NITROGEN DIOXIDE TRENDS IN SELECTED CHATTANOOGA COMMUNITIES

Ву

C.E. Decker and T.M. Royal Research Triangle Institute Research Triangle Park, N.C. 27711

Contract No. 68-02-1737

Project Officer

William F. Barnard
Exposure Assessment Branch
Population Studies Division
Health Effects Research Laboratory
Research Triangle Park, N.C. 27711

Y - Alticon - A, No 2000

U.S. ENVIRONMENTAL PROTECTION AGENCY OFFICE OF RESEARCH AND DEVELOPMENT HEALTH EFFECTS RESEARCH LABORATORY RESEARCH TRIANGLE PARK, N.C. 27711

DISCLAIMER

This report has been reviewed by the Health Effects Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

The many benefits of our modern, developing, industrial society are accompanied by certain hazards. Careful assessment of the relative risk of existing and new man-made environmental hazards is necessary for the establishment of sound regulatory policy. These regulations serve to enhance the quality of our environment in order to promote the public health and welfare and the productive capacity of our Nation's population.

The Health Effects Research Laboratory, Research Triangle Park conducts a coordinated environmental health research program in toxicology, epidemiology, and clinical studies using human volunteer subjects. These studies address problems in air pollution, non-ionizing radiation, environmental carcinogenesis and the toxicology of pesticides as well as other chemical pollutants. The Laboratory develops and revises air quality criteria documents on pollutants for which national ambient air quality standards exist or are proposed, provides the data for registration of new pesticides or proposed suspension of those already in use, conducts research on hazardous and toxic materials, and is preparing the health basis for non-ionizing radiation standards. Direct support to the regulatory function of the Agency is provided in the form of expert testimony and preparation of affidavits as well as expert advice to the Administrator to assure the adequacy of health care and surveillance of persons having suffered imminent and substantial endangerment of their health.

In an effort to document the health effects attributable to atmospheric nitrogen dioxide, the Health Effects Research Laboratory of the Environmental Protection Agency established an aerometry network in Chattanooga, Tennessee. This area was chosen because a point source for nitrogen oxides, a trinitrotoluene, TNT, plant is located just beyond the northeastern fringes of the city. As a by-product if the TNT production process, substantial atmospheric concentrations of oxides of nitrogen are emitted and are generally channeled between the ridges of the Appalachian foothills running north and south. Because of local meteorological conditions and topography, and the frequency of thermal inversions, the situation is often aggravated and the pollutants become trapped in the valley.

This report describes the air monitoring program in Chattanooga from June 1974 until June 1976. It discusses not only the sampling techniques but presents data showing the reduction in the levels of NO₂.

hn H. Knelson, M.D.

Director,

Health Effects Research Laboratory

ABSTRACT

The objectives of this project were to operate air monitoring stations and collect air quality data in the Chattanooga, Tennessee area to support epidemiological studies during the period June 15, 1974 to June 14, 1976. This ongoing project was begun in 1969 under the sponsorship of the U.S. Environmental Protection Agency and was designed to gather air quality data for use in studies relating health effects to ambient concentrations of oxides of nitrogen. Initially, the aerometric program consisted of particulate (high volume method) and nitrogen dioxide (CHESS bubbler method) measurements at ten stations located in and about the Chattanooga area. In 1972 Research Triangle Institute upgraded the aerometric monitoring program in Chattanooga through a joint project sponsored by the Environmental Protection Agency and the Coordinating Research Council. Chemiluminescent $NO-NO_x-NO_y$ analyzers and data acquisition systems were installed in environmentally-controlled shelters at seven of the nine monitoring sites operating at that time. Research Triangle Institute has operated and maintained the nine-station monitoring network and provided aerometric data to the Environmental Protection Agency under Contract 68-02-1737 through May 1976.

TABLE OF CONTENTS

		Page
ABSTRAC	т	i
LIST OF	FIGURES	v
LIST OF	TABLES	vi
AC KNOWL	EDGMENT	viii
Section		
1.0	INTRODUCTION	1
	1.1 Background/Objective/Summary	1
	1.2 Aerometric Measurement Program	2
2.0	SITE LOCATIONS	5
3.0	DESCRIPTION OF INSTRUMENTATION/FACILITIES	9
	3.1 Shelters/Ambient Air Sampling System	9
	3.2 Chemiluminescent NO-NO _x -NO ₂ Analyzers	9
	3.3 Calibration Technique/Apparatus	12
	3.4 Data Acquisition Systems	14
4.0	OPERATIONAL PROTOCOL	17
5.0	PROCESSING OF FIELD DATA	19
6.0	DATA VALIDATION AND QUALITY CONTROL	23
7.0	SUMMARY OF NITROGEN DIOXIDE DATA (September 1972 to	
	June 1976)	25
	7.1 Data Recovery	36
	7.2 Observations and Conclusions	38
8.0	REFERENCES	41
Appendi	xes	
Α.	OPERATING PROCEDURES FOR CHEMILUMINESCENT ANALYZERS AND DATA ACQUISITION SYSTEMS	43
В.	DETAILED CALIBRATION PROCEDURES (BENDIX NO-NO _X -NO ₂ ANALYZER)	51
C.	DETAILED MAINTENANCE PROCEDURES (BENDIX NO-NO _x -NO ₂ ANALYZER)	55

LIST OF FIGURES

Figure		Page
1	Site locations	7
2	Shelter exterior	10
3	Shelter interior	11
4	Schematic diagram of Bendix NO-NO -NO analyzer and data acquisition scheme	12
5	Gas phase titration system for calibrating NO-NO -NO analyzers	13
6	Photograph of Metrodata DL-630-3 data logger and remote control unit	15
7	Functional diagram of Metrodata DL-630-3 and remote control unit	16
8	Data processing flow chart	20
9	Hourly and 24-hour average data printout	21
10	Graphical presentation of quarterly mean NO concentrations for site 0621	29
11	Graphical presentation of quarterly mean NO concentrations for site 0622	30
12	Graphical presentation of quarterly mean NO ₂ concentrations for site 0631	31
13	Graphical presentation of quarterly mean NO ₂ concentrations for site 0632	32
14	Graphical presentation of quarterly mean NO ₂ concentrations for site 0633	33
15	Graphical presentation of quarterly mean NO ₂ concentrations for site 0634	34
16	Graphical presentation of quarterly mean NO ₂ concentrations	35

LIST OF TABLES

<u>Table</u>		Page
1	Sampling site locations and coordinates	6
2	Annual NO ₂ arithmetic means	26
3	Ratio of annual NO ₂ arithmetic means	27
4	Quarterly mean NO ₂ concentrations (µg/m ³)	
5	Ratio of quarterly mean NO ₂ concentrations $(\mu g/m^3)$	36
6	Percent of valid NO ₂ data by year	37

ACKNOWLEDGMENTS

The work on this project was performed by personnel in the Environmental Measurements Department, Systems and Measurements Division, Research Triangle Institute for the U.S. Environmental Protection Agency under Contract 68-02-1737 during the period June 15, 1974 to June 14, 1976. Mr. C. E. Decker, Manager, Environmental Measurements Department, was the Project Leader and responsible for the coordination and conduct of the program. Mr. T. M. Royal, Mr. R. W. Murdoch, and Mrs. B. A. Grimes participated in the data acquisition program in Chattanooga. Mr. Royal provided technical support for calibration and operation of instrumentation, data processing and validation; Mr. Murdoch performed field calibrations and repaired instrumentation; and Mrs. Grimes served as the RTI coordinator, on-site in Chattanooga and supervised the day-to-day operations of the network.

The Research Triangle Institute acknowledges the cooperation and assistance of Messrs. F. B. Benson, Jr., W. B. Steen, R. C. Dickerson, W. F. Barnard, and K. D. Kyle--Health Effects Research Laboratory, Environmental Protection Agency; Messrs. J. B. Cole and W. H. Pope--Chattanooga State Technical Community College; and the citizens and organizations in Chattanooga that provided the sites for the aerometric program.

1.0 INTRODUCTION

1.1 Background/Objectives/Summary

The following technical report describes the efforts and activities for operating an air monitoring program in Chattanooga, Tennessee, during the period June 15, 1974, through June 14, 1976. The ongoing project was begun in 1969 under the sponsorship of the U.S. Environmental Protection Agency (EPA) and was designed to gather air quality data in the Chattanooga area and examine health effects attributable to atmospheric oxides of nitrogen. 1,2/ This study was designed to investigate the effects of atmospheric NO $_2$ in a community exposed to a large stationary source (i.e., Volunteer Army Munitions Plant). Initially, the aerometric monitoring program consisted of particulate (high volume method) and nitrogen dioxide (NO $_2$) (CHESS bubbler method) measurements at 10 monitoring sites located in and about the Chattanooga area. Continuous NO $_2$ measurements were recorded at two stations using the Technicon Air Monitor II (Saltzman Method). Operation of the air monitoring network was conducted for EPA by the Chattanooga State Technical Community College.

In September 1972 Research Triangle Institute participated in a joint EPA-Coordinating Research Council (CRC) program to upgrade the aerometric monitoring program by incorporation of chemiluminescent NO-NO,-NO, analyzers and data acquisition systems in shelters at seven of the nine monitoring sites operating at that time in Chattanooga. $\frac{3}{}$ The motivating factor behind this program involved questions raised with respect to the accuracy and validity of NO, data collected over the past decade by the Federal Reference Method for monitoring NO, in ambient air (i.e., modified Jacob-Hochheiser Method). Investigations conducted by EPA and by various organizations 4-6/ had shown that the reference method possessed inherent deficiencies. The major objections to the reference method were the low and variable collection efficiency and the interference of nitric oxide with the measurement. Research Triangle Institute obtained and provided NO2 data using chemiluminescent NO2 analyzers to EPA under this program from September 1972 until December 14, 1973. On December 15, 1973, Research Triangle Institute was contracted by the Health Effects Research

Laboratory, EPA, Research Triangle Park, North Carolina, to assume the responsibility for the coordination and operation of the entire Chattanooga aerometric monitoring program. Funding for 6 months for the air monitoring program was provided to Research Triangle Institute under EPA Contract No. 68-02-0335, "Effects of Nitrogen Oxide Levels on Health Characteristics of Persons in Chattanooga, Tennessee."

On June 15, 1974, Contract No. 68-02-1737 was awarded to Research Triangle Institute to continue to operate and maintain air monitoring stations and collect air quality data in the Chattanooga area. Data acquisition was concluded on May 31, 1976. The aerometric network was dismantled, and all equipment was returned to Research Triangle Park, North Carolina, by June 14, 1976. This final report summarizes all activities related to the operation of the air monitoring program in Chattanooga under Contract No. 68-02-1737 during the period June 15, 1974, through June 14, 1976. To provide continuity, all relevant activities and chemiluminescent NO₂ data collected during the years 1973, 1974, 1975, and part of 1976 have been included in subsequent discussions.

1.2 Aerometric Measurement Program

The aerometric measurement program for the Chattanooga Health Effects Study as it existed in April 1972 consisted of NO $_2$ and particulate measurements from 10 monitoring sites located in and about the Chattanooga area. Twenty-four-hour integrated NO $_2$ and suspended particulate samples were collected at these stations using the CHESS modification of the Jacobs-Hochheiser Method and the High Volume Sampler Method. Continuous NO $_2$ measurements were recorded at two stations using the Technicon Air Monitor II (Saltzman Method). During the third quarter of 1972 the monitoring program was upgraded to include chemiluminescent NO-NO $_x$ -NO $_z$ monitoring instrumentation and data acquisition systems in shelters equipped to maintain the environment necessary to insure proper operation of the monitoring equipment at seven of the nine monitoring sites in Chattanooga. Sites were selected to include upgraded NO $_z$ monitoring facilities in high, medium, and low NO $_z$ exposure areas. The aerometric measurement

program was again modified in December of 1973. The major changes included the deletion of the Technicon Air Monitor II (continuous NO_2 measurements by the Saltzman Method) at stations 0632 and 0633 and the addition of RSP samplers at all nine sites.

Site locations and a description of the instrumentation and facilities are described in sections 2.0 and 3.0, respectively. The operational protocol and procedures used to obtain NO, and particulate data, computer programs used to process the field data, and data validation and quality control procedures used to insure the collection of quality data are presented in sections 4.0, 5.0, and 6.0. Although the Scope of Work for Contract 68-02-1737 required only that aerometric data (NO_2 and particulate) be collected and provided to the Environmental Protection Agency in computer-compatible format, Research Triangle Institute decided that a preliminary summary of the NO_2 data obtained during the program was warranted. A graphical presentation and description of chemiluminescent NO, data obtained during the calendar years of 1973, 1974, 1975, and the first 5 months of 1976 are presented in section 7.0. Detailed operating, calibration, and maintenance procedures used in this program are presented in Appendixes A, B, and C, respectively. Hardcopy printouts and magnetic tapes containing formatted hourly and 24-hour average chemiluminescent $\ensuremath{\text{NO}}_2$ data for the entire program have been provided to the project officer.

2.0 SITE LOCATIONS

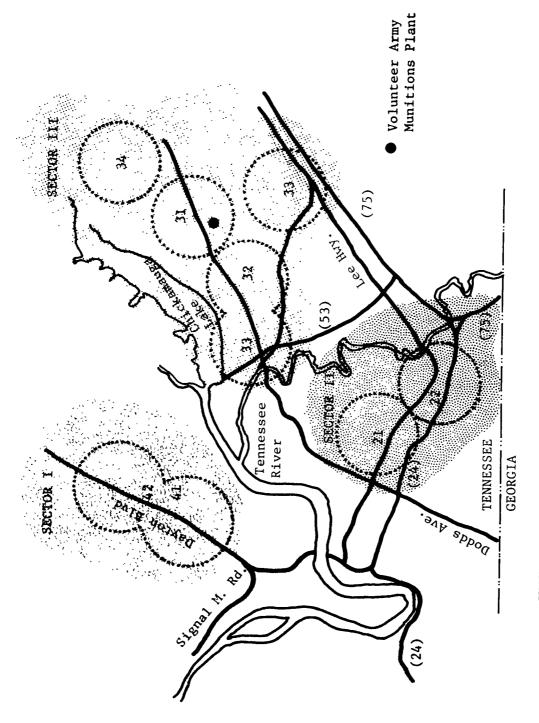
To provide continuity for the measurement program, EPA decided to retain the reference sampling site locations used in the original NO₂ study, ½ when upgraded facilities (i.e., 2.4-m by 3.7-m shelters, chemiluminescent NO-NO_x-NO₂ analyzers, and data acquisition systems) were installed at seven sites selected by the EPA project officer from the nine permanent monitoring sites operating in Chattanooga during the fourth quarter of 1972. Two of the nine sampling sites used 3- by 4-m shelters and contained high volume, RSP, and bubbler samplers. The addresses of the nine sampling sites and location coordinates obtained from U.S. Department of Interior Geological Survey Contour Maps are presented in table 1. The locations of the sampling sites with respect to the Volunteer Army Munitions Plant and the city of Chattanooga are shown in figure 1.

Table 1. Sampling site location and coordinates

Site No.	Address	Coordinates		
Site No.	Address	Latitude	Longitude	
0621*	Children's Home 421 Gillespie Avenue Chattanooga, Tennessee	35°01'47"	85°14'42"	
0622*	Jewish Community Center 5326 Lynneland Terrace Chattanooga, Tennessee	35°0'21"	85°13'14"	
0631*	Clark Road Harrison, Tennessee	35°06'37"	85°08'46"	
0632*	3729 Briarwood Drive Chattanooga, Tennessee	35°05'05"	85°11 ' 27''	
0633*	2708 Hickory Valley Road Chattanooga, Tennessee	35°03'40"	85°09'22"	
0634*	Loret Villa, Highway 58N 5 Miles Northeast of Chattanooga, Tennessee	35°08'21"	85°07'25"	
0635	4409 Murray Hills Drive Chattanooga, Tennessee	35°05'12"	85°12'26"	
0641*	3319 Dayton Boulevard Red Bank, Tennessee	35°06'37"	85°17'44"	
0642	Santeelah Road Red Bank, Tennessee	35°07'41"	85°17'00"	

^{*}Upgraded facility (2.3- x 3.7-m shelters, chemiluminescent NO-NO $_{\rm x}$ -NO analyzer, data acquisition system).

Obtained from U.S. Department of Interior Geological Survey Contour Maps.



CHATTANOOGA STUDY SECTORS AND MONITORING ZONES

Figure 1. Site locations.

3.0 DESCRIPTION OF INSTRUMENTATION/FACILITIES

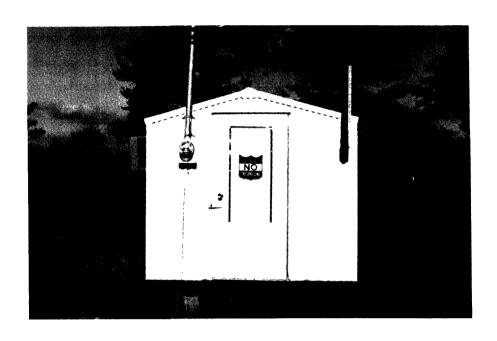
3.1 Shelters/Ambient Air Sampling System

The shelter used to house the instrumentation in seven of the nine air monitoring stations was a $2.3-\times3.7-\times2.3-m$ factory-assembled, aluminum-sided building. The building included an automatic switching 18,000 Btu heating/cooling unit, an electrical system to accommodate 240 V, single-phase service for the heating and cooling unit, 120 V circuits for fluorescent lights and wall receptacles inside and outside, an 8-ft instrument table and 5-ft workbench, and an air-sampling Pyrex glass manifold system. Pictures of the shelter exterior and interior complete with instrumentation are shown in figures 2 and 3.

The ambient air sampling system consisted of a cane (to prevent moisture and particulates from settling into the inlet), a particulate trap (glass bottle) to remove large suspended particulates, three 4-m sections of 3.8 cm o.d. glass manifold (one section having four sampling ports), and a blower. Ambient air was aspirated through the manifold by the blower at a rate of approximately 0.1 m³/min. Sampling ports made of 12/5 ball and socket joints were used for easy hookup of instrument inlet lines.

3.2 <u>Chemiluminescent NO-NO_-NO_2 Analyzers</u>

Bendix Model 8101-B chemiluminescent NO-NO $_{\rm x}$ -NO $_{\rm 2}$ analyzers equipped with teflon particulate filters (MACE FILTER) were used to monitor NO $_{\rm 2}$ concentrations at the seven stations indicated in section 2.0. The principle of operation of the Bendix analyzer is based on the chemiluminescent gas phase reaction between nitric oxide (NO) and ozone (O $_{\rm 3}$). A schematic diagram of the gas flow and detection system of the Bendix analyzer is shown in figure 4. The measurement of NO $_{\rm 2}$ concentrations by this instrument requires that NO $_{\rm 2}$ be reduced to NO prior to the reaction with O $_{\rm 3}$. The sum of the NO measurement plus that produced by reducing NO $_{\rm 2}$ to NO is the nitrogen oxide (NO $_{\rm x}$) concentration. Subtraction of the previous NO measurement from the NO $_{\rm x}$ measurement gives the NO $_{\rm 2}$ concentration. The chemiluminescent reaction is pressure dependent and the



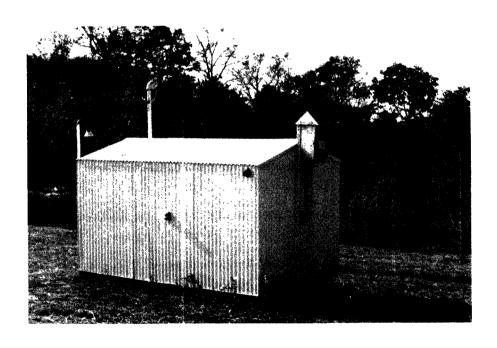


Figure 2. Shelter exterior.

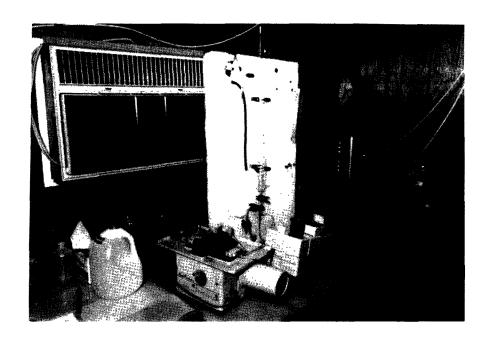




Figure 3. Shelter interior.

maximum absolute operating pressure of the Bendix analyzer is approximately 17.8 cm of mercury. At this pressure the minimum detectable concentration of the Bendix analyzer has been determined to be approximately 10 $\mu g/m^3$.

3.3 Calibration Technique/Apparatus

Due to problems associated with field use of NO $_2$ permeation tubes and the need to determine periodically the efficiency of the heated carbon converter (i.e., reduces NO $_2$ to NO), the gas phase titration procedure was used for routine dynamic calibration of the chemiluminescent NO-NO $_x$ -NO $_z$ analyzers. $\frac{7}{}$ The gas phase titration technique is based upon application

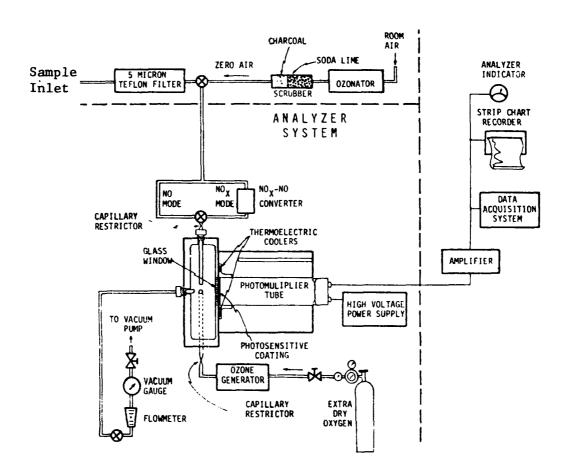


Figure 4. Schematic diagram of Bendix NO-NO $_{
m x}$ -NO $_{
m 2}$ analyzer and data acquisition scheme.

of the rapid gas phase reaction between NO and 0_3 to produce a stoichiometric quantity of NO $_2$. Nitric oxide from a cylinder of NO in NO $_2$ (100 ppm) was diuted with a constant flow of clean air to provide 0.5 ppm and used to calibrate the NO and NO $_{\rm x}$ channels of the chemiluminescent NO-NO $_{\rm x}$ -NO $_2$ analyzer. By incorporation of a calibrated ozone generator in the calibration apparatus upstream from the point of NO addition, precise NO $_2$ concentrations can be generated by oxidation of NO to NO $_2$ with 0_3 . As long as a slight excess of NO is present, the concentration of 0_3 added is equivalent to the concentration of NO consumed, and is equivalent to the concentration of NO $_2$ generated. A diagram of the gas phase titration apparatus used in this program for calibration of the NO $_2$ analyzers is shown in figure 5.

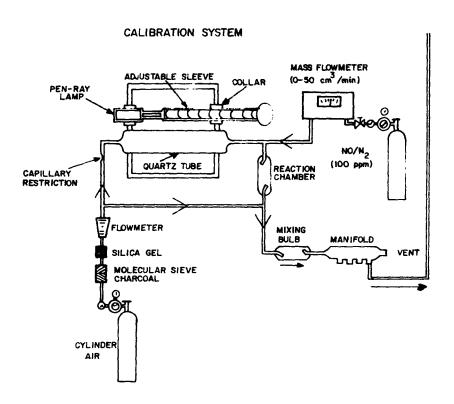
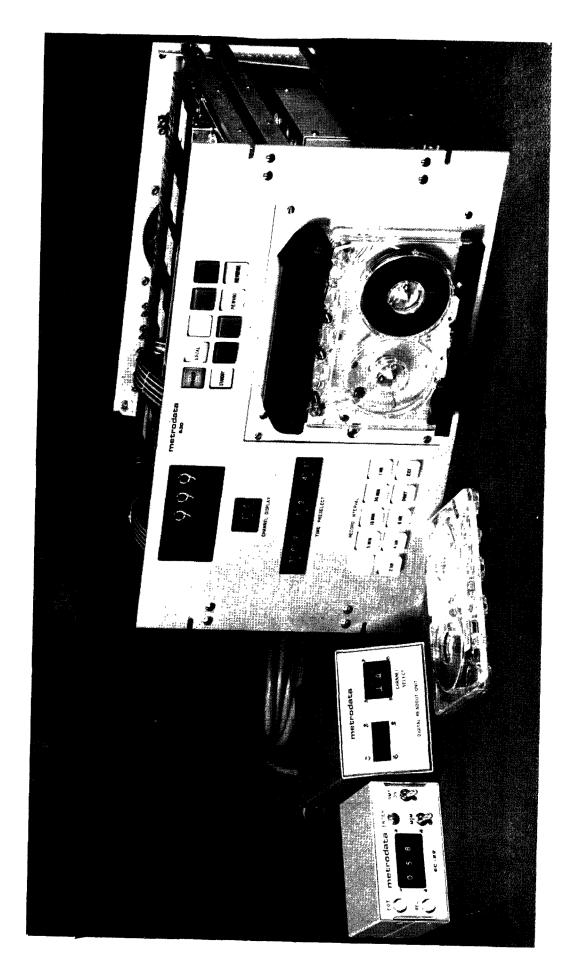


Figure 5. Gas phase titration system for calibrating $NO-NO_x-NO_2$ analyzers.

Primary calibration of the NO concentration in the pressurized cylinders containing nitrogen as a diluent was accomplished initially by gas phase titration and later by reference to a primary standard of NO in nitrogen (National Bureau of Standards SRM-1684). Once the NO concentration in a cylinder had been determined, the cylinder could be used over its lifetime to provide a working standard for routine calibration;—/ however, to insure validity of data, the NO concentration was reverified at 2-month intervals.

3.4 Data Acquisition Systems

The Metrodata Model DL-630-3 data logger was used to acquire and store data on magnetic tape. The data logger is a complete data acquisition system that records on magnetic tape 25 channels of analog data plus a time code, station identification, and manual data entry. Data are recorded on magnetic tape at 5-minute intervals. Manual data can be entered immediately upon actuation of the switch on a manual data unit (EC-22) which initiates the recording of one scan. A photograph of the data logger with the remote control unit is shown in figure 6. The data logger is shown without a cabinet (cabinets were installed on all units). A functional diagram of the data logger system is shown in figure 7. The system can be interrogated remotely from a control site through a voice grade telephone line and standard telephone data couplers. The interrogation feature was utilized initially, but was deleted after the RTI coordinator was located in Chattanooga in June of 1974.



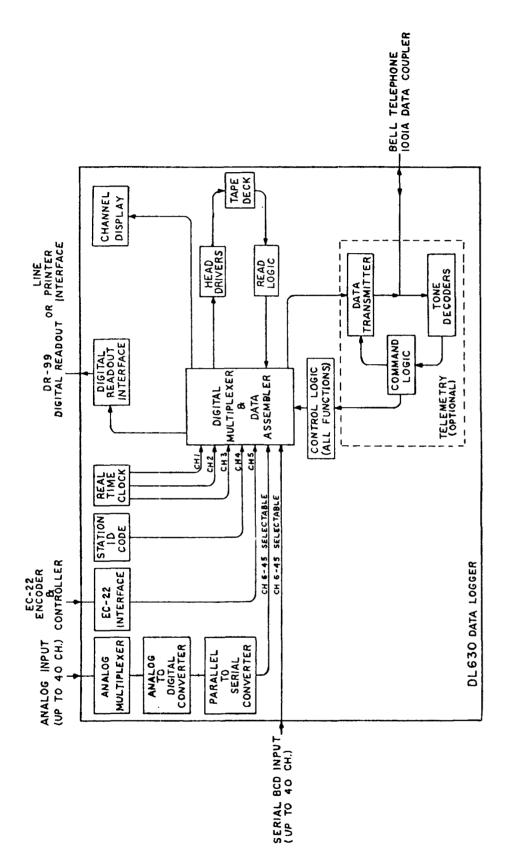


Figure 7. Functional diagram of Metrodata DL-630-3 data logger and remote control unit.

4.0 OPERATIONAL PROTOCOL

During the period of performance of Contract 68-02-1737 (June 15, 1974 to June 14, 1976), the following protocol was used to operate and maintain the aerometric measurement program in Chattanooga. Chattanooga State Technical Community College operators under the supervision of Mrs. Bobbie Grimes, RTI coordinator in Chattanooga, performed the daily tasks required to operate and maintain the aerometric measurement program. High volume, RSP, and NO₂ bubbler samples were collected on a daily basis and forwarded to Rockwell International, Thousand Oaks, California, for analysis. Maintenance procedures were implemented for samplers and equipment as specified in the Operational Procedures supplied by EPA.

Daily procedures associated with operation of the chemiluminescent analyzers and data acquisition systems included zeroing of the analyzer, strip chart recorder annotation, data logger time/date check, and analyzer log entry. Magnetic tapes for the data acquisition systems were replaced and returned with tape logs and analyzer data sheets via air mail to RTI for data processing on a weekly schedule. Oxygen cylinder pressure, instrument cell pressure, measurement range, and other operational status checks were recorded on the analyzer data sheet to facilitate assessment of instrument performance.

Chemiluminescent analyzers were zeroed daily and spanned once per week. A multipoint calibration was performed on a routine basis every 3 weeks. Nonroutine calibrations were performed whenever a replacement analyzer was set up or whenever testing was required to determine malfunctions or questionable instrument performance. During each calibration period, the converter efficiency (NO $_2 \rightarrow$ NO) of the analyzer and span drift from the previous calibration period were determined. Calibration data were compared with previous data to determine long-term drift for data quality control. Nitrogen dioxide data were also recorded on strip chart recorders, which served as backup recording systems in case of failure of the data acquisition systems. Data from the strip chart recorders were also used for validation purposes to insure that the data integrity was maintained throughout the data processing sequence of events.

5.0 PROCESSING OF FIELD DATA

In this program, field data were recorded as digital voltages on magnetic tape cassettes, which were forwarded to RTI weekly for processing. Field data were translated by RTI personnel using EPA's Metrodata Translator and temporarily stored on nine track magnetic tape for the various processing phases required to convert digital voltages to concentration units $(\mu g/m^3)$ and produce both a computer-compatible data tape and a hardcopy printout. The flow diagram shown in figure 8 describes the treatment of the data from the time magnetic tape cassettes were received until a printout of data in various useful forms was obtained.

The tape translator extracts edited data records from logical records on field tapes. The translator is programmed to count the number of characters in each logical record in the tape-reading routine. The edit and flag program verifies data within a given range, time, station identification, and valid manual data entry codes. The transfer equation program converts instrument voltage to the appropriate concentration units (i.e., ppm or $\mu g/m^3$). The general form of the transfer function utilized in the program was

Concentration =
$$m(v - v_0)$$
.

The output of this program was a tape and printout of 5-minute data.

The merge and average data program allows hourly averages from strip chart records to be inserted as required and combined with existing data to yield 24-hour average concentration values. A tape was generated in this program for future use. A typical printout of the merge and average program is shown in figure 9. Ten days of hourly averages are printed per page for each site.

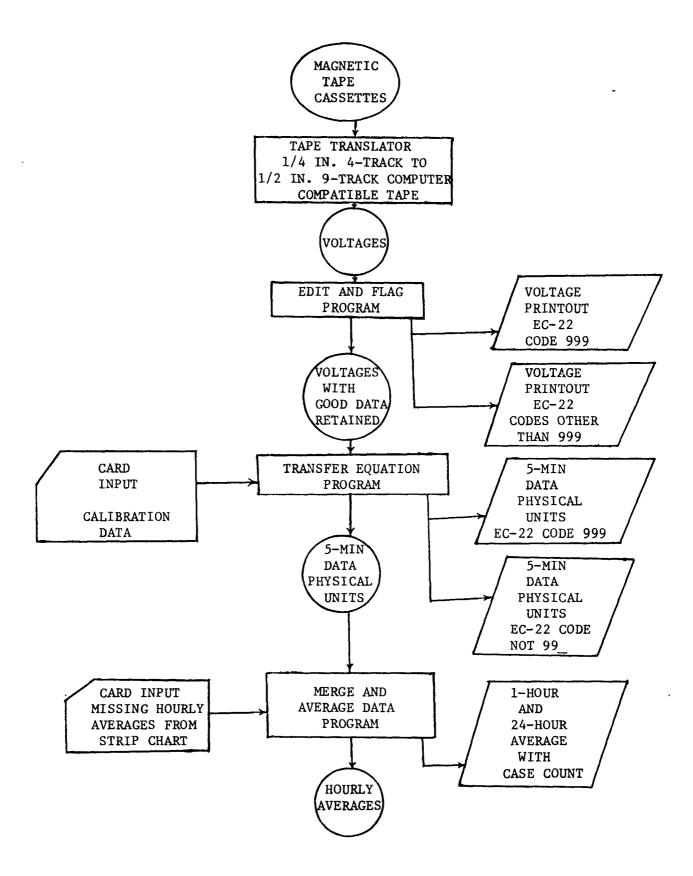


Figure 8. Data processing flow chart.

2		:	:	ري ا	47600F 3	AVERAUFS ((2**//5:				
31 (***) 1					C	EA9 197					
40.5 40.5	:۔	÷.	Q.	A	A	-1	·4		٠,	ĺ.	4
40.5 39.5 37.9 37.9 37.9 37.9 37.9 37.9 37.9 37.9					4	0	0				<u>_</u>
45.1 45.1 45.2 45.2 45.2 45.3 45.2 45.4 45.5 45.6 45.7	_	0	6	7.	•	~	•	•	1		•
45.2 45.2 45.2 45.2 45.2 45.3 45.4 45.5 45.6 45.6 45.7 46.7 46.7 46.7 46.7 46.7 46.7 46.7 46.7 46.7 47.7 47.7 47.7 47.7 47.7 47.7 47.7 47.7 47.7 47.7 47.7	ں بر	v.	Ġ	۵.	0	'n	•	•		٠,	,
75.5 71.7	30	, M	5	~		ċ	•	•		٠.	
71.7 20.2 40.9 40.5 40.5 7.0 1 40.5 10.1 10.1 10.1 10.1 10.1 10.1 10.1 1	1	٠,	٠.	۰.	4		•	•	• • ⊶		•
33.8 34.7 34.7 34.7 41.4 44.6	S C	ä	٠ :	0	9.	5	•				•
73.7 12.4 34.3 41.9 56.4 70.7 47.0 22.0 4.6 22.4	S	~,	ė	ж ж	٠,	٧.	7.		٠,	•	•
45.1 23.6 44.2 50.4 69.6 24.4 4 4.6 82.5 82.6 41.4 10.9 10.9 10.9 10.9 10.9 10.9 10.9 10.9	<u>ر</u>			ສໍ		٠,	·	•	٠	•	٠,
#4.9 #1.4 72.1 \$60.2 \$2.6 \$2.7 \$ \$2.6 \$2.7 \$	c.	เม	٠ د	4	ပ	ò	4	•	· /	•	4
# # # # # # # # # # # # # # # # # # #	ŝ	3.	-	2	·	~	۶.	•	•	7.	• د.
70.8 43.c 19.3 127.9 10.9 16.9 5.7 7.4.7 7	ت	4	•	73.	÷	<u>ت</u> •		•	• زم	174	٠,
74.0 10.7 99.6 10.9 15.0 7.4 10.8 10.8 10.8 20.9 20.0 7.4 10.8 10.8 10.8 10.8 10.8 10.8 10.8 10.8	יי	5	^{ال}	6.	27.	0	ŝ	•	•	•	3
26.6 13.7 41.4 18.8 999.9 2.0.4 44.4 10.8 11.9 11.0 11.0 11.0 11.0 11.0 11.0 11.0	ر	4.	ъ ъ	ė	.66	•	3.	•	ر	٠	.5
26.5 14.7 11.9 10.8 19.6 17.2 14.8 16.7 10.8 10.8 10.8 10.8 10.8 10.8 10.8 10.8	S	ŗ.	Ġ	~	÷	å	99.		•	o	•
18.8 21.e 12.6 15.0 20.7 10.8 14.3 15.0 14.3 15.0 14.3 15.0 14.3 15.0 14.3 15.0	4	٠ د	4	÷	•	an an	.60	<i>.</i> .	•	•	• ئ
10.1 30.2 14.3 13.2 14.8 13.5 11.0 10.6 17.0 10.6 17.0 10.6 17.0 10.3 10.9 20.7 20.0 20.0 20.0 20.0 20.0 20.0 20.0	υ Ο	x,	ä	ċ	ů.	·	ò	٠	•	• J	3
25.6 39.2 21.4 11.3 15.3 15.9 2.7 16.9 20.7 20.7 20.7 20.7 20.7 20.7 20.7 20.7	C	٥	ċ	4.	٠ <u>.</u>	· ၁	÷	•	•,	i	•
74.5 46.9 29.3 13.2 13.3 3.5 3.0 50.7 70.7 70.7 70.7 70.7 70.7 70.7 70	7 û	'n	ċ	-	, 4		٥	•	ن	.*	÷
20.4 31.7 51.4 20.7 20.7 35.7 21.4 79.0 6.17 175.4 12.7 45. 24.0 75.3 104.0 50.7 79.0 6.17 125.4 12.7 94.0 54.5 70.2 104.0 62.0 16.9 116.4 9.0 114.7 12.7 10.7 94.0 65.1 65.1 65.1 15.6 97.8 9.4 92.1 3.4 12.7 12	()	4.	٠.	ċ	۳,	. - ,	٠ <u>,</u>	٠	• د	,	5
24.0 75.1 173.9 47.0 20.7 79.0 6n 175.4 12:0 PC. 54.5 75.5 104.0 104.0 1104.4 90 1104.7 10.1 94.6 PC.2 70.2 104.7 10.1 15.5 104.0 104.7 10.1 15.5 104.7 10.1 15.5 104.7 10.1 15.5 104.7 104.	7	٠ ت	÷	÷	0	ů.	ς.	•	,	,	ċ
54.5 75.5 104.0 62.0 16.9 118.4 9.19 134.7 10.7 94.6 65.2 70.2 101.7 92.1 15.5 101.5 7.0 10.7 10.7 10.7 10.7 10.7 10.7 10.7	္	4	'n	٦3.	:	Ġ	٠ ک	•	31 12	٠,	÷
65.2 70.2 15.5 13.5 13.5 12.6 38.7 65.1 65.4 97.8 9.4 92.1 3.4 12. 13. 64. 43.7 36.4 75.7 84.6 9.4 90.2 77.1 77.0 13. 47. 74 24 24 24 24 24 74. 74. 74. 74. 85.5 34.3 53.3 54.7 77.3 74.9 4 74. 74.	7	4	ŝ	с 4	ċ	ò	10.		4.	:	4
38.7 65.1 75.6 97.8 9.4 92.1 3.4 7.5 15. 54. 43.7 36.4 75.7 84.6 5.4 90.2 7.1 77.5 15. 47. 74 24 24 24 32 7.1 77.5 34.9 4.1 45.6 5.1 35.	ပ (V	د،	0	<u>.</u>	·	٠ د کا	į	•	().	بد	,
43.7 36.4 75.7 84.6 5.4 90.2 7.1.1 77.0 75. 47. 77. 37.3 74.9 4.1 45.0 7.1 50.0 50.0 50.0 50.0 50.0 50.0 50.0 50	ς,	à	ż	ر	7	Ċ	·	٠	ن		•
74 24 24 24 24 25 24 24 25 24 24 25 25 25 25 25.5 3d·) 53·3 54·7 27·3 34·9 d·· dɔ·c oɔ·c sui	4	* ,	•	ż	4	•	0	•	•	11	
35.5 30.3 53.3 54.7 27.3 34.9 4 15.0	CLUNT						3.5			.	
	V5.kAGE	Ġ		3.	4	7	4		15	•	30.5

Figure 9. Hourly and 24-hour average data printout.

6.0 DATA VALIDATION AND QUALITY CONTROL

In order to achieve and maintain a high level of data confidence, it was essential to routinely monitor as many instrument parameters as feasible and to maintain appropriate records. Quality control for this program included verification of calibration cylinder concentrations, performing dynamic calibration at specified intervals, maintaining adequate records that describe instrument performance, and thorough training of field operators. Equipment deficiencies and failures were promptly corrected, and new operational parameters were added when feasible to alert field operators for degradation of performance.

Calibration data were examined for excessive zero and span drift. If the zero drift exceeded \pm 1 percent of full scale (\pm 9.4 $\mu g/m^3$ NO $_2$) per 24-hour period, the data of the preceding 24-hour period were of questionable validity and action was taken to determine the cause. Span drift was determined from span calibration data each week. Span drift exceeding \pm 10 percent of full scale per week was usually associated with instrument malfunction, and the previous week's data were invalidated.

Quality assurance performance audits were conducted periodically at each station during the reporting period by EPA and an independent RTI auditing team. The results of these audits have been documented in the quarterly reports submitted to the project officer. All audit results were satisfactory (i.e., analyzer response was within 10 percent of the audit concentration. No data were invalidated due to results of any performance audit. National Bureau of Standards SRM (NO in nitrogen, NO permeation tubes) and gas phase titration were used to generate reference concentrations of NO and NO 2.

To verify data logger accuracy, a constant voltage data input standard was recorded every 5 minutes in conjunction with the NO₂ analog data. It was not necessary to delete any ambient air data due to analog-to-digital conversion errors.

At the completion of each computer program set, the processed data were compared with strip chart data for selected periods. More intensive data checks were performed against strip chart and operational records

after the hourly averages program. A typical check included comparison of computer-processed data and strip chart data for two selected 1-hour averages per day. The recorded data on strip charts were edited for signs of equipment malfunctions, excessive pollutant levels, or unusual diurnal patterns.

Data quality is a function of instrument and operator errors plus small additional inaccuracies in the calibration system. The maximum error resulting from the calibration procedures was estimated to be less than \pm 7 percent.

Data confidence near zero pollutant level is estimated to be in error by less than \pm 9.4 $\mu g/m^3$, while at levels greater than 50 $\mu g/m^3$ the error was estimated to be less than 5.0 percent of the measurement level.

7.0 SUMMARY OF NITROGEN DIOXIDE DATA (January 1973 to June 1976)

The Scope of Work for contract 68-02-1737 required only that NO $_2$ data be collected by the chemiluminescent method and provided in hard copy and computer-compatible format to the Environmental Protection Agency. Therefore, computer programs were written only to routinely process NO $_2$ data, as shown in figure 9. However, certain observations and analyses were performed manually, using NO $_2$ data obtained from January 1973 to May 1976, and are as follows:

- 1. Annual arithmetic means (1973, 1974, 1975, January-May 1976),
- Ratio of arithmetic means,
- 3. Quarterly means,
- 4. Ratio of quarterly means, and
- Percent data recovery by station (1973, 1974, 1975, January-May 1976).

These observations and results are summarized in the following paragraphs. Whenever appropriate, results are shown graphically as well as in tabular form.

Annual arithmetic means were computed for each monitoring station and are presented in table 2 for 1973, 1974, 1975, and January-May 1976. These data show a substantial reduction in NO, exposure levels in the Chattanooga areas where the sampling sites are located when compared to the mean NO, data reported in the original 1968-1969 Chattanooga Study. $\frac{1}{2}$ Mean NO, concentrations decreased approximately 36 percent in sector I, approximately 56 percent in sector II, and approximately 68 percent in sector III when data for 1973 were compared with data reported for the original study. The most dramatic decrease in mean NO_2 concentration occurred at site 0631located nearest the Volunteer Army Munitions Plant. The significant decrease in NO, concentration at site 0631 from 1974 to 1975 can be correlated with a slowdown in TNT production and installation of control equipment at the Volunteer Army Munitions Plant. The lowest annual mean was observed during all years at site 0634. Site 0634 was located in a rural area northeast of Chattanooga and used as a control site. The data presented in table 2 clearly indicate that the ${
m NO}_{
m p}$ ambient air quality standard

Table 2. Annual NO₂ arithmetic means $(\mu g/m^3)$

	Annual	NO ₂ Arithme	etic Mean ((μg/m ³)	
Site No.	1973	1974	1975	1976*	
0621	42.9	42.7	35.6	41.5	
0622	63.8	49.4	46.1	46.2	
0631	58.0 [†]	76.3	40.5	38.9	
0632	43.2	45.9	32.5	37.8	
0633	37.9	39.1	26.6	31.2	
0634	33.5	34.9	23.2	23.8	
0641	54.9	45.8	40.4	46.9	

^{*5-}month mean (January 1-May 30, 1976)

of 100 $\mu g/m^3$ was not approached at any monitoring station during any of these reported years. In general, NO₂ concentrations have remained almost constant at site 0621; have decreased at site 0622 in 1974, 1975, and 1976; have decreased substantially from 1973 to 1976 at sites 0631, 0632, 0633, and 0634 (these four sites are directly affected by emissions from the VAM Plant); and have decreased slightly at site 0641. Sites 0622 and 0641 are both located near busy roadways and should correlate with and be affected by local traffic.

Ratios of arithmetic means between sites for each year are presented in table 3. The ratios presented in this matrix allow the reader to quickly compare mean values between respective sites.

Quarterly mean NO₂ concentrations were computed for each site for 1973, 1974, 1975, and January-May 1976 and are presented in table 4. These data are also presented in graphical form in figures 10-16. Data for the fall quarter of 1972 were retrieved and are included to show the

[†]Volunteer Army Munitions Plant on strike (January-March 1973)

Table 3. Ratio of annual ${\rm NO}_2$ arithmetic means

Site No.	Year	0621	0622	0631	0632	0633	0634	0641
0621	1973	1.00	1.49	1.35	1.01	0.88	0.78	1.28
	1974	1.00	1.16	1.78	1.07	0.91	0.82	1.07
	1975	1.00	1.29	1.13	0.91	0.75	0.65	1.13
	1976*	1.00	1.35	0.94	0.91	0.75	0.57	1.13
0622	1973		1.00	0.90	0.67	0.59	0.52	0.86
	1974		1.00	1.54	0.93	0.79	0.71	0.92
	1975		1.00	0.88	0.70	0.58	0.50	0.88
	1976*		1.00	0.69	0.67	0.55	0.42	0.83
0631	1973			1.00	0.75	0.65	0.58	0.95
	1974			1.00	0.60	0.51	0.46	0.60
	1975			1.00	0.80	0.66	0.57	1.00
	1976*			1.00	0.97	0.80	0.61	1.20
0632	1973				1.00	0.87	0.78	1.27
	1974				1.00	0.85	0.76	1.00
	1975				1.00	0.82	0.71	1.24
	1976*				1.00	0.82	0.63	1.24
0633	1973					1.00	0.88	1.45
	1974					1.00	0.89	1.17
	1975					1.00	0.87	1.52
	1976*					1.00	0.76	1.50
0634	1973						1.00	1.63
	1974						1.00	1.31
	1975						1.00	1.74
	1976 *						1.00	1.97
0641	1973							1.00
	1974							1.00
}	1975	1						1.00
	1976*					·		1.00

^{*5-}month mean (January 1-May 30, 1976).

effect of the shutdown of the VAM Plant on certain stations. Ratios of quarterly mean NO_2 concentrations between stations were also calculated and are presented in table 5. All ratios presented in table 5 were calculated in relation to the quarterly mean for site 0621. The effect or influence of the VAM Plant shutdown can be seen in table 4 (i.e., site 0631 quarterly mean of 22.2 $\mu\mathrm{g/m}^3$ for the first quarter of 1973) and in

Table 4. Quarterly mean NO_2 concentrations $(\mu g/m^3)$

				<u>_</u>				
Year	Quarter*				Site No.			
lear	Vuarter*	0621	0622	0631	0632	0633	0634	0641
1973	1	40.2	59.3	22.2	36.4	26.2	23.4	53.4
	2	38.3	64.0	63.0	45.2	28.5	32.4	66.2
	3	51.3	70.5	65.3	39.6	43.1	42.2	49.2
	4	41.7	61.4	81.7	51.4	53.7	35.8	50.7
1974	1	49.5	61.1	90.7	48.7	42.7	45.3	51.7
!	2	39.4	54.4	71.2	37.6	34.0	30.6	49.7
	3	36.5	45.3	70.0	44.0	37.0	28.6	44.7
<u> </u> 	4	45.2	37.4	71.6	52.0	42.6	33.4	36.9
1975	1	31.9	38.0	38.1	21.9	27.2	25.4	36.5
	2	39.9	55.6	44.3	35.6	28.2	22.9	43.0
	3	34.7	44.9	33.6	34.5	21.4	15.2	35.8
	4	35.5	45.4	45.6	37.4	31.0	23.2	45.3
1976	1	40.6	56.4	37.4	40.1	35.0	24.6	46.4
	21	42.4	56.0	40.3	35.4	27.4	22.9	47.3

^{*}Quarter 1 - January-March; Quarter 2 - April-June; Quarter 3 - July-September; Quarter 4 - October-December.

[†]April-May data only.

[†]VAM Plant Shutdown.

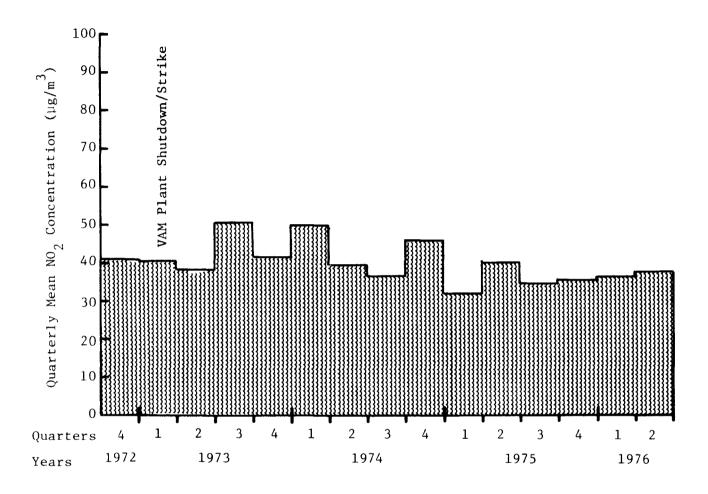


Figure 10. Graphical presentation of quarterly mean $\ensuremath{\text{NO}}_2$ concentrations for site 0621.

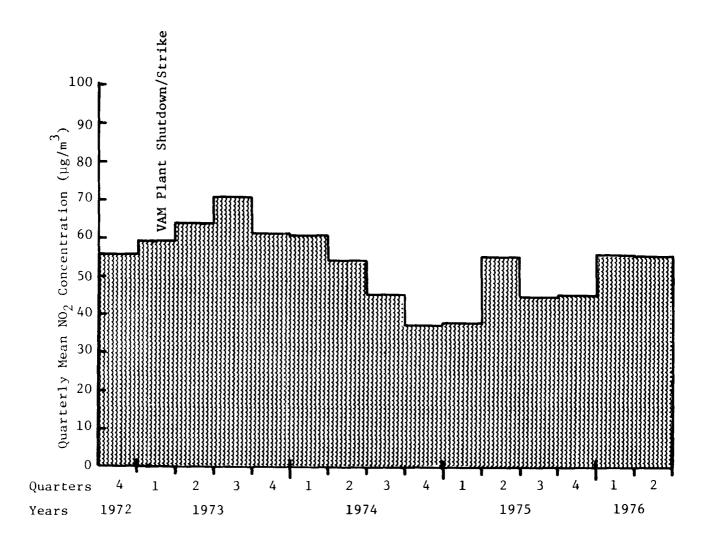


Figure 11. Graphical presentation of quarterly mean $^{\rm NO}2$ concentrations for site 0622.

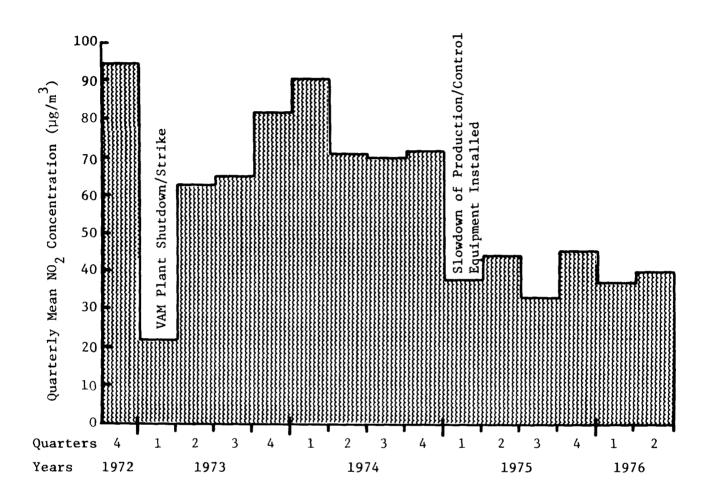


Figure 12. Graphical presentation of quarterly mean \mbox{NO}_2 concentrations for site 0631.

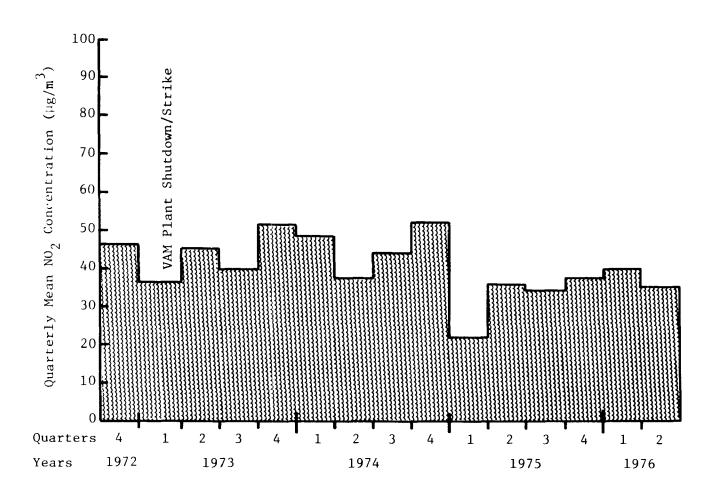


Figure 13. Graphical presentation of quarterly mean $\ensuremath{\text{NO}}_2$ concentrations for site 0632.

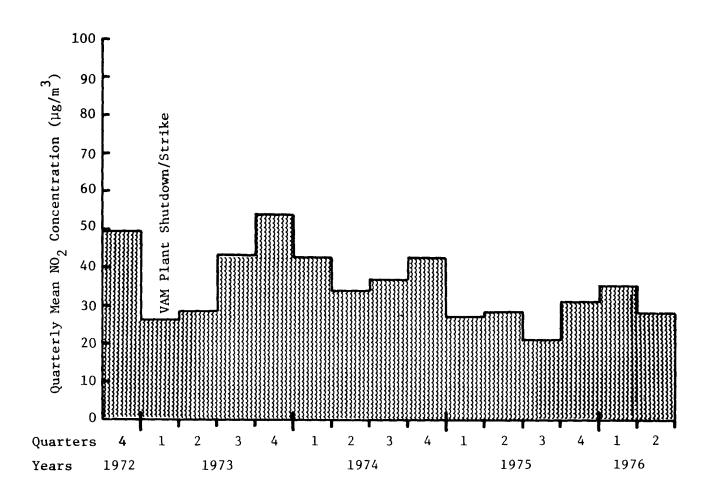


Figure 14. Graphical presentation of quarterly mean $\ensuremath{\text{NO}}_2$ concentrations for site 0633.

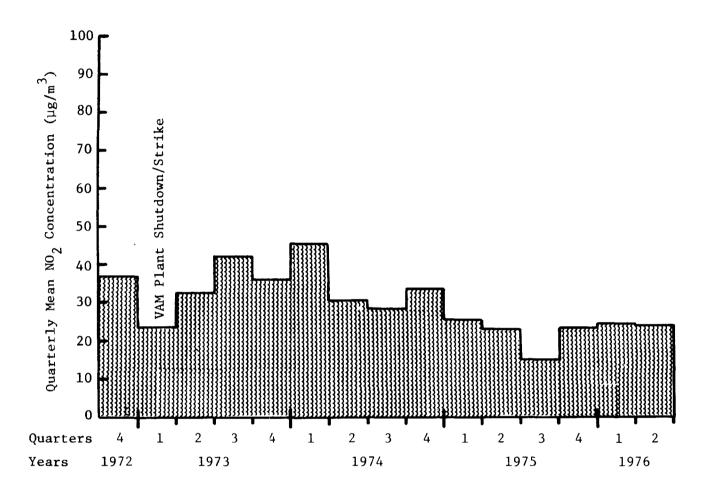


Figure 15. Graphical presentation of quarterly mean $\ensuremath{\text{NO}}_2$ concentrations for site 0634.

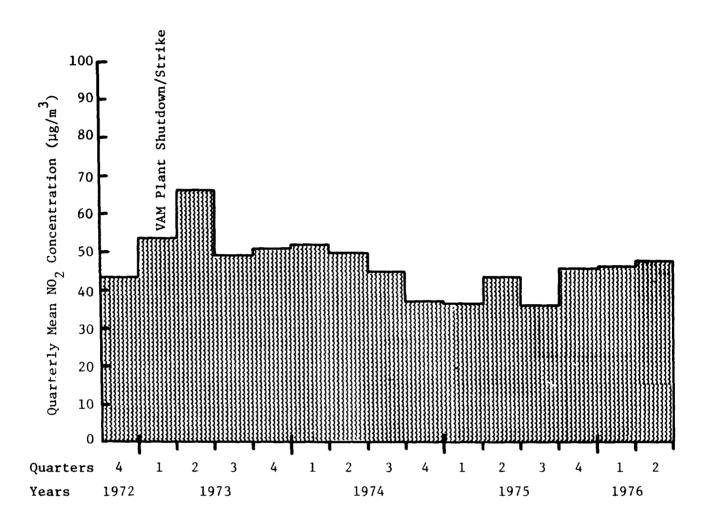


Figure 16. Graphical presentation of quarterly mean NO_2 concentrations for site 0641.

table 5 in the ratio of means for the first quarter of 1973. Also, the ratio of quarterly means for site 0631 compared to site 0621 is now running below 1.00 for the first 5 months of 1976.

7.1 Data Recovery

The percentage of valid NO_2 data recovery achieved during each year of this program is summarized in table 6. These records show that significant improvements in the percentage of data recovery occurred from year to

Table 5. Ratio of quarterly mean NO_2 concentrations ($\mu g/m^3$)

Voar Quartor*		Site No. [†]						
Year Quarter*	0621	0622	0631	0632	0633	0634	0641	
1973	1	1.00	1.48	0.55‡	0.91	0.65	0.58	1.32
	2	1.00	1.67	1.64	1.18	0.74	0.85	1.73
	3	1.00	1.37	1.27	0.77	0.84	0.82	0.96
	4	1.00	1.47	1.96	1.23	1.29	0.86	1.22
1974	1	1.00	1.23	1.83	0.98	0.86	0.92	1.04
	2	1.00	1.38	1.80	0.95	0.86	0.77	1.26
	3	1.00	1.24	1.92	1.21	1.01	0.78	1.22
	4	1.00	0.83	1.58	1.15	0.94	0.74	0.82
1975	1	1.00	1.19	1.19	0.69	0.85	0.79	1.14
	2	1.00	1.39	1.11	0.89	0.71	0.57	1.08
	3	1.00	1.29	0.96	0.99	0.62	0.44	1.03
	4	1.00	1.28	1.28	1.05	0.87	0.65	1.28
1976	1	1.00	1.39	0.92	0.99	0.86	0.61	1.14
	2 [§]	1.00	1.32	0.95	0.83	0.65	0.54	1.12

^{*}Quarter 1 - January-March; Quarter 2 - April-June; Quarter 3 - July-September; Quarter 4 - October-December.

 $^{^{\}dagger}$ Ratio = $\frac{\text{Site mean}}{\text{Site 0621 mean}}$

[†]Volunteer Army Munitions Plant on strike.

[§]April-May data only.

Table 6. Percent of valid NO_2 data by year

Site No.	Year	Operational Period (days)	Valid NO ₂ Data (days)	Data Recovery (%)
0621	1973	365	259	71.0+
	1974	365	316	86.6
	1975	365	347	95.1
	1976*	152	151	99.3
0622	1973	365	296	81.0 [†]
	1974	365	343	94.0
	1975	365	344	94.2
	1976*	152	148	97.3
0631	1973	365	302	82.7 [†]
	1974	365	331	90.7
	1975	365	343	94.0
Ì	1976 *	152	90	59.2
0632	1973	365	344	94.2
	1974	365	311	85.2
	1975	365	357	97.8
	1976*	152	151	99.3
0633	1973	365	319	87.3
	1974	365	352	96.4
	1975	365	264	72.3
	1976*	152	131	86.2
0634	1973	365	235	64.4
	1974	365	321	87.9
	1975	365	277	75.6
	1976*	152	151	99.3
0641	1973	365	207	56.7 [†]
	1974	365	269	73.7
	1975	365	314	86.1
	1976*	152	148	97.3

^{*}January-May
†Single operator error accounted for 12.0 percent of instrument downtime at 0621; 10.8 percent at 0622; 15 percent at 0631; and 11 percent at 0641.

year. Notable exceptions include 1976 at site 0631; 1975 at 0633; 1975 at 0634; and 1974 at site 0641. The best percentage data recovery occurred during the first 5 months of 1976. With the exception of site 0631, better than 97 percent valid data were recovered from the network. The overall data recovery averaged over all sites for each year are as follows: 70.7 percent for 1973; 87.8 percent for 1974; 87.9 percent in 1975; and 91.1 for the first 5 months of 1976.

Logical explanations can be given to account for the improvement or lack thereof in percent data recovery and are as follows:

- 1. The main reason for the improvement in percent data recovery resulted from RTI locating a field coordinator in Chattanooga to supervise the local operators supplied by Chattanooga State Technical Community College; considerable data were lost during 1973 due solely to local operator errors.
- 2. The primary reason for loss of data was due to failure of the NO_2 analyzers, which caused 99 percent of downtime (i.e., loss of data). Less than 1 percent of lost data could be attributed to failure of the dual recording systems (i.e., data acquisition and stripchart recorders). Insufficient NO_2 analyzers were available for use on this program (i.e., eight analyzers were provided by EPA to operate seven stations). In 1976 two additional analyzers were provided by EPA for use on the program and better than 97 percent valid data were recovered at all sites, except sites 0631 and 0633.

7.2 Observations and Conclusions

Certain observations and conclusions can be drawn from the limited amount of data presented in the previous paragraphs. These are as follows and are by no means intended to be all inclusive:

1. Mean NO_2 concentrations in Chattanooga have decreased significantly in all three study sectors (figure 1 of this report) when compared to the mean NO_2 data reported for each section in the original 1968-1969 Chattanooga Study. Mean NO_2 concentrations in 1973 have decreased 36 percent in sector I, 56 percent in sector II, and 68 percent in sector III. Year-to-year decreases have continued for all sites in all sectors. The reader is cautioned that percentage decreases are approximate, since the numbers used

to compute the decrease in NO $_2$ levels for each sector were obtained using different methods (i.e., the CHESS modification to the Jacobs-Hochheiser Method in the 1968-69 Study and the chemiluminescent method in the 1972-1976 Study). Inaccuracies inherent in the measurement method used to obtain each set of data for the three sectors will influence the absolute percentage decrease. In addition, the sampling sites presently used in Chattanooga are not necessarily the same as those used in the original 1968-1969 Chattanooga Study $^{1/}$; however, all sites used in the comparison are located within the same sectors.

- 2. The slowdown in TNT production at the Volunteer Army Munitions Plant and gradual installation of control equipment have been accompanied by a decrease in NO $_2$ concentration for the sector III study area. The data show that the ambient air quality standard of $100~\mu g/m^3$ was not approached at any site in sector III during the measurement period. The highest annual mean was $76.3~\mu g/m^3$ at site 0631 in 1974 (site nearest the point source) and the lowest mean was $23.2~\mu g/m^3$ at site 0634 (control site).
- Based on the data and prevailing wind patterns for this area, emissions from the TNT plant appear to be the major source of NO, in the high NO exposure area (sector III). The influence or effect of the TNT plant contribution on the NO, levels measured at each of the four sites in section III can be correlated with wind direction from the TNT plant to the site. The TNT plant was shut down by a strike during the first calendar quarter (January-March 1973) and its impact on the quarterly mean for each of the surrounding sites was apparent. The quarterly mean for site 0631 located adjacent to and generally downwind of the TNT plant decreased 47 percent, and for site 0634 decreased 38 percent. The quarterly mean for sector III (i.e., average mean for sites 0631, 0632, 0633, and 0634) for the first calendar quarter of 1973 was 27 $\mu\text{g/m}^3$ as opposed to $57 \, \mu g/m^3$ for the fourth quarter of 1972 and 42 $\mu g/m^3$ for the second quarter of 1973. Mean nitrogen dioxide concentrations at site 0631 in 1975 and 1976 were significantly lower than for previous years and approximate ${\rm NO}_2$ levels observed at other sites not influenced by the VAM Plant. These data indicate that control equipment installed at the VAM Plant has been effective.

4. Based on the data obtained during this period of time (table 2), there does not appear to be significant difference in NO_2 exposure between the health study areas (i.e., sectors I, II, or III); however, a significant difference in exposure within sector III existed until the end of 1974. This observation can readily be seen by examining data presented in table 2. Sector III is comprised of sites 0631, 0632, 0633, and 0634.

In summary, the ambient air quality standard of $100~\mu\text{g/m}^3$ (annual arithmetic mean) was not exceeded nor closely approached during the measurement program at any of the seven monitoring sites, where chemiluminescent NO_2 analyzers were located. Short-term maximum hourly average concentrations did occur at site 0631 in excess of 1,000 $\mu\text{g/m}^3$, but the overall mean for site 0631 has decreased by more than 50 percent since 1973. In general, mean NO_2 concentrations measured in the Chattanooga area have decreased significantly from those levels measured during the 1968-1969 Chattanooga study. Slowdown in TNT production and installation of control equipment at the VAM Plant have been accompanied by a decrease in NO_2 concentrations at sites located in sector III near the point source.

8.0 REFERENCES

- 1. Shy, C. M., J. P. Creason, M. E. Pearlman, K. E. McClain, F. B. Bensen, and M. Y. Young, "The Chattanooga School Children Study: Effects of Community Exposure to Nitrogen Dioxide: Methods, Description or Pollutant Exposure, and Results of Ventilatory Function Testing,"

 Journal Air Pollution Control Association 20 (1970):539.
- 2. Pearlman, M. E., and J. P. Finklea, "Nitrogen Dioxide in Lower Respiratory Illness," Ecological Research Branch, DHER, National Air Pollution Control Administration (1970).
- 3. Decker, C. E., T. M. Royal, and J. B. Tommerdahl, "Program for Upgrading the Instrumentation Employed in the 1972 Chattanooga NO Exposure Study," Final Report, Research Triangle Institute, CRC-APRAC Project No. CAPM-10-71, May 1973.
- 4. Purdue, L. J., J. E. Dudley, J. B. Clements, and R. J. Thompson, "Reinvestigation of the Jacobs-Hochheiser Procedure for Determining Nitrogen Dioxide in Ambient Air," Environmental Science and Technology 6(1972):152.
- 5. Merryman, E. L., C. W. Spicer, and A. Ling, "A Reevaluation of the Jacobs-Hochheiser Procedure: Effects of NO, CO₂, CH₄, H₂O, and Sodium Arsenite on NO Analysis." In <u>Proceedings of 2nd Conference on Natural Gas Research and Technology</u>, AGA, Atlanta, Ga., June 5-7, 1972.
- 6. Hauser, T. J., and C. M. Shy, "Position Paper: NO Measurement," Environmental Science and Technology 6 (1972):890.
- 7. U. S. Environmental Protection Agency, "Ambient Air Quality Standards: Reference Method for Determination of Nitrogen Dioxide, <u>Federal</u> Register 38, No. 110 (June 8, 1973).
- 8. Hodgeson, J. A., R. E. Baumgardner, B. E. Martin, and K. A. Rheme, "Stoichiometry in the Neutral Iodometric Procedure for Ozone by Gas-Phase Titration with Nitric Oxide," <u>Analytical Chemistry</u> 43 (1971):1123.
- 9. Rheme, K. A., B. E. Martin, and J. A. Hodgeson, "The Application of Gas Phase Titration in the Simultaneous Calibration of NO, NO, NO, and O, Atmospheric Monitors." Paper presented at the 164th ACS Meeting, New York, September 1972.

APPENDIX A

OPERATING PROCEDURES

(As supplied to Chattanooga State Technical Community College Operators)

APPENDIX A

OPERATING PROCEDURES FOR CHEMILUMINESCENT ANALYZERS AND DATA ACQUISITION SYSTEMS

A. DAILY OPERATING PROCEDURES

 Indicate date, time, and station number on strip chart recorder replace paper at end of roll and mail to RTI. Chart paper box should be labeled with start and stop date and time and station I.D.

2. Instrument Status

- a) Check status of power, pump, ozone generator lights (should be on).
- b) Note 0_2 pressure (20 psi, reset if not 20 psi).
- c) Note range for NO, NO $_2$, NO $_{\mathbf{x}}$ (should be identical).
- d) Read oxygen cylinder pressure (psi) (outside dial scale nearest cylinder valve).
- e) If #1, 2, 3 are correct, operational status of instrument is okay.
- f) Turn ozone generator on zero module ON.
- 3. Operational Status Data Logger System
 - a) Check date and time* if date and time do not agree with clock or wristwatch - correct date and time must be entered using time preselect digits and <u>time preset</u> switch (green button).
 - b) Check channel 18 for reading of 500; if value changes + 50, replace battery.
- 4. Enter operational status of Bendix analyzer on tape using EC-22 switch. Leave switch in up position at least 3 seconds each time. If operational status is sampling, enter 9 as third digit; if status is inoperative, enter 7 as third digit (see code definitions for manual data inputs).

	Example	Channel #	Instrument ID Number	Status (if sampling)
	NO	8	12	129
Bendix	NO_2	9	13	139
	NOx	21	25	259
Technicon	NO ₂	22	26	269
	* if inop	erative, en	ter	
	$^{NO}_2$	127		
Bendix	NO ₂	137		
	$^{ m NO}_{ m x}$	257		
Technicon	NO ₂	267		

5. Instrument Zero Procedure

- a) Switch instrument mode switch to zero.
- b) Enter code using EC-22 unit

$$NO_2 - 138 - scan$$

$$NO_{x} - 258 - scan$$

* This means analyzer is stabilizing on zero air

c) After 10 minutes check zero voltages on channels 8, 9, 21; enter millivolt readings on analyzer data sheet. Enter code on tape using EC-22 unit;

$$NO_2 - 130 - scan$$

$$NO_{x} - 250 - scan$$

If "zero" reads 0.0 ± 10 millivolt do not adjust. If zero exceeds limit, readjust zero using zero control potentiometer located on meter. Signify adjustment for NO, NO₂, NO_y by appropriate code.

NO - 128
$$\rightarrow$$
 perform zero adjust \rightarrow NO - 123

$$NO_2$$
 - 135 \rightarrow perform zero adjust \rightarrow NO_2 - 133

$$NO_{x}$$
 - 258 \rightarrow perform zero adjust $\rightarrow NO_{x}$ - 253

- d) Switch instrument input back to ambient and enter 128, 138, 258 on EC-22 and note "zero period" on strip chart. If adjustment is made state zero "adjusted" for NO $_2$ on strip chart.
- e) After analyzer has sampled ambient air for two minutes, turn off ozone generator and enter on EC-22, 129, 139, 259, if instrument is operating properly. If instrument is not operating properly, enter the following codes:

NO - 127 - scan

 $NO_2 - 137 - scan$

 $NO_{x} - 257 - scan$

f) Place EC-22 unit digits to 999 and initiate scan prior to leaving station. If any difficulty is experienced, call RTI for instructions. (919)549-8311 Ext. 671 - C. E. Decker Ext. 588 - Tom Royal

B. WEEKLY OPERATING PROCEDURES

- 1. Change magnetic tapes on data acquisition system at seven (7) day intervals (on Friday). Mark date and time on tape logs and mail tapes to RTI on Friday.
- 2. Magnetic Tape Change Procedures
 - a) Place data logger in STAND-BY MODE
 - b) Remove tape from recorder; place tape and tape log inside carton.
 - c) Place new tape on recorder being careful not to crimp tape; check to see that tape drive pins are inserted into tape orive wheels.
 - d) Close plastic door.
 - e) Tape should advance to start position (i.e., aluminum strip should be rocated just past tape head EOT/BOT light will stop flashing). If tape does not advance, manual tape advance may be accomplished by using EOT/BOT button until aluminum strip is properly located.
 - f) Place data logger in RECORD mode.
 - g) Check to see that recorder scans at five (5) minute intervals.

h) Magnetic Tape Log Instructions

- 1. Note start, date and time for tape on tape log, cassette number, data logger ID, and station number.
- 2. Note power failures on tape log.
- 3. Indicate stop date and time off.
- 4. If problems develop and unit will not work call T. M. Royal or C. E. Decker (919)549-8311 for further instructions.

C. CODE DEFINITIONS FOR MANUAL DATA INPUTS

SENSOR IDENTIFICATION

- Identify environmental sensors with <u>first</u> and <u>second</u> digits of the EC-22.
- 2. Identify operational mode of sensors with third digit of the ${\rm EC}{\text -}22$.

Nitrogen Oxide (NO) (Bendix) Nitrogen Dioxide (NO ₂) (Bendix) Oxides of Nitrogen (NO _X) (Bendix) DATA INPUT STANDARD Nitrogen Dioxide (NO ₂) (Technicon)	/ 1 / 2 / / / 2 / 3 / / / 2 / 5 / / / 2 / 2 / / / 2 / 6 / /
OPERATIONAL MODE	
Zero	/ / / 0 /
Span	/ / / 1 /
Calibrate	/ / / 2 /
Adjusted Zero	/ / / 3 /
Adjusted Span	/ / / 4 /
Mistake Made	/ / / 5 /
Spare	/ / / 6 /
Inoperative	/ / / 7 /
Stabilizing (Transition Period)	////
Ambient Sampling	/ / 9/

D. DATA LOGGER SAMPLING SEQUENCE

Channel Number

v umb e	<u></u>
1	DAY - JULIAN DATE
	(1st and 2nd Digit - Hours
2	\[\begin{aligned} \text{1st and 2nd Digit - Hours} \\ \text{3rd Digit - Tens of Minutes} \end{aligned}
3	\begin{aligned} \begin{aligned} \text{St Digit - Units of Minutes} \\ \text{2nd and 3rd Digit - Seconds} \end{aligned}
4	STATION IDENTIFICATION NUMBER
5	MANUAL DATA ENTRY
6	
7	
8	Nitric Oxide (NO) (Bendix)
9 -	Nitrogen Dioxide (NO ₂) (Bendix)
10	-
11	
12	
13	
14	
15	
16	
17	
18 -	DATA INPUT STANDARD (Test Voltage)
19	
20	
21 -	Oxides of Nitrogen (NO _X) (Bendix)
22 -	Nitrogen Dioxide (NO ₂) (Technicon)
23	
24	
25	
26	
27 -	Calibration Value Multiplier
	+ 15 Volts
29 -	Calibration Values (ppm)

APPENDIX B

DETAILED CALIBRATION PROCEDURES (BENDIX NO-NO_X-NO₂ ANALYZER)

APPENDIX B DETAILED CALIBRATION PROCEDURE (BENDIX NO-NO_X-NO₂ ANALYZER)

- 1. Turn on ozone generator and Hastings mass flow meter and allow them to warm up for approximately 30 minutes.
- 2. Connect instrument inlet line to manifold of calibration apparatus. Connect compressed air cylinder to calibration apparatus and allow zero air (air filtered through charcoal) to flow through system. Connect NO/N_2 gas regulator to cylinder and evacuate with pump to prevent the formation of NO_2 in the regulator.
- 3. Allow analyzer to sample zero air for 5-10 minutes. Average zero output for NO, NO_x, and NO₂ channels for at least 5 cycles (i.e., 5 minutes). If instrument zero deviates from zero by more than ± 10 mV, readjust to zero. Indicate proper entry codes for zero and/or zero adjust on magnetic tape using EC-22 unit.
- 4. Prepare 0.1 ppm NO concentration by metering sufficient NO in nitrogen into 5 liter/min diluent stream. Allow 10 minutes for system and analyzer to equilibrate at that concentration and then average the instrument output for at least 5 cycles. Enter proper codes on magnetic tape with EC-22 unit. Enter calibration concentration on magnetic tape using 10-turn potentiometer. Both NO and NO, channels are calibrated simultaneously.
- 5. Proceed to next calibration concentration and repeat Step No. 4 (i.e., 0.1, 0.2, 0.4, 0.5 ppm NO, etc).
- 6. After completing the multipoint calibration with NO, generate NO₂ concentrations as described in the previous discussion. Enter proper codes and calibration concentrations on magnetic tape using mode switches and 10-turn potentiometer. Repeat for additional calibration points for NO₂ channel (i.e., 0.1, 0.2, 0.4, 0.5 ppm NO₂, etc).
- 7. Return sample inlet line to sample manifold.

APPENDIX C

DETAILED MAINTENANCE PROCEDURES (Bendix NO-NO_X-NO₂ Analyzer)

APPENDIX C

DETAILED MAINTENANCE PROCEDURES (BENDIX NO-NO_X-NO₂ ANALYZER)

1.0 AMBIENT AIR FILTER (TEFLON) REPLACEMENT

The ambient air filter contains a Teflon element. This element should be inspected weekly and replaced as required. Frequent replacement will be necessary in a dirty or high particulate concentration area. Replace the element as follows:

- a. Place the PUMP switch and the POWER switch in the off position (down).
- b. Loosen the wingnuts and open the filter assembly.
- c. Remove the Teflon filter element.
- d. Install the new filter element, close the assembly and tighten the wingnuts.

2.0 EXHAUST FILTER (CHARCOAL) REPLACEMENT

The charcoal in the exhaust filter should be replaced on a monthly basis. Replace the charcoal as follows:

- a. Place the PUMP switch and the POWER switch in the off position (down).
- b. Reposition the instrument to gain access to the filter which is mounted on the back panel. Exercise caution to avoid applying excessive strain to the tubing connections.
- c. Disconnect the input and output lines from the filter.
- d. Loosen the mounting brackets and remove the filter holder.
- e. Unscrew the top portion of the filter.
- f. Empty the charcoal and make sure the glass wool in the bottom of the filter holder is in place before refilling.
- g. Refill the filter holder using no. 10 mesh charcoal.
- h. Reinstall the filter and reapply power.
- i. Recheck the calibration.

3.0 OXYGEN FILTER (SINTERED)

The oxygen filter is a sintered stainless steel mesh element that is housed within a 1/8-in. tubing connector on the input of the capillary. The element should be replaced when the oxygen cylinder is changed or when the particulate buildup restricts the oxygen flow from the output of the capillary to less than 30 cm³ per minute with OXYGEN pressure gage reading of 20 $1b/in^2$. Replace the filter element as follows:

- a. Shut off the oxygen cylinder.
- b. Place the PUMP switch and the POWER switch in the off position (down).
- c. Remove the four (4) screws from the top cover of the instrument and lift the cover from the unit.
- d. Loosen the fitting from the input end of the capillary in the oxygen line.
- e. Remove the stainless steel mesh filter from within the fitting.
- f. Install a new element and reconnect the fitting.
- g. Replace the top cover and reapply power.
- h. Recheck the calibration.

4.0 OXYGEN CYLINDER REPLACEMENT

The oxygen cylinder should be replaced when the cylinder pressure decreases to $100~{\rm lb/in}^2{\rm g}$. The procedure for cylinder replacement is presented below:

- a. Place the PUMP switch and the POWER switch in the off position (down).
- b. Close the oxygen cylinder valve.
- c. Turn the two-stage regulator adjustment fully counterclockwise.
- d. Remove the two-stage regulator from the cylinder.
- e. Replace the oxygen cylinder (verify that the new cylinder contains welding grade or better oxygen).

- f. Connect the two-stage regulator to the cylinder.
- g. Open the cylinder valve.
- h. Adjust the two-stage regulator to 30 $1b/in^2g$.
- i. Place the POWER switch and the PUMP switch in the ON position.
- j. Allow 10 minutes for any air to be purged from the system.
- k. Perform the calibration procedure.

5.0 EVACUATION PUMP MAINTENANCE

The evacuation pump used in the Bendix $NO-NO_x-NO_2$ analyzer is a two-stage diaphragm-type vacuum pump. The pumping element and motor require no lubrication and should not be dismantled in the field. However, if the pump performance degrades to the point that it will not maintain a vacuum of 23 in. Hg, the cause may be foreign particles under the reed valves or a ruptured diaphragm. Correcting either of the aforementioned problems may be accomplished as follows:

- a. Place the PUMP switch and the POWER switch in the off position (down).
- b. Disconnect the pump power cord from the jack on the rear panel of the instrument.
- c. Disconnect the Teflon tubing from the pump intake and the polyethylene tubing from the pump exhaust. The copper tubing remains connected between the two heads.
- d. Remove the eight (8) screws from the two heads (four in each head) and remove the two heads.
- e. The reed valve assemblies are mounted in the head. Note the orientation of the reed valves with respect to the input and output of each head.
- f. Remove the reed valve assembly from each head by removing the four (4) Phillips head screws attaching the assembly to the head.

- g. Remove the two (2) screws that secure the reed valves to each assembly. Use caution to prevent distorting the reeds.
- h. Wipe the reeds and the assemblies with a clean, lintfree cloth.
- i. Reassemble the reed valve assemblies utilizing the screws removed in step g.
- j. Reinstall the reed valve assemblies in the heads utilizing the screws removed in step f. Insure that the proper orientation of the reed valves is observed, as noted in step e.
- k. Inspect each diaphragm for evidence of deterioration or holes. Remove any foreign matter from the diaphragm.
- 1. If either or both diaphragms require replacement, remove the four (4) Phillips head screws that attach the diaphragm to the piston and replace the diaphragm.
- m. Install a new diaphragm utilizing the screws removed in step 1.
- n. Reinstall the heads on the pump utilizing the screws removed in step d. Insure that the diaphragms are properly seated in the grooves of the pump body prior to installing the heads.
- o. Reinstall the tubing removed in step c and reconnect the pump power cord.
- p. Service the exhaust filter (charcoal) in accordance with paragraph 2.0.
- q. Apply power to the instrument and pump and recheck the pump vacuum.
- r. Recheck the calibration.

	TECHNICAL REPORT DAT APplease read Instructions on the reverse before	A e completing,
1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/1-76-034		
4. TITLE AND SUBTITLE		5. REPORT DATE
Nithogon Diovido Thonds i	October 1976	
Nitrogen Dioxide Trends in Selected Chattanoog Communities		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)		8. PERFORMING ORGANIZATION REPORT NO.
C.E. Decker and T.M. Roya	al	
9. PERFORMING ORGANIZATION NAME	AND ADDRESS	10. PROGRAM ELEMENT NO.
Bosopych Twippalo Institu	1AA601	
Research Triangle Institu	11. CONTRACT/GRANT NO.	
Research Triangle Park, N.C. 27709		68-02-1737
12. SPONSORING AGENCY NAME AND A	DDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Health Effects Research L	_aboratory	
Office of Research and Development		14. SPONSORING AGENCY CODE
U.S. Environmental Protec		EPA-ORD
Research Triangle Park, N		

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The objectives of this project were to operate air monitoring stations and collect air quality data in the Chattanooga, Tennessee area to supportepidemiological studies during the period June 15, 1974 to June 14, 1976. This ongoing project was begun in 1969 under the sponsorship of the U.S. Environmental Protection Agency and was designed to gather air quality data for use in studies relating health effects to ambient concentrations of oxides of nitrogen. Initially, the aerometric program consisted of particulate (high volume method) and nitrogen dioxide (CHESS bubbler method) measurement at ten stations located in and about the Chattanooga In 1972 the Research Triangle Institute upgraded the aerometric monitoring program in Chattanooga through a joint project sponsored by the Environmental Protection Agency and the Coordinating Research Council. Chemiluminescent NO-NO_x-NO₂ analyzers and data acquisition systems were installed in environmentally-controlled shelters at seven of the nine monitoring sites operating at that time. Research Triangle Institute has operated and maintained the nine-station monitoring network and provided aerometric data to the Environmental Protection Agency under contract 68-02-1737 through May 1976.

7. KEY WORDS AND DOCUMENT ANALYSIS					
a. DESCRIPTORS	b.IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field, Group			
Nitrogen oxides Nitrogen dioxide air pollution analyzers monitors		13 B 14 B			
13. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report) UNCLASS IF IED	21. NO. OF FAGES			
RELEASE TO PUBLIC	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE			