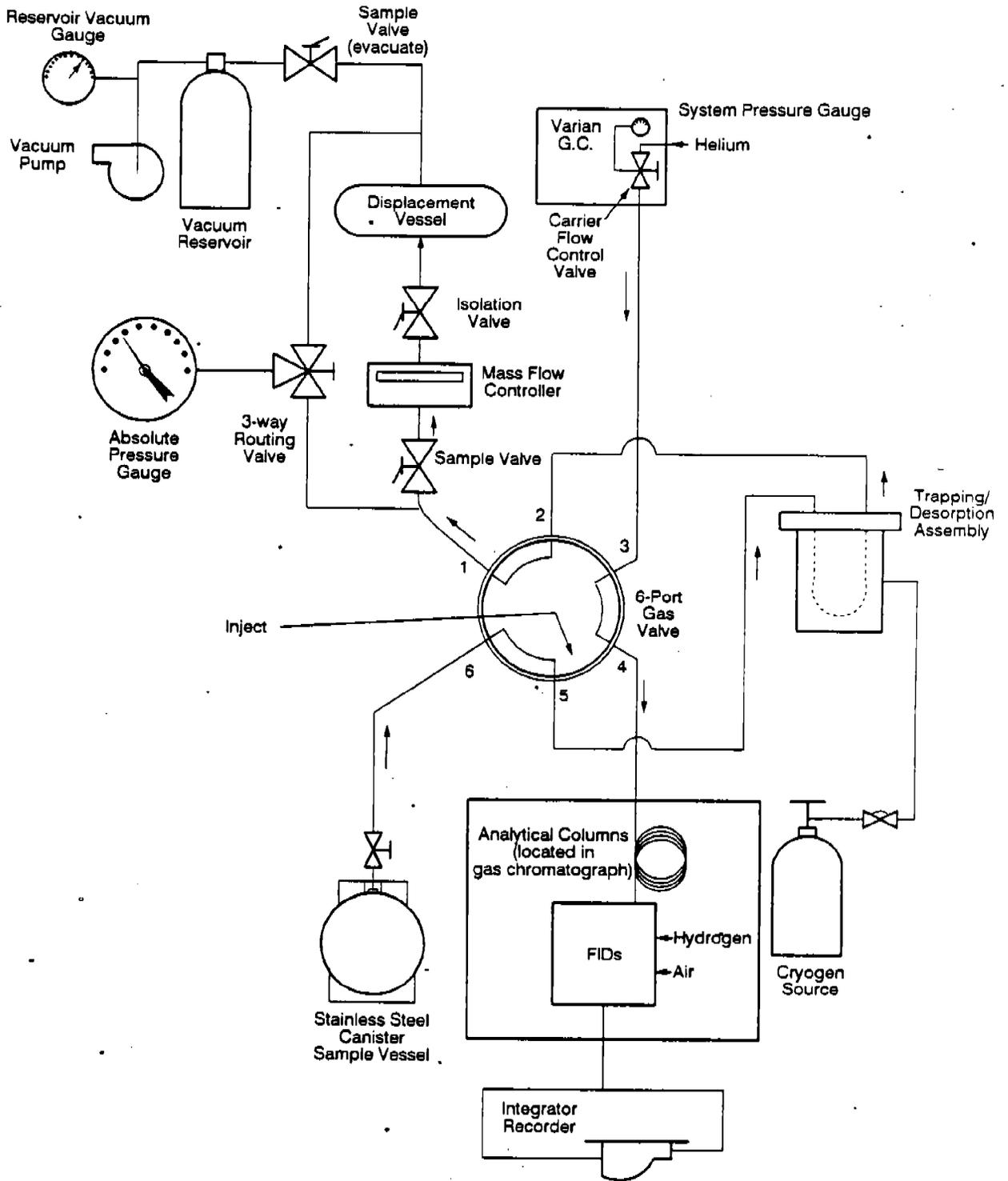


Figure 11-2. Radian Sample Interface in Sample Load Mode

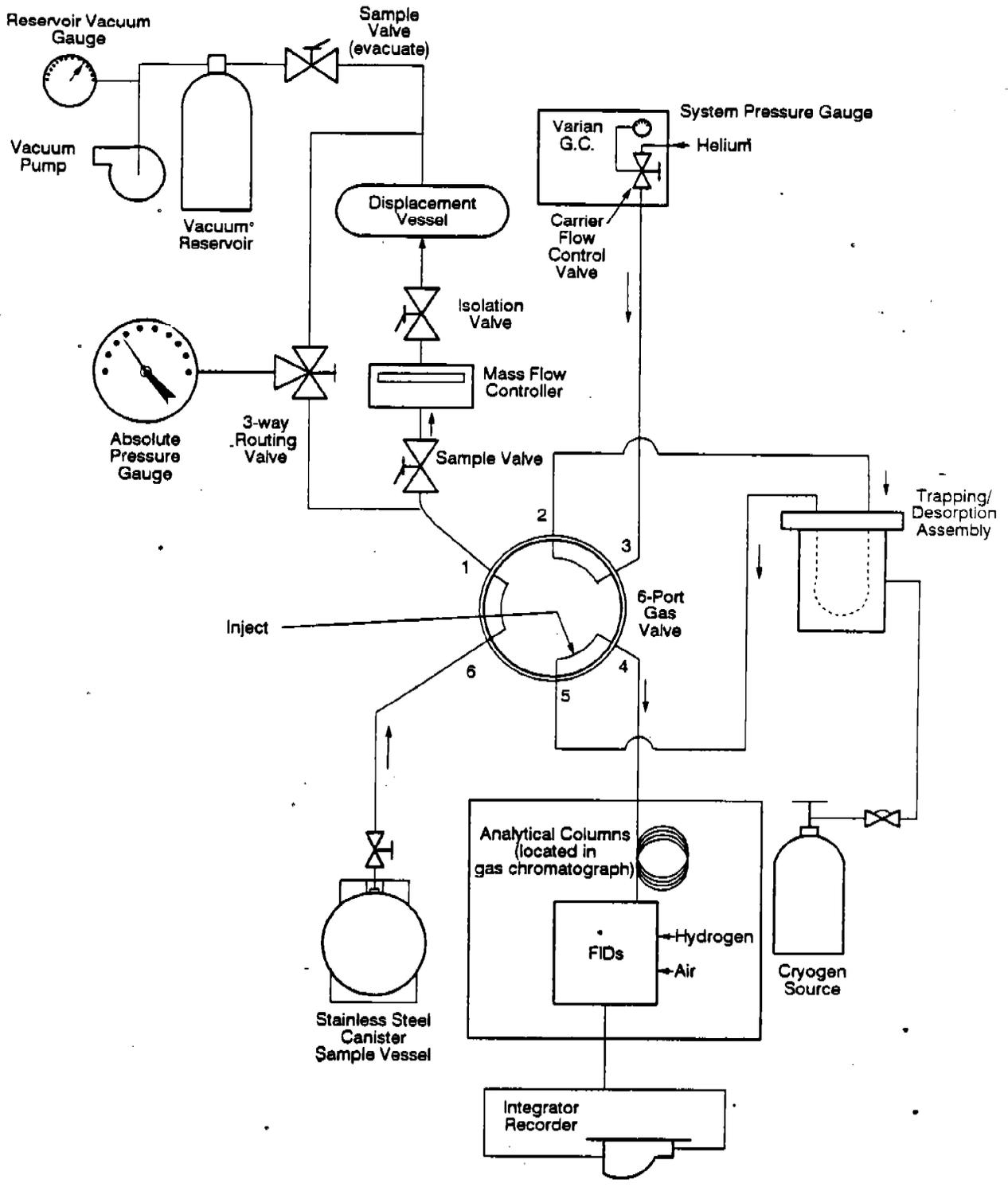


Figure 11-3. Radian Sample Interface in Sample Inject Mode

5115056R

focused water and organic compounds are thermally desorbed and swept by helium carrier gas to the head of the GC column. The GC oven is programmed so the sample is refocused on the column at subambient temperatures and then C₂ to C₁₄ hydrocarbons are chromatographically separated.

The Varian® 3400 gas chromatograph has two fused silica capillary columns each connected to a flame ionization detector (FID). The sample is split 1:1 between the columns with a J&W three-way glass union (Megabore®/0.32 mm/0.32 mm). Each column has a J&W DB-1® phase, the difference being phase thicknesses of 1 μm and 5 μm in the two columns. The column with the 5-μm-phase thickness serves to separate the C₂ hydrocarbons consistently, and give some confirmation retention time information. The column with the 1-μm-phase thickness is used to separate C₃ to C₁₄ hydrocarbons effectively.

Table 11-1 gives the operating conditions for the GC/FID used in the speciated NMOC analyses.

11.4 QUALITY ASSURANCE PROCEDURES

Quality assurance procedures were implemented for this program to ensure the collection of ambient air samples in a prescribed way and to measure the speciated concentrations with known precision and accuracy.

11.4.1 Calibration Standards Preparation

Calibration of the speciated NMOC analytical system was done by analyzing humidified propane calibration standards prepared at levels of about 25, 65, and 125 ppbv propane from Scott Specialty Gases certified standards. These standards were prepared by using gas-tight syringes to inject aliquots of the certified standard into clean, evacuated stainless steel canisters. The canisters were filled to ambient pressure with humidified air from a standard preparation flow dilution system, then pressurized with nitrogen to approximately 35 psig from a canister dilution system.

Table 11-1

1991 Speciated NMOC GC/FID Operating Conditions

Parameter	Operating Value
Sample Volume	800 mL
<u>J&W DB-1® Capillary Columns</u>	
Column A: Film Thickness Length Inside Diameter	1 μm 60 m 0.32 mm
Column B: Film Thickness Length Inside Diameter	5 μm 60 m 0.32 mm
Oven Temperature Program	-60° for 5 min. Then: 8°C/min. to 150°C, hold for 5 min., 8°C/min. to 180°C.
Analysis Time	45 min.
Detector Temperatures 2 FIDs	 300°C
Gas Flow Rates Helium Carrier Gas Helium Make-Up H ₂ to FID Air to FID	 3 mL/min. 30 mL/min. 30 mL/min. 300 mL/min.

11.4.2 GC/FID Monthly Calibration

Propane calibration curve standards with approximate concentrations of 25, 65, and 125 ppbv-propane were analyzed on a monthly basis. Data from these standard analyses along with a humidified air analysis gave a four-point calibration curve for each FID. A known volume (in liters) of the propane standard was loaded into the chromatograph for each calibration point. The area count recorded by each FID detector was correlated to the nanoliters (L) of propane by a linear regression. The slope of the regression line was used as the initial average response factor for the four calibration points. Linear regression analysis was done to get a propane response factor for each detector. The response factors were considered valid if the coefficient of correlation for the four points was equal to or greater than 0.995. The resulting response factors were divided by three (carbons/molecule of propane) to get a per carbon response factor for each detector. This response factor is used to calculate sample concentrations for the following month.

The monthly propane calibration curves for the speciated NMOC FIDs are given in Appendix K, along with the supporting data showing area counts and nanoliters (L) of propane standard.

11.4.3 Daily Calibration Check

A daily propane calibration check of a mid-level (30 to 60 ppbv) propane standard was performed prior to sample analysis to assure the validity of the current monthly response factor. A monthly control chart was used to accumulate propane response factor information and calculate the standard deviation on a daily basis. Means and two-sigma limits were calculated on a cumulative basis, i.e., as new data were added, the number of data by which the means and standard deviations were calculated increased. Two-sigma limits about the cumulative mean was established for propane response factor quality control.

Should the first daily response factor fall outside the two-sigma limits of the control chart, a second QC analysis is done the same day. If the second daily response factor falls outside the two-sigma limits, the system is checked for proper operation and after corrections and adjustments necessary are made to the instrument, another standard propane sample can be analyzed to see if the system is operating within the control limits. If the

response remains outside the two-sigma control limits, the instrument should be recalibrated and/or corrective action taken.

Daily calibration checks are given in Appendix L for the Speciated NMOC FID response factors. A separate table is given for each detector. For each month a new calibration is given. In Table L-1, for example the calibration date was June 6, 1991, and the response factor for each calibration point is shown in terms of area counts per nanoliter of propane standard per carbon (AC/nL-C). The monthly response factor was calculated from the calibration curve regression slopes displayed in Appendix K. After the first calibration point, both the mean response factor and the standard deviation of the response factors were accumulated. The "2s Range" in Table L-1 is the two-sigma limits of the control chart used in the daily calibration check. The "low" and "high" values shown in Table L-1 show the lower control limit and the upper control limit, respectively. The control limits were calculated daily using $\bar{X} \pm 2s$, where \bar{X} is the cumulative mean of all the monthly calibration response factors and the daily response factors to date (within the month), and s is their standard deviation. The final column in Table L-1 is the percentage difference between the response factor and the monthly response factor calculated from the slope of the calibration curve.

11.4.4 Speciated NMOC Comparison with EPA Results

Nine speciated NMOC samples were randomly chosen and given to the EPA's AREAL laboratory at Research Triangle Park, North Carolina, for analysis. The results of this comparison are given in Tables 11-2 and 11-3. Table 11-2 displays the comparisons in ppbC units of concentration. Table 11-3 shows the results expressed as a percent bias, using the AREAL results as the reference method. Table 11-4 gives the absolute percent differences.

Twenty-five compounds are compared, plus NMOC is given for the EPA measurements and NMHC (no oxygenates or halogenates) is given for the Radian measurement. Radian measurements range from 0.90 ppbv for 1,3,5-trimethylbenzene to 466.57 ppbv for n-butane. In Table 11-3 the comparisons

**Table 11-2
Speciated NMOC Compared to EPA Results**

SITE ID SAMPLE ID	H1TX 2200		BMTX 2201		BRLA 2205		BRLA 2206		EPTX 2211		H1TX 2213		BRLA 2224		JUMX 2228		JUMX 2229	
	Radian	EPA	Radian	EPA	Radian	EPA	Radian	EPA	Radian	EPA	Radian	EPA	Radian	EPA	Radian	EPA	Radian	EPA
Propylene	8.13	10.01	7.04	8.26	29.41	28.68	28.61	30.43	26.59	28.36	20.45	21.39	6.21	6.92	12.15	12.26	11.48	11.75
Propane	49.11	58.69	39.10	41.85	82.18	97.74	87.01	99.51	161.78	158.01	39.03	46.50	45.51	52.21	78.96	77.70	76.57	77.83
Isobutane	21.93	23.22	23.45	24.37	96.79	96.82	97.46	99.08	29.19	29.04	26.10	26.25	25.54	25.96	12.12	12.45	12.04	12.40
1-Butene	6.97	7.49	5.57	5.94	18.53	18.67	18.55	19.24	17.32	17.44	14.05	14.24	4.09	4.28	7.22	7.43	7.10	7.35
n-Butane	34.08	36.42	39.56	40.46	458.99	443.22	466.57	458.44	84.22	80.78	42.16	39.21	81.96	82.10	35.13	35.65	35.06	35.54
Isopentane	63.81	66.46	61.57	63.18	208.86	197.27	208.86	205.05	105.89	107.61	73.24	75.64	53.14	53.06	45.73	44.88	44.91	44.47
n-Pentane	18.54	19.00	19.75	20.02	87.50	85.19	87.82	87.97	62.22	61.18	18.33	18.73	24.67	25.43	25.78	32.72	25.35	32.67
2,2-Dimethylbutane	2.81	2.56	3.02	3.32	12.60	12.18	12.46	12.55	2.41	2.71	3.03	2.87	6.23	6.68	1.52	1.35	1.13	1.34
2,3-Dimethylbutane	4.69	4.50	5.52	6.13	11.38	11.16	11.35	11.54	13.40	13.01	5.43	4.91	3.73	3.77	6.34	6.73	6.22	6.73
2-Methylpentane	17.40	17.79	20.58	21.22	38.34	40.18	38.14	42.12	39.12	41.25	20.46	22.39	10.99	11.21	19.61	22.17	19.25	21.44
3-Methylpentane	10.10	11.42	12.55	13.52	21.74	21.01	21.78	21.63	24.80	24.93	11.93	12.70	6.24	7.47	12.73	12.26	12.54	12.22
n-Hexane	11.51	12.22	10.00	10.12	25.24	24.84	25.36	25.65	33.14	32.05	13.36	12.23	11.29	11.90	16.28	16.27	14.97	16.18
Methylcyclopentane	6.39	7.05	6.83	9.30	11.88	12.30	11.82	12.70	18.89	19.11	6.44	6.62	4.20	4.53	9.45	9.62	9.29	9.58
Benzene	16.05	17.46	14.78	15.66	17.24	17.73	17.26	18.33	46.63	47.12	31.22	31.92	4.54	4.66	23.22	23.66	22.99	23.59
2-methylhexane	4.71	6.00	5.47	6.94	5.97	7.07	6.16	7.42	11.77	15.59	5.45	6.32	3.12	3.40	5.69	7.81	5.87	7.59
3-Methylhexane	5.45	8.19	6.43	8.22	6.65	7.99	6.85	8.42	17.31	17.31	6.08	8.92	3.10	4.79	7.76	9.81	7.69	9.26
n-Heptane	5.68	5.69	5.88	4.81	6.80	7.57	7.15	7.79	16.62	14.17	5.81	6.00	5.69	6.32	6.73	7.42	6.73	7.58
Methylcyclohexane	6.67	7.60	4.62	4.87	7.52	8.84	7.53	8.55	8.56	9.58	4.28	4.59	3.73	5.12	4.15	6.04	4.07	6.28
Toluene	46.74	49.45	35.84	36.93	26.85	27.96	26.94	28.62	117.24	113.93	36.08	36.36	17.37	18.44	71.31	70.01	70.16	69.84
Ethylbenzene	8.23	9.30	8.57	9.57	6.31	6.96	6.37	7.96	22.53	23.06	8.02	8.65	5.83	6.58	12.91	13.26	12.69	13.24

**Table 11-2
Speciated NMOC Compared to EPA Results**

SITE ID SAMPLE ID	HITX		BMTX		BRLA		EPTX		HITX		BRLA		JUMX		JUMX		
	Radlan	EPA	Radlan	EPA	Radlan	EPA	Radlan	EPA	Radlan	EPA	Radlan	EPA	Radlan	EPA	Radlan	EPA	
Compound FN	2200	2200	2201	2201	2205	2205	2211	2211	2213	2213	2224	2224	2228	2228	2229	2229	
m/p-Xylene	30.00	28.68	28.99	27.65	10.38	9.95	10.37	10.90	64.73	24.59	34.34	9.65	9.20	40.84	37.60	40.21	42.0
o-Xylene	9.48	10.52	9.93	10.40	1.22	3.44	2.70	3.54	22.96	8.07	8.73	2.57	3.22	12.55	13.49	13.90	13.1
n-Nonane	2.21	2.34	1.56	1.60	1.81	2.02	1.83	2.27	8.15	1.30	1.20	2.12	2.43	3.46	3.23	3.35	3.0
1,3,5-Trimethylbenzene	3.56	4.57	4.62	5.87	0.92	0.57	0.90	2.82	8.62	3.42	3.71	0.92	2.07	3.80	4.82	3.72	5.6
1,2,4-Trimethylbenzene	10.35	13.30	12.82	18.30	2.06	3.19	2.05	3.54	27.53	10.63	12.88	2.39	3.45	13.60	16.03	13.23	17.5
TOTAL NMOC	1	903	824	824	1567	1703	2139	845	609	992	97	758	777	777	758	758	97
TOTAL NMHC	0	611	614	614	1391	1412	1738	640	427	427	427	427	427	427	427	427	427

FOOTNOTES

- a Radlan reported as 1-Butene + Isobutene coeluting.
- b 2,2-Dimethylbutane was not on Radlan's 1991 database, but peak could be matched to reported UnID.
- c 2-Methylpentane = Isohexane.
- d 2-Methylhexane = Isoheptane
- e 1,2,4-Trimethylbenzene + 1-Decene show tendencies to coelute.
- f NMOC = Nonmethane Organic Compounds
- g NMHC = Nonmethane Hydrocarbons

Table 11-3
Percent Difference Between Radian
and EPA Analyses

SITE ID SAMPLE ID Compound	H1TX 2200	BMTX 2201	BRLA 2205	BRLA 2206	EPTX 2211	H1TX 2213	BRLA 2224	JUMX 2228	JUMX 2229	Average for Compound
Propylene	-20.73	-15.95	2.51	-6.17	-6.44	-4.49	-10.81	-0.90	-2.32	-7.26
Propane	-17.77	-6.79	-17.30	-13.40	2.36	-17.47	-13.71	1.61	-1.63	-9.35
Isobutane	-5.71	-3.85	1.01	-1.65	0.52	-0.57	-1.63	-2.69	-2.95	-1.95
1-Butene	-7.19	-6.43	-0.75	-3.65	-0.69	-1.34	-4.54	-2.87	-3.46	-3.44
n-Butane	-6.64	-2.25	3.50	1.76	4.17	7.25	-0.17	-1.47	-1.36	0.53
Isopentane	-4.07	-2.58	5.71	1.84	-1.61	-3.22	0.15	1.88	0.98	-0.10
n-Pentane	-2.45	-38.02	2.68	-0.40	1.69	-2.16	-3.03	-23.73	-25.23	-10.07
2,2-Dimethylbutane	8.53	-9.46	3.39	-0.72	-11.72	5.42	-6.97	11.85	-17.00	-1.85
2,3-Dimethylbutane	4.13	-10.47	1.95	-1.66	2.95	10.06	-1.07	-5.97	-7.88	-0.88
2-Methylpentane	-2.22	-3.06	-4.69	-9.92	-5.30	-9.01	-1.98	-12.25	-10.76	-6.58
3-Methylpentane	-12.27	-7.44	3.42	0.69	-0.52	-6.25	-17.94	3.76	2.58	-3.78
n-Hexane	-5.98	-1.19	1.60	-1.14	3.34	8.83	-5.26	0.06	-7.77	-0.83
Methylcyclopentane	-9.82	-30.63	-3.47	-7.18	-1.16	-2.76	-7.56	-1.78	-3.07	-7.49
Benzene	-8.42	-5.78	-2.80	-6.01	-1.05	-2.22	-2.61	-1.88	-2.58	-3.70
2-methylhexane	-24.09	-23.69	-16.87	-18.56	-27.92	-14.78	-8.59	-28.03	-25.56	-20.90
3-Methylhexane	-40.18	-24.44	-18.31	-23.49	0.00	-37.87	-42.84	-23.34	-18.53	-25.44
n-Heptane	-0.18	20.02	-10.72	-8.57	15.91	-3.22	-10.49	-9.75	-11.88	-2.10
Methylcyclohexane	-13.03	-5.27	-16.14	-12.69	-11.25	-6.99	-31.41	-37.10	-42.71	-19.62
Toluene	-5.63	-3.00	-4.05	-6.05	2.86	-0.77	-5.98	1.84	0.46	-2.26
Ethylbenzene	-12.21	-11.03	-9.80	-22.19	-2.33	-7.56	-12.09	-2.67	-4.24	-9.35
m/p-Xylene	1.07	4.73	4.23	-4.98	11.56	-33.09	4.77	8.26	-5.18	-0.96
o-Xylene	-10.40	-4.62	-95.28	-26.92	-4.76	-7.86	-22.45	-7.22	1.89	-19.74
n-Nonane	-5.71	-2.53	-10.97	-21.46	4.90	8.00	-13.63	6.88	9.70	-2.76
1,3,5-Trimethylbenzene	-24.85	-23.83	46.98	-97.73	-35.42	-8.13	-76.92	-23.67	-41.70	-31.70
1,2,4-Trimethylbenzene	-24.95	-35.22	-43.05	-53.31	-5.99	-19.14	-36.30	-16.40	-27.79	-29.13
AVERAGE FOR SAMPLE	-10.03	-10.11	-7.09	-13.74	-2.64	-5.97	-13.32	-6.62	-9.92	-8.83 *

* Average of accumulated compound averages.

Table 11-4
Absolute Percent Difference Between
Radian and EPA Analyses

SITE ID	H1TX	BMTX	BRLA	BRLA	EPTX	H1TX	BRLA	JUMX	JUMX	Average
SAMPLE ID	2200	2201	2205	2206	2211	2213	2224	2228	2229	for
Compound										Compound
Propylene	20.73	15.95	2.51	6.17	6.44	4.49	10.81	0.90	2.32	7.81
Propane	17.77	6.79	17.30	13.40	2.36	17.47	13.71	1.61	1.63	10.23
Isobutane	5.71	3.85	1.01	1.65	0.52	0.57	1.63	2.69	2.95	2.29
1-Butene	7.19	6.43	0.75	3.65	0.69	1.34	4.54	2.87	3.46	3.44
n-Butane	6.64	2.25	3.50	1.76	4.17	7.25	0.17	1.47	1.36	3.17
Isopentane	4.07	2.58	5.71	1.84	1.61	3.22	0.15	1.88	0.98	2.45
n-Pentane	2.45	38.02	2.68	0.40	1.69	2.16	3.03	23.73	25.23	11.04
2,2-Dimethylbutane	8.53	9.46	3.39	0.72	11.72	5.42	6.97	11.85	17.00	8.34
2,3-Dimethylbutane	4.13	10.47	1.95	1.65	2.95	10.06	1.07	5.97	7.88	5.13
2-Methylpentane	2.22	3.06	4.69	9.92	5.30	9.01	1.98	12.25	10.76	6.58
3-Methylpentane	12.27	7.44	3.42	0.69	0.52	6.25	17.94	3.76	2.58	6.10
n-Hexane	5.98	1.19	1.60	1.14	3.34	8.83	5.26	0.06	7.77	3.91
Methylcyclopentane	9.82	30.63	3.47	7.18	1.16	2.76	7.56	1.78	3.07	7.49
Benzene	8.42	5.78	2.80	6.01	1.05	2.22	2.61	1.88	2.58	3.70
2-methylhexane	24.09	23.69	16.87	18.56	27.92	14.78	8.59	28.03	25.56	20.90
3-Methylhexane	40.18	24.44	18.31	23.49	0.00	37.87	42.84	23.34	18.53	25.44
n-Heptane	0.18	20.02	10.72	8.57	15.91	3.22	10.49	9.75	11.88	10.08
Methylcyclohexane	13.03	5.27	16.14	12.69	11.25	6.99	31.41	37.10	42.71	19.62
Toluene	5.63	3.00	4.05	6.05	2.86	0.77	5.98	1.84	0.46	3.40
Ethylbenzene	12.21	11.03	9.80	22.19	2.33	7.56	12.09	2.67	4.24	9.35
m/p-Xylene	1.07	4.73	4.23	4.98	11.56	33.09	4.77	8.26	5.18	8.65
o-Xylene	10.40	4.62	95.28	26.92	4.76	7.86	22.45	7.22	1.89	20.16
n-Nonane	5.71	2.53	10.97	21.46	4.90	8.00	13.63	6.88	9.70	9.31
1,3,5-Trimethylbenzene	24.85	23.83	46.98	97.73	35.42	8.13	76.92	23.67	41.70	42.14
1,2,4-Trimethylbenzene	24.95	35.22	43.05	53.31	5.99	19.14	36.30	16.40	27.79	29.13
AVERAGE FOR SAMPLE	11.13	12.09	13.25	14.09	6.66	9.14	13.72	9.51	11.17	11.19 *

* Average of accumulated compound averages.

are given in percent difference, using the EPA measurement as the reference value. Note that most of the percent differences are negative, indicating that the Radian measurements are lower than the EPA measurements. This may be because the Radian measurement of NMHC does not include oxygenates or halogenates. The overall percent differences range from zero to -76.92 percent difference with an average percent difference of -8.83. Percent differences are averaged on all samples for each compounds, and over all compounds for each sample. Average percent differences for compounds range from -31.70 for 1,3,5-trimethylbenzene to +0.53 for n-butane, with an overall average of -8.83 percent difference. Sample ID percent differences range from -13.74 for Sample ID #2206 (BRLA) to -2.64 for Sample ID #2211 (EPTX).

Table 11-4 compares the Radian analyses on an absolute percent difference basis. The overall absolute percent difference is 11.19. These are excellent results, and show excellent quality control procedures in both laboratories.

11.4.5 Precision of Analyses -- Replicates

A number of the samples were analyzed twice to measure the precision of the analyses. Table 11-5 summarizes the statistics for the replicate analyses in terms of average concentrations, pooled standard deviations of the differences, and pooled coefficient of variations. In general, the coefficients of variation (precisions) for the speciated NMOC compound measurements are higher than the measurements for the UATMP. This is as expected because in the UATMP, each of the compounds identified has its separate calibration standard and calibration curve. In the speciated NMOC program, all of the quantitations are relative to the propane standard only.

11.4.6 Precision of Sampling and Analysis -- Duplicates

Sampling and analyses precision was estimated from the replicate analyses of duplicate samples. The pooled % CVs, seen in Table 11-6, are about equal for every compound to the replicate pooled % CVs, seen in Table 11-5. This shows that the sampling procedure for duplicates provides representative ambient air samples.

11.5 SPECIATED MONITORING RESULTS

Speciated monitoring results are treated in this section in two ways:
1) Site-specific statistics are presented in Section 11.5.1 for BMTX, BRLA,

Table 11-5. Replicate Statistics for 1991

Compound	Replicate Pairs	Overall Mean ppbv	Pooled Standard Deviation ppbv	Pooled %CV
Ethylene	90	29.18	9.37	32.11
Acetylene	90	13.95	6.31	45.23
Ethane	90	37.21	9.46	25.42
Propylene	92	16.47	2.86	17.36
Propane	92	46.98	6.30	13.41
Isobutane	92	21.76	1.91	8.78
1-Butene + Isobutene	92	6.84	1.37	20.03
1,3-Butadiene	62	3.19	0.34	10.66
n-Butane	92	40.49	2.57	6.35
t-2-Butene	76	3.35	0.40	11.94
c-2-Butene	68	2.76	0.53	19.20
Isopentane	92	53.18	3.37	6.34
n-Pentane	92	21.03	1.34	6.37
t-2-Pentene	78	4.26	0.65	15.26
c-2-Pentene	68	2.27	0.33	14.54
Cyclopentane	78	2.35	0.24	10.21
2,3-Dimethylbutane	90	4.88	5.65	115.78
Isohexane	92	14.71	1.55	10.54
3-Methylpentane	92	9.97	1.13	11.33
n-Hexane	92	12.85	1.55	12.06
Methylcyclopentane	92	6.22	0.32	5.14
2,4-Dimethylpentane	70	2.64	0.24	9.09
Benzene	92	14.44	1.51	10.46
Cyclohexane	88	3.51	0.39	11.11
Isoheptane	86	4.18	1.08	25.84
2,3-Dimethylpentane	60	3.57	0.72	20.17
3-Methylhexane	90	5.04	0.49	9.72
1-Heptene	10	1.73	0.11	6.36
2,2,4-Trimethylpentane	88	7.99	0.66	8.26
n-Heptane	90	5.07	0.30	5.92
Methylcyclohexane	84	4.13	0.47	11.38
2,2,3-Trimethylpentane	64	2.10	0.24	11.43
2,3,4-Trimethylpentane	84	3.03	0.28	9.24
Toluene	92	35.17	2.63	7.48
3-Methylheptane	74	2.68	0.18	6.72

Table 11-5. (Continued)

Compound	Replicate Pairs	Overall Mean ppbv	Pooled Standard Deviation ppbv	Pooled %CV
n-Octane	82	3.09	0.39	12.62
Ethylbenzene	92	7.20	0.42	5.83
p-Xylene + m-Xylene	92	21.61	1.80	8.33
Styrene	64	2.57	0.27	10.51
o-Xylene	90	7.40	0.74	10.00
n-Nonane	68	2.34	0.34	14.53
n-Propylbenzene	88	4.70	1.58	33.62
p-Ethyltoluene	88	6.44	2.43	37.73
1,3,5-Trimethylbenzene	78	3.33	0.67	20.12
o-Ethyltoluene	60	2.20	0.40	18.18
1,2,4-Trimethylbenzene	36	7.80	1.54	19.74
1-Decene	74	7.83	1.00	12.77
n-Decane	54	2.37	0.35	14.77
1,2,3-Trimethylbenzene	62	3.20	0.99	30.94
p-Diethylbenzene	48	3.36	0.94	27.98
Tridecene	24	2.34	0.25	10.68
Propyne	0	-	-	-
1-Pentene	60	3.30	0.87	26.36
2-Methyl-1-butene	76	3.69	0.45	12.20
2-Methyl-2-butene	72	4.81	0.79	16.42
Cyclopentene	20	1.57	0.15	9.55
1-Hexene	20	2.67	0.20	7.49
1-Undecene	82	3.94	1.25	31.73
n-Tridecane	20	1.03	0.11	10.68
1-Octene	40	2.81	0.29	10.32
m-Ethyltoluene	50	1.97	0.13	6.60
n-Undecane	70	2.94	0.67	22.79
Dodecene	36	2.34	0.36	15.38
Tetradecene	0	-	-	-
2-Ethyl-1-butene	0	-	-	-
n-Dodecane	46	0.56	0.55	98.21

Table 11-6. Duplicate Statistics for 1991

Compound	Duplicate Pairs	Overall Mean ppbv	Pooled Standard Deviation ppbv	Pooled %CV
Ethylene	45	29.18	9.84	33.72
Acetylene	45	13.95	6.43	46.09
Ethane	45	37.21	8.94	24.03
Propylene	46	16.47	3.36	20.40
Propane	46	46.98	6.42	13.67
Isobutane	46	21.76	2.45	11.26
1-Butene + Isobutene	46	6.84	1.49	21.78
1,3-Butadiene	31	3.19	0.35	10.97
n-Butane	46	40.49	2.99	7.38
t-2-Butene	38	3.32	0.46	13.86
c-2-Butene	34	2.76	0.49	17.75
Isopentane	46	53.18	3.63	6.83
n-Pentane	46	21.03	1.66	7.89
t-2-Pentene	39	4.26	0.62	14.55
c-2-Pentene	34	2.27	0.36	15.86
Cyclopentane	39	2.35	0.23	9.79
2,3-Dimethylbutane	45	4.88	4.65	95.29
Isohexane	46	14.71	1.59	10.81
3-Methylpentane	46	9.97	1.18	11.84
n-Hexane	46	12.85	1.58	12.30
Methylcyclopentane	46	6.22	0.43	6.91
2,4-Dimethylpentane	35	2.64	0.23	8.71
Benzene	46	14.44	1.46	10.11
Cyclohexane	44	3.51	0.38	10.83
Isoheptane	43	4.18	1.07	25.60
2,3-Dimethylpentane	30	3.57	0.63	17.65
3-Methylhexane	45	5.04	1.24	24.60
1-Heptene	5	1.73	0.11	6.36
2,2,4-Trimethylpentane	44	7.99	0.69	8.64
n-Heptane	45	5.07	0.61	12.03
Methylcyclohexane	42	4.13	0.44	10.65
2,2,3-Trimethylpentane	32	2.10	0.26	12.38
2,3,4-Trimethylpentane	42	3.03	0.30	9.90
Toluene	46	35.17	2.95	8.39
3-Methylheptane	37	2.68	0.39	14.55