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INVESTIGATION OF HIGH OZONE CONCENTRATION IN THE VICINITY  
OF GARRETT COUNTY, MARYLAND AND PRESTON COUNTY, WEST  
VIRGINIA

Research Triangle Institute  
Durham, North Carolina

January 1973

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INVESTIGATION OF HIGH OZONE CONCENTRATION IN THE  
VICINITY OF GARRETT COUNTY, MARYLAND AND  
PRESTON COUNTY, WEST VIRGINIA

PHASE I

FINAL REPORT  
JANUARY 1973

Environmental Studies Center  
Research Triangle Institute  
Research Triangle Park, North Carolina 27709

Prepared for the  
Environmental Protection Agency  
Research Triangle Park, North Carolina 27711

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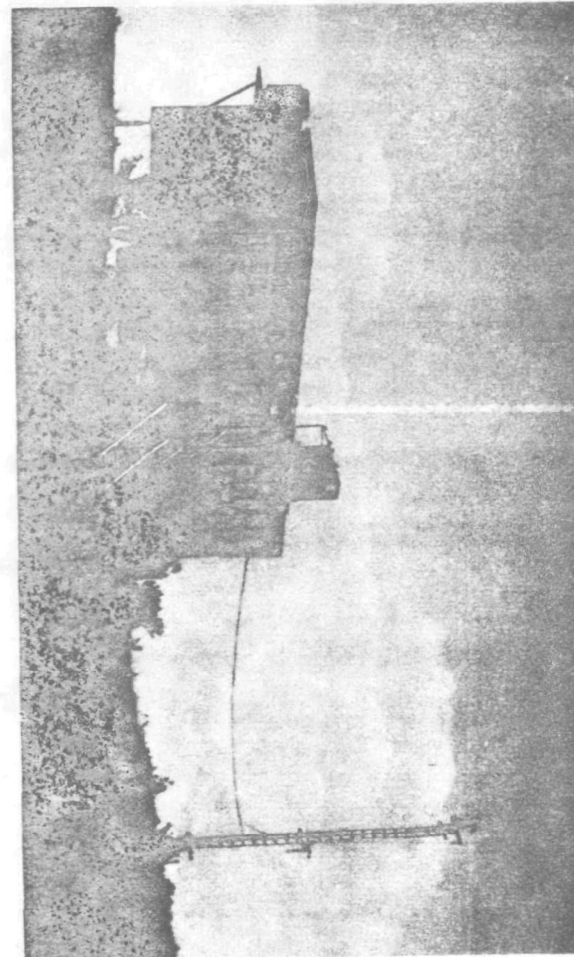
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# ABSTRACT

A seven-week program of field measurements was carried out between August 4 and September 25, 1972 to investigate the source of high ozone concentration in the vicinity of Garrett County, Maryland and Preston County, West Virginia. Approximately 11 percent of the hourly ozone concentrations measured at the Garrett County Maryland Airport exceeded the 0.08 ppm National Air Quality Standard. In one episode of high ozone concentration, the Standard was exceeded for 26 consecutive hours. The mean hourly ozone concentration for the study period was 0.057 ppm and the maximum hourly concentration was 0.119 ppm. High ozone concentrations persisted through the night; the nighttime mean was 0.055 ppm. Nitrogen dioxide and nonmethane hydrocarbon concentrations were at or near background levels throughout the study period. It was concluded that local photochemical synthesis could not account for the observed high ozone concentrations in the study area. Analysis of meteorological data indicated that the high ozone concentrations were associated with air masses arriving in the study area after passing over urban-industrial regions.

Research Triangle Institute Environmental Monitoring  
Laboratory at Garrett County Maryland Airport



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This project was conducted by the Research Triangle Institute, Research Triangle Park, North Carolina, pursuant to Contract No. 68-02-0624 with the Environmental Protection Agency. The statements, findings, conclusions, and recommendations presented in this report do not necessarily reflect the views of the Environmental Protection Agency.

Many individuals contributed to the research described in this report. Principal among these and the areas in which they made their contribution are:

Walter D. Bach, Jr.	Meteorology
Clifford E. Decker	Analytical chemistry
Harry L. Hamilton, Jr.	Meteorology
Linda K. Matus	Data processing
Lyman A. Ripperton	Atmospheric chemistry
Thomas M. Royal	Instrumentation
James J. B. Worth	Meteorology, field operations

In addition, R. W. Murdoch operated the Environmental Monitoring Laboratory, S. R. Stilley operated the mobile unit, C. E. Moore installed the meteorological instrumentation, and W. K. Poole and S. B. White provided assistance with statistical problems. The contributions of these individuals are also acknowledged.

The Board of County Commissioners of Garrett County, Maryland authorized the use of the Garrett County Airport as a location for the Environmental Monitoring Laboratory; their cooperation is appreciated. The active interest and willing cooperation of John Kreuzwieser, the airport manager, are gratefully acknowledged.

E. C. Tabor, Environmental Protection Agency, served as Project Officer; his guidance is very much appreciated.

Donald R. Johnston  
Project Manager

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INVESTIGATION OF HIGH OZONE CONCENTRATION IN THE  
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PRESTON COUNTY, WEST VIRGINIA

## SECTION 1

## INTRODUCTION

In the course of a study of injury to Christmas trees, Environmental Protection Agency (EPA) investigators were surprised to find oxidant concentrations at rural sites in western Maryland and eastern West Virginia frequently exceeding the National Air Quality Standard (0.08 ppm) during the period May 29-September 28, 1970 (EPA, 1971). High oxidant concentrations were observed at three sites--the Stony River farm in Grant County, West Virginia, and the Steyer No. 2 and Weise-McDonald farms in Garrett County, Maryland. Measurements made with a chemiluminescent ozone meter at the Steyer No. 2 farm showed that virtually all of the oxidant at that site was ozone (Richter, 1970). Of particular interest was the fact that the high ozone concentration persisted into the dark hours; i.e., ozone concentration did not exhibit the typical diurnal pattern in which it decreases to near zero at night. Nitrogen oxide concentrations during this period were reported to be near background levels (EPA, 1971).

The high surface ozone concentration could result from local synthesis or from vertical or horizontal transport from another location. Ozone synthesis, in situ, from naturally occurring or manmade precursors is a possible explanation. However, the reported low nitrogen oxide concentrations together with high ozone concentrations persisting long after nightfall argue against this explanation. Advective transport of ozone from the stratosphere to the surface is unlikely, given the extremely high temperatures that would result from the accompanying adiabatic compression. In contrast, horizontal transport of ozone from a remote tropospheric source region appears possible. For example, it has been shown that ozone rich layers occur within elevated but low-level inversion layers (Lea, 1968). Further, Lea suggested that the high ozone concentrations observed aloft at Pt. Mugu, California, could be attributed to

precursors originating in the Los Angeles area. More recently, the transport of photochemical smog from Fresno to the Mineral King Valley of California has been suggested (Miller, et al., 1972).

From the above considerations, the following hypothesis evolved: Ozone precursors are released into the troposphere at a location remote from the study area. Given appropriate meteorological conditions, the precursors are transported to the study area. During transport and in the presence of sunlight, ozone is synthesized. The hypothesis further assumes that by sundown the precursors (which are also destructive agents) are consumed, leaving high residual ozone concentrations which are transported to the surface by mechanical turbulence.

Testing the hypothesis stated above involved accomplishing several specific research objectives. These objectives were:

- 1) to verify the high concentrations of ozone previously found in the Mt. Storm, West Virginia area;
- 2) to define the horizontal and vertical extent of regions of high ozone concentration;
- 3) to determine the rates of photochemical synthesis, destruction and transport of ozone, and
- 4) to attempt to determine the sources of ozone in the area.

## SECTION 2

### STUDY PLAN

The study plan described in this section was designed to accomplish the research objectives stated in Section 1, above.

The study plan provided for a seven-week field program consisting of fixed ground-level, mobile ground-level, and upper air measurements of selected constituents of the air and meteorological parameters. The air constituents measured at the fixed ground-level site were ozone, carbon monoxide, methane, nitric oxide, nitrogen dioxide, sulfur dioxide, and total hydrocarbons. Meteorological parameters measured at the fixed ground-level site were ambient temperature, dewpoint temperature, solar radiation, wind speed and direction, and vertical temperature difference. Mobile ground-level measurements included ozone, wet and dry bulb temperature, and wind speed and direction. Balloon-borne sensors were used to obtain upper air measurements of oxidant, ambient temperature and atmospheric pressure.

Measurement of ozone at the fixed ground-level site was undertaken to verify the high concentrations of ozone previously found in the Mt. Storm, West Virginia area, while mobile ground-level measurements were obtained in order to explore the horizontal extent of regions of high ozone concentration. Likewise, upper air measurements were made with the intent of investigating the vertical extent of regions of high ozone concentration.

A Continuous Stirred Tank Reactor (CSTR) experiment (Jeffries, 1971) was employed to determine the rates of photochemical synthesis, destruction, and transport of ozone.

Since corona discharge from high voltage electric power transmission lines was considered to be a possible contributor to ambient ozone concentration, ozone measurements were made underneath, upwind and downwind of 500-KV power transmission lines.

A determination of the source of ozone in the area in terms of location, i.e., local, upper atmospheric, or remote surface layer, would result from an examination of the concentrations and diurnal



characteristics of ozone and its precursors, nitrogen dioxide and non-methane hydrocarbons; the rates of ozone synthesis, destruction, and transport provided by the CSTR experiment; the upper air measurements; and meteorological analysis.

### SECTION 3 DESCRIPTION OF STUDY AREA

The study area included Garrett County, Maryland and the easternmost portion of Preston County, West Virginia. Bounded on the east by the North Branch of the Potomac River, it consisted primarily of a high plateau with an average elevation of 2500 feet above mean sea level. The geographical and topographical features of the study area are shown in Fig. 1.

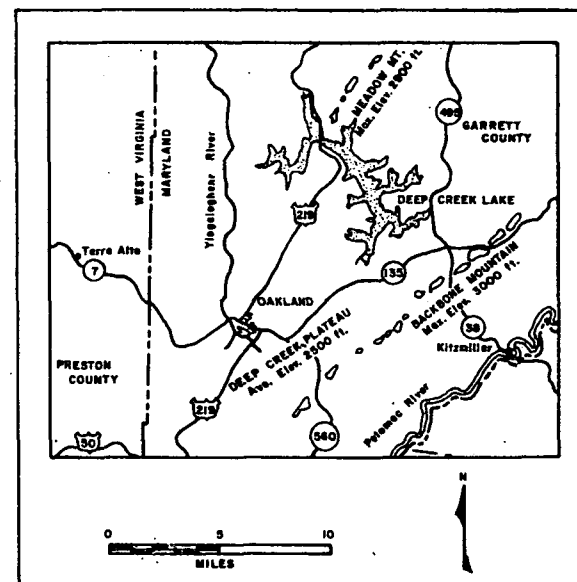


Figure 1. Geographical and topographical features of study area.  
(Source: EPA, 1971)

Remote from urban centers, the area is decidedly rural in character. In 1970, Garrett County, Maryland had a population of 21,476, while Oakland, the county seat, had a population of 2,300. Preston County, West Virginia had a 1970 population of 25,455.

Most of the study area is forested, with commercial Christmas tree growing a principal source of income. In addition, Deep Creek Lake in Garrett County provides recreation for many people from the tri-state area of Maryland, Pennsylvania, and West Virginia.

Estimated annual emissions of carbon monoxide, hydrocarbons, oxides of nitrogen, and sulfur dioxide in Garrett County are 11, 2, 1, and 2 thousand tons, respectively. Estimated annual emissions of carbon monoxide, hydrocarbons, oxides of nitrogen, and sulfur dioxide in Preston County are 1, 1, 10, and 54 thousand tons, respectively.\* Figure 2 identifies some major pollutant sources within an 80-mile radius of the study area.

The relationship between the present study area and the area of concern in the 1970 EPA investigation is illustrated in Fig. 3.

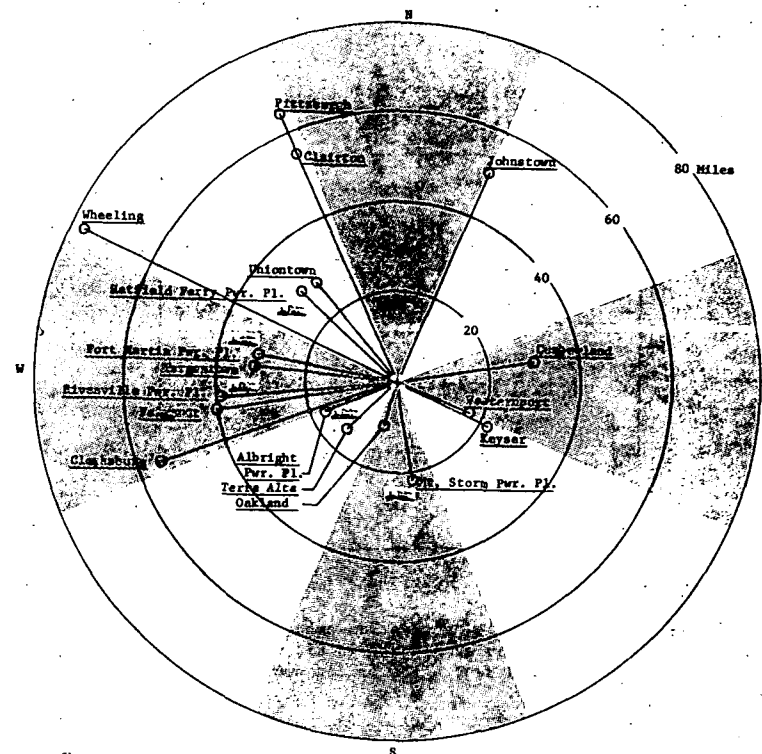


Figure 2. Major pollutant sources in the vicinity of the study area.

\* Data provided by EPA.

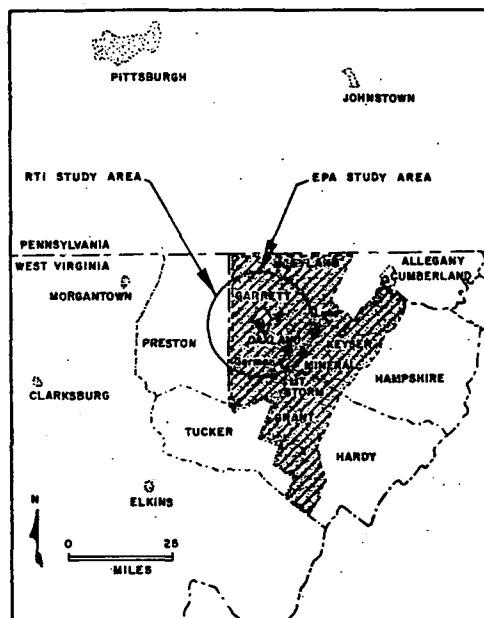


Figure 3. Relationship between Research Triangle Institute (RTI) study area and 1970 EPA study area (circles with dots denote EPA oxidant measurement sites).

#### SECTION 4 PROCEDURE

This section describes the procedures employed to obtain fixed ground-level, mobile ground-level, and upper air measurements of air quality and meteorological parameters.

##### 4.1 Fixed Ground-Level Measurements

###### 4.1.1 Site Selection

The site selected for fixed ground-level measurements was the Garrett County Airport near McHenry, Maryland. The airport elevation is approximately 2900 ft above mean sea level. Consisting of a 2500-ft paved landing strip, an apron, hangars, and terminal building, it is used principally by small private aircraft. The Research Triangle Institute (RTI) Environmental Monitoring Laboratory and a 30-ft guyed tower were located to the south of the parking area. Figure 4 is a sketch of the airport which shows the location of the Laboratory and tower. The site provided excellent exposure of monitoring instruments with minimal obstruction to air movement.

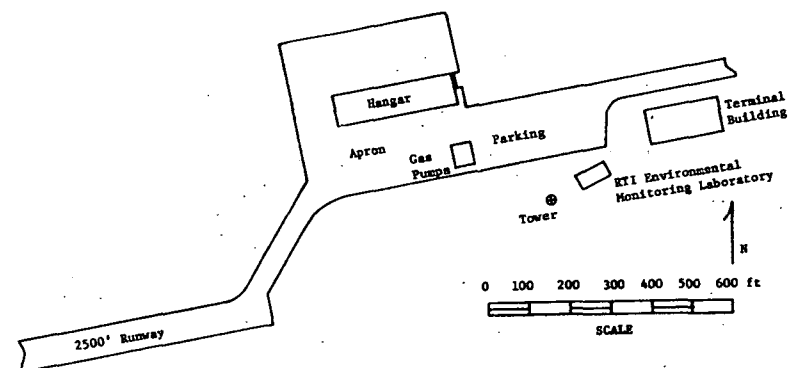


Figure 4. Garrett County Maryland Airport site.

#### 4.1.2 Air Quality Measurements

Ozone, nitric oxide, nitrogen dioxide, total hydrocarbon, methane, carbon monoxide, and sulfur dioxide\* concentrations were measured continuously by instruments housed in the RTI Environmental Monitoring Laboratory. Non-methane hydrocarbon concentration was obtained by subtracting the methane concentration from the total hydrocarbon concentration.

Ozone concentration was measured with a solid-phase chemiluminescent ozone meter and a Bendix Model 8300 flame photometric analyzer was used to measure sulfur dioxide concentration. Nitric oxide and nitrogen dioxide concentrations were measured with a Bendix Model 8101-B Chemiluminescent NO-NO<sub>x</sub>-NO<sub>2</sub> Analyzer. Total hydrocarbon, methane, and carbon monoxide concentrations were measured with the Beckman Model 6800 Gas Chromatographic Flame Ionization Detector (GC-FID). The calibration procedures used throughout and at the termination of the measurement program are summarized in Table 1 and detailed in Appendix A. Air for analysis was drawn from the 17-ft level on the tower through a one-inch I.D. teflon tube to a glass sampling manifold inside the Laboratory. Air for each instrument was drawn from this manifold.

Table 1. CALIBRATION METHODS AND SCHEDULE

Parameter	Calibration method	Frequency	
		Zero and span	Multipoint
Ozone	Ultra-violet ozone generator referenced to the neutral-buffered potassium iodide method	Every 2 days	Bi-weekly
Nitric oxide/ nitrogen dioxide	Gas phase titration of nitric oxide with ozone	Every 2 days	Bi-weekly
Sulfur dioxide	National Bureau of Standards permeation tube	Every 2 days	Bi-weekly
Total hydrocarbon/ methane	Certified cylinder gas <sup>a</sup> (methane in zero air)	Every 2 days	Bi-weekly
Carbon monoxide	Certified cylinder gas <sup>a</sup> (carbon monoxide in zero air)	Every 2 days	Bi-weekly

<sup>a</sup> Purchased from Scott Research Laboratories

\* Since sulfur dioxide is a quantitative interference in oxidant determinations, it was measured for the purpose of correcting the balloon-borne oxidant measurements.

Performance characteristics and operational summaries for the air quality monitoring instruments are presented in Appendix B.

#### 4.1.3 Meteorological Measurements

Ambient temperature was measured at heights of 5.5, 16, and 28.5 ft with shielded, aspirated thermistors, allowing the determination of temperature differences between 5.5 and 16, and 5.5 and 28.5 ft. Wind speed and wind direction were measured at heights of 17.5 and 31 ft with Bendix Aerovanes. Dewpoint temperature was measured with a Foxboro Dew Point Measuring System at a height of 7 ft on the tower. Solar radiation was measured with a Kipp and Zonen solarimeter located on the roof of the Laboratory.

#### 4.1.4 Continuous Stirred Tank Reactor (CSTR)

Two 72-liter pyrex glass flasks were used as CSTR vessels. One was exposed to sunlight, the other was kept in darkness. Air flow through the reactor vessels was 2 lpm. Air for each reactor was drawn from a common manifold which in turn was supplied with 300 lpm of air through a 1-inch I.D. teflon tube from a height of 17 ft on the tower. Solid-phase chemiluminescent ozone meters were used to measure ozone concentrations at the manifold and at the exit of each vessel. A description of the CSTR system is included as Appendix C.

#### 4.1.5 Data Acquisition

The signals from all fixed ground-level instruments were digitized and recorded on magnetic tape for subsequent reduction by computer. Strip chart recorders were used with all instruments as a backup to the data acquisition system, and to provide the operator with a convenient historical record.

#### 4.1.6 Data Processing

Data were sent weekly from the Environmental Monitoring Laboratory to RTI at Research Triangle Park, N. C. in the form of digital voltages recorded on magnetic tape. Computer programs were developed which edited, applied transfer functions, corrected lag time and drift, and computed hourly averages, frequency distributions, and diurnal averages.

#### 4.2 Mobile Ground-Level Measurements

##### 4.2.1 Satellite Locations

Satellite locations selected for mobile ground-level measurements are shown in Fig. 5, and described in Table 2. The satellite locations are arrayed along the circumference of an approximate 12.5-mile radius circle. The Steyer No. 2 and Weise-McDonald farms, locations 8 and 1, respectively, in Fig. 5 were selected to provide a link between the earlier EPA investigation (See Fig. 3) and this effort. The criteria used in selecting the remaining locations were that they be free of local obstructions to air movement, that they be at relatively high elevation, and in particular that they be well exposed to winds from the southwest.

The sampling schedule followed for mobile ground-level measurements is presented in Table 3. A detailed schedule is shown in Table 3a. One-hour measurements were made at satellite locations.

##### 4.2.2 Power Transmission Lines

A site north of Accident, Maryland was selected for the purpose of evaluating the contribution of ozone from high voltage power transmission lines. At this site, 500-kilovolt power transmission lines run southeast to northwest across Pud Miller Road (Fig. 5); i.e. at a right angle to a prevailing southwest wind. At this site the transmission lines pass over the road at a height of approximately 40 feet. The sampling protocol called for fifteen-minute measurements taken in the following sequence: underneath the lines, fifty yards downwind, fifty yards upwind, 140 yards downwind, and 140 yards upwind (northeast and southwest were considered downwind and upwind, respectively). This procedure was repeated three times, providing a maximum of 15 fifteen-minute ozone measurements at the power transmission lines for each day of sampling. The sampling schedule is shown in Table 3.

##### 4.2.3 Description of Mobile Unit

An International Harvester Scout was used as the mobile unit. It was equipped with a solid-phase chemiluminescent ozone meter with a strip chart recorder, and a Bendix Aerovane with a dual-channel strip chart recorder for wind speed and direction. Air for analysis was drawn through an inverted glass funnel extending 1 ft above the

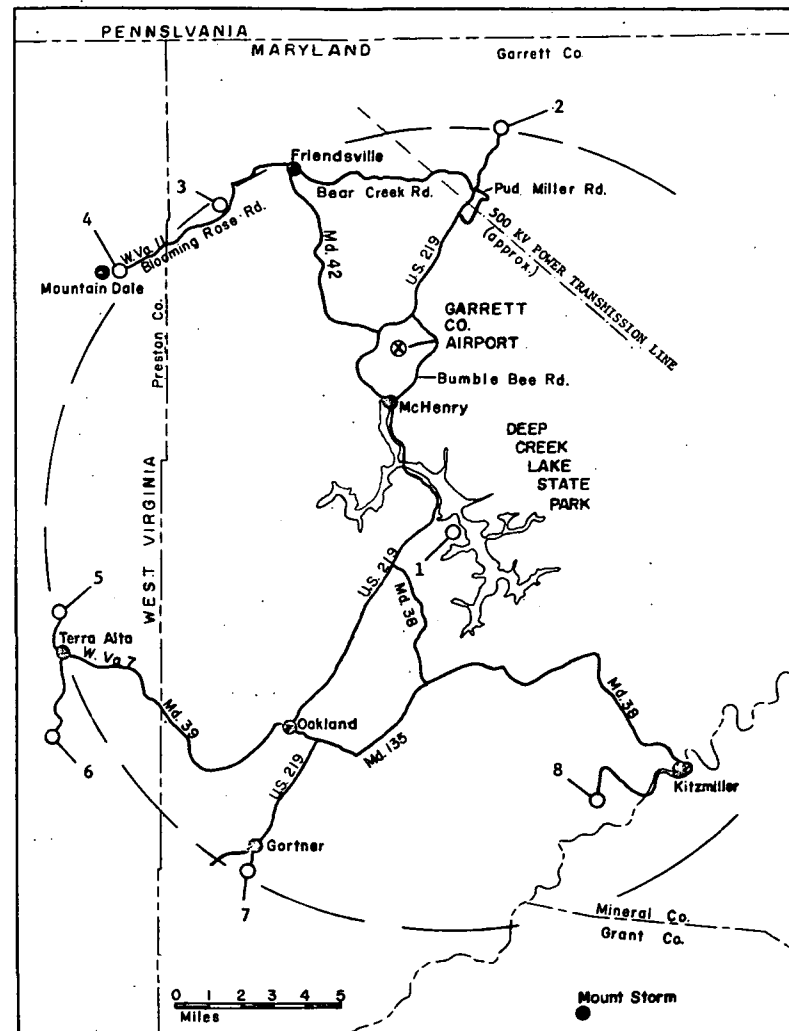


Figure 5. Satellite locations for ozone measurement and roads travelled.

Table 2. DESCRIPTION OF SATELLITE LOCATIONS

Location number	Description	Approximate elevation(ft)
1	Zaddock Miller Rd. (called Weise-McDonald farm in EPA report), at power pole next to Miller residence	2660
2	On west side of U.S. Rt. 219, 3.2 miles south of intersection of U.S. Rt. 219 & U.S. Rt. 40, 55 yards from road pavement	2720
3	0.8 miles south of Blooming Rose Church on Frantz and Blooming Rose Roads	2120
4	0.3 miles east of Mountain Dale intersection on West Virginia County Rt. 11	2540
5	Forman Field north of Terra Alta on W. Va. County Rt. 3, at entrance lane, approximately 10 yards off of W. Va. County Rt. 3	2546
6	4 miles south of Terra Alta on W. Va. County Rt. 53	2300
7	0.5 mile south of U.S. Rt. 219 on Blue Ribbon Road	2440
8	Steyer No. 2 Farm (at EPA site)	2540

Table 3. SCHEDULE FOR MOBILE GROUND-LEVEL UNIT

Date	Satellite Locations	Power Transmission Lines
August 4	X	
5		
6		
7	X	
8	X	
9		X
10	X	
11		
12		
13	X	
14	X	
15		X
16	X	
17	X	
18		X
19	X	
20		
21		
22	X	
23	X	
24		X
25	X	
26		
27		
28	X	
29	X	
30		X
31	X	
September 1		
2		
3	X	
4	X	
5		X
6	X	
7	X	
8		X
9	X	
10		
11		
12	X	
13	X	
14		X
15	X	
16	X	



Table 3a. DETAILED SAMPLING SCHEDULE FOR  
SATELLITE LOCATIONS

Date		Location <sup>a</sup>			
		Starting Time - EDT			
		1000	1200	1400	1600
August	4	1	2	3	4
	7	5	6	7	8
	8	2	3	4	1
	10	6	7	8	5
	13	3	4	1	2
	14	7	8	5	6
	16	4	1	2	3
	17	8	5	6	7
	19	1	2	3	4
	22	5	6	7	8
	23	2	3	4	1
	25	6	7	8	5
	28	3	4	1	2
	29	7	8	5	6
	31	4	1	2	3
September	3	8	5	6	7
	4	1	2	3	4
	6	5	6	7	8
	7	2	3	4	1
	9	6	7	8	5
	12	3	4	1	2
	13	7	8	5	6
	15	4	1	2	3
	16	8	5	6	7

<sup>a</sup> Location numbers correspond to those of Fig. 5.

vehicle roof and connected to the ozone meter with teflon tubing. The mobile unit ozone meter was calibrated using the procedure listed in Table 1, above. The power supply for the instruments was four 12-volt batteries in parallel combined with a DC-AC inverter. The instruments remained on throughout the period of a run; however, the Scout engine was turned off while measurements were made. A Bendix Psychron was employed to measure wet and dry bulb temperatures.

#### 4.3 Upper Air Measurements

Vertical soundings of atmospheric temperature and ozone were made in the near-surface environment and through the troposphere using a NOAA-type radiosonde with a Mast Model 730-7 ozonesonde attached as the sensor. For the near surface measurements, an aerodynamically-shaped balloon, tethered from the ground, was used to carry the instrumentation aloft. A full description of tethered balloon procedures is given in Appendix D. For tropospheric measurements, the same instrumentation was attached to a 1200-gm rubber balloon and released. Signals transmitted by the radiosonde were received and recorded on a 5-inch strip chart recorder operating at a chart speed of 1/2 inch per minute.

Tethered and free balloon releases were made at the Garrett County Maryland Airport as weather circumstances, in particular rain and high winds, permitted. A special effort was made to obtain both day and night soundings.

## SECTION 5

### SUMMARY OF OBSERVATIONS

A summary of observations obtained during the seven-week field measurement program is presented below.

#### 5.1 Fixed Ground-Level Measurements

##### 5.1.1 Air Quality Measurements

Five-minute average concentrations for the air quality measurements were printed out by computer. A sample of this printout is given in Fig. 6.\* Summary statistics for hourly air quality measurements made at the Garrett County Maryland Airport are given in Table 4. The maximum hourly concentrations of carbon monoxide, nitrogen dioxide, ozone, and sulfur dioxide were 0.804, 0.038, 0.119, and 0.161 ppm, respectively.

Table 4. STATISTICAL SUMMARY OF HOURLY AIR QUALITY MEASUREMENTS AT GARRETT COUNTY MARYLAND AIRPORT  
August 4-September 25, 1972

Pollutant	Mean (ppm)	Standard deviation (ppm)	Case count
Carbon monoxide	.219	.149	686
Methane	1.521	.115	571
Nitric oxide	-.010 <sup>a</sup>	.004	1,140
Nitrogen dioxide	.007	.005	1,140
Nonmethane hydrocarbon	-.058	0.120	553
Oxides of nitrogen	-.004	.007	1,140
Ozone	.057	.018	1,043
Sulfur dioxide	.005	.011	945
Total hydrocarbon	1.452	.096	782

<sup>a</sup> The data acquisition system acknowledges both positive and negative voltages. An entry preceded by a negative sign should be regarded as zero concentration.

\* The complete tabulation of five-minute values is too voluminous to present here. A copy has been delivered to the Project Officer, and interested parties may contact RTI to arrange to see the tabulation.

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NOT REPRODUCIBLE

The values for carbon monoxide, methane, non-methane hydrocarbon and total hydrocarbon concentration shown in Table 4 should be interpreted with some caution.\* Of these values, those for carbon monoxide are believed to be most nearly correct; hence they are reported in greater detail.

Daytime and nighttime mean concentrations of carbon monoxide, nitrogen dioxide, ozone and sulfur dioxide are shown in Table 5, while mean diurnal concentration curves for these pollutants are presented as Figs. 7, 8, 9, and 10, respectively.

In Table 6 frequency distributions for the several air quality parameters are presented.

### 5.1.2 Meteorological Measurements

Mean diurnal curves for ambient temperature, solar radiation, and 30-ft wind speed for the study period are shown in Figs. 11, 12, and 13, respectively.

The mean temperature for all hours of the study period was 18.5°C (65.3°F). The mean nighttime temperature was 16.7°C, or 3.2°C lower

Table 5. DAYTIME AND NIGHTTIME MEANS FOR SELECTED AIR QUALITY MEASUREMENTS AT GARRETT COUNTY MARYLAND AIRPORT August 4-September 25, 1972

Measurement	Mean (ppm)	
	Daytime <sup>a</sup>	Nighttime <sup>b</sup>
Carbon monoxide	0.227 (382) <sup>c</sup>	0.208 (304)
Nitrogen dioxide	0.006 (645)	0.007 (495)
Ozone	0.059 (591)	0.055 (452)
Sulfur dioxide	0.004 (530)	0.006 (415)

<sup>a</sup> 0600 to 1955 EDT

b 2000 to 0555 EDT

<sup>c</sup> Number in parentheses is the case count.

\* Following completion of the field program, the instrument manufacturer determined that water vapor permeating the neoprene diaphragm of the hydrogen regulator could have contaminated the analytical column with a consequent shift in retention time and error in indicated concentration.

Table 6. FREQUENCY DISTRIBUTION OF ONE-HOUR AVERAGES AT  
GARRETT COUNTY MARYLAND AIRPORT  
August 4-September 25, 1972

Concentration (ppm)	Percent of samples > stated concentration					
	Ozone	Nitrogen oxides	Nitric oxide	Nitrogen dioxide	Sulfur dioxide	Carbon monoxide
.0050	100.00 %	7.98 %	0.00 %	47.46 %	25.71 %	94.02 %
.0100	99.81 %	2.98 %	0.00 %	15.35 %	11.53 %	93.73 %
.0200	98.64 %	.70 %	0.00 %	2.37 %	4.13 %	93.29 %
.0300	92.43 %	.18 %	0.00 %	.35 %	2.75 %	91.98 %
.0400	81.84 %	0.00 %	0.00 %	0.00 %	2.12 %	91.55 %
.0500	66.80 %	0.00 %	0.00 %	0.00 %	1.27 %	90.96 %
.0600	40.58 %	0.00 %	0.00 %	0.00 %	.74 %	89.65 %
.0700	22.23 %	0.00 %	0.00 %	0.00 %	.63 %	88.34 %
.0800	11.26 %	0.00 %	0.00 %	0.00 %	.42 %	87.17 %
.0900	4.56 %	0.00 %	0.00 %	0.00 %	.32 %	85.86 %
.1000	1.75 %	0.00 %	0.00 %	0.00 %	.21 %	84.26 %
.1100	.68 %	0.00 %	0.00 %	0.00 %	.21 %	81.34 %
.1200	0.00 %	0.00 %	0.00 %	0.00 %	.21 %	77.41 %
.1300	0.00 %	0.00 %	0.00 %	0.00 %	.11 %	73.91 %
.1400	0.00 %	0.00 %	0.00 %	0.00 %	.11 %	70.26 %
.1500	0.00 %	0.00 %	0.00 %	0.00 %	.11 %	64.72 %
.2000	0.00 %	0.00 %	0.00 %	0.00 %	0.00 %	46.50 %
.3000	0.00 %	0.00 %	0.00 %	0.00 %	0.00 %	24.49 %
.4000	0.00 %	0.00 %	0.00 %	0.00 %	0.00 %	14.43 %
.6000	0.00 %	0.00 %	0.00 %	0.00 %	0.00 %	1.02 %
Case count	1043	1140	1140	1140	945	686

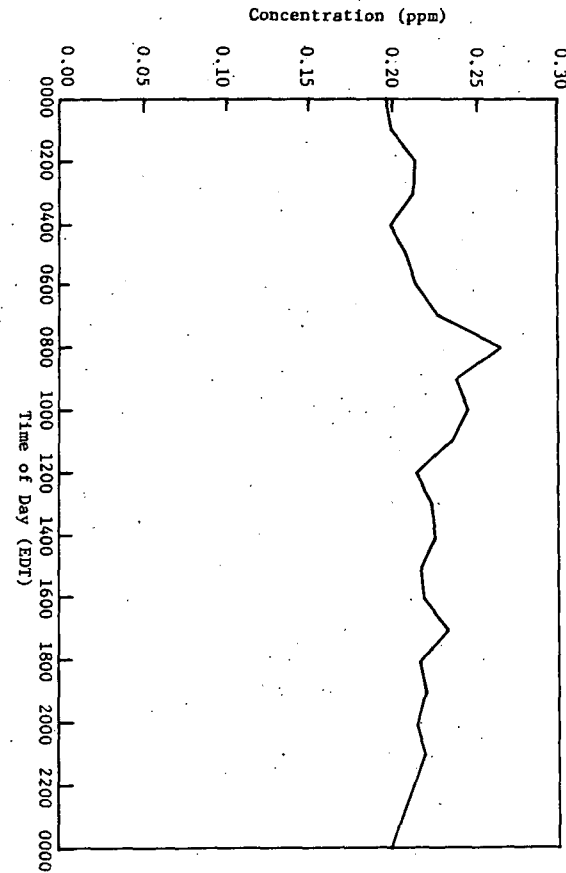


Figure 7. Diurnal mean carbon monoxide concentration at Garrett County  
Maryland Airport for August 4-September 25, 1972.

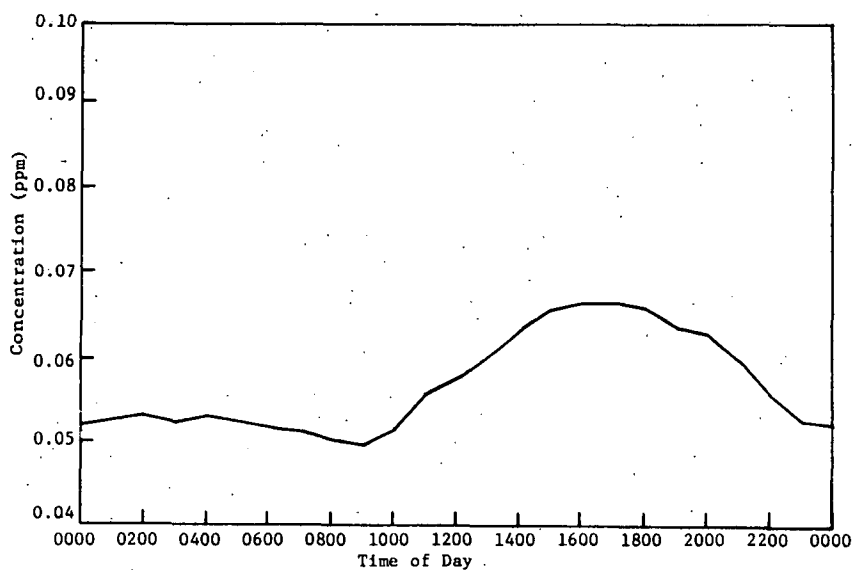


Figure 9. Diurnal mean ozone concentration at Garrett County Maryland Airport for August 4 to September 25, 1972.

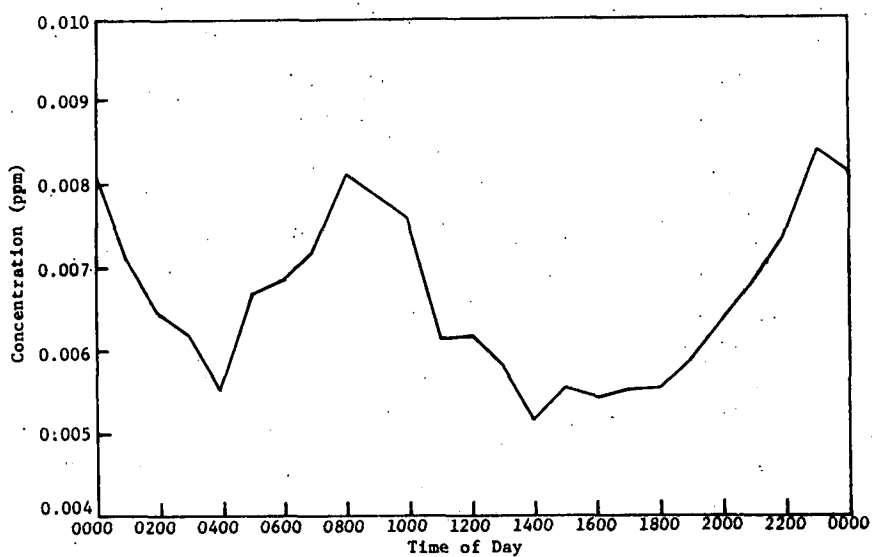


Figure 8. Diurnal mean nitrogen dioxide concentration at Garrett County Maryland Airport for August 4-September 25, 1972.

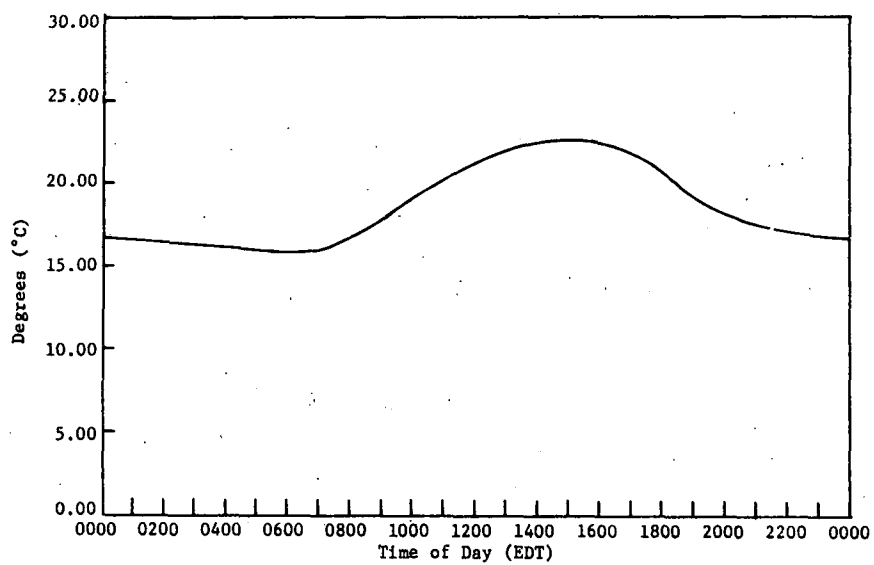


Figure 11. Diurnal mean ambient temperature at Garrett County Maryland Airport for August 4-September 25, 1972.

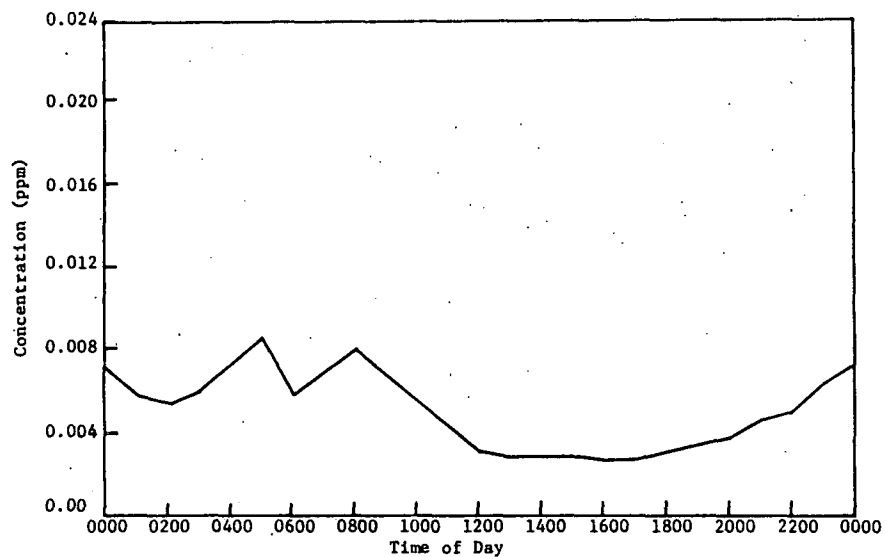


Figure 10. Diurnal mean sulfur dioxide concentration at Garrett County Maryland Airport for August 4-September 25, 1972.



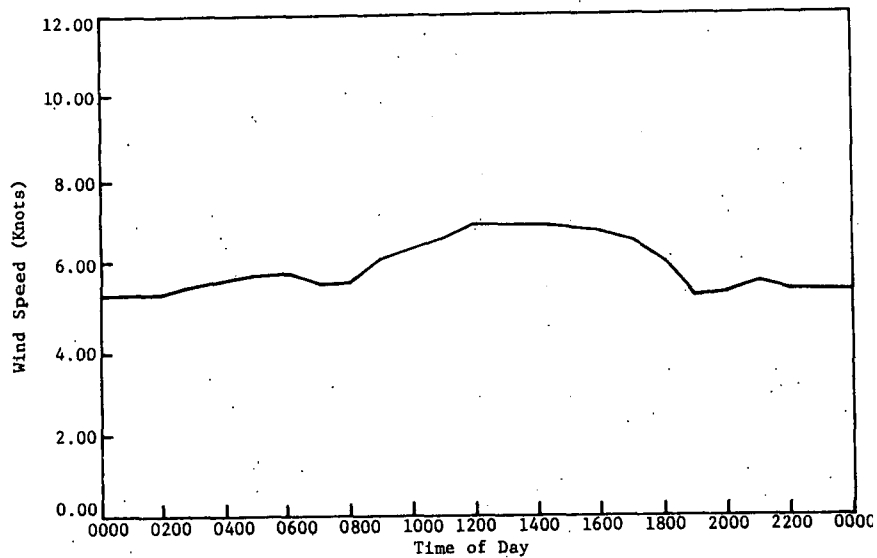


Figure 13. Diurnal mean thirty-foot wind speed at Garrett County Maryland Airport for August 4-September 25, 1972.

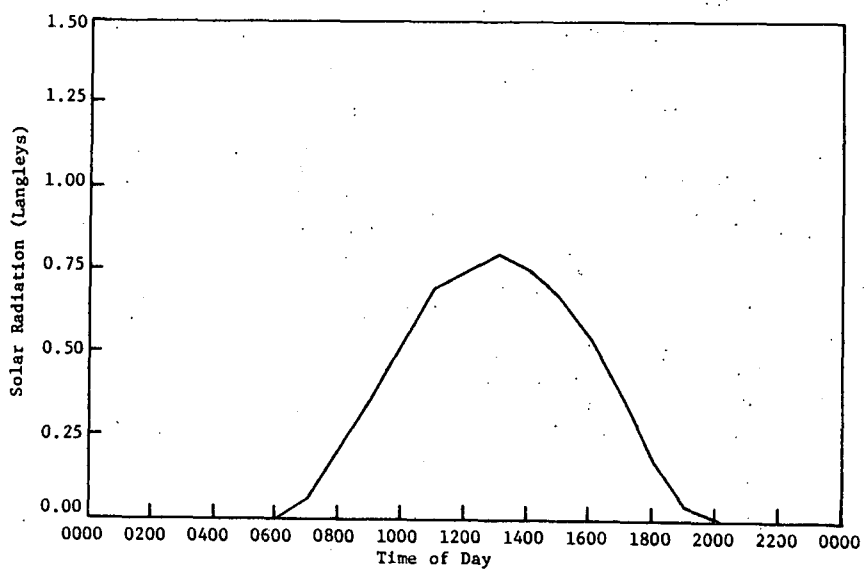


Figure 12. Diurnal mean solar radiation at Garrett County Maryland Airport for August 4-September 25, 1972.

than the mean daytime temperature of 19.8°C. The difference between the maximum (22.5°C) and the minimum (15.7°C) on the diurnal temperature curve is also small (6.8°C). The small range of average temperature indicates the presence of clouds both day and night. The high nighttime temperature suggests that strong radiation inversions occurred only infrequently at the airport.

Mean solar radiation during the study period was 0.417 Langley's.

The average wind speed at the 30-ft level for all hours was 5.9 kt. On the average, winds reached a peak of 7.0 kt at mid-day, with a lull at 5.2 kt near sunset. Only 23 hours of calm winds (< 1 kt) were calculated (representing 1.8 percent of the observations) and the hourly vector average wind speed never exceeded 17 kt. Evaluation of wind speed observations indicates that the site was well ventilated and that separation of winds aloft from the near surface circulation by nocturnal inversions occurred infrequently.

The frequency of occurrence of wind direction by 22.5°C sectors and the average wind speed for each sector is shown in Fig. 14. Southwest through northwest winds are clearly the predominant wind directions, accounting for 59 percent of the 1,139 hourly wind observations. The next most frequent directions were southeast and south-southeast, accounting for an additional 19 percent of the observations. Northerly to northeasterly winds rarely occurred and never exceeded a speed of 3 kts. Southeasterly winds occurred much more frequently and westerly winds slightly less frequently than during the previous study (EPA, 1971).

## 5.2 Mobile Ground-Level Measurements

### 5.2.1 Satellite Locations

A total of 49 one-hour ozone measurements were obtained at the satellite locations. Those measurements, as well as the corresponding meteorological measurements, are presented in chronological order in Table 7.

### 5.2.2 Power Transmission Lines

Seventy 15-minute ozone measurements in the vicinity of 500-KV power transmission lines were obtained. The measurements are shown in Table 8.



Figure 14. Frequency of occurrence of wind direction 30 ft above ground at Garrett County Maryland Airport, August 6 to September 24, 1972. Average wind speed for each direction shown at extremity of the radials. Calm conditions occurred 1.8 percent of the time.

Table 7. OZONE AND METEOROLOGICAL MEASUREMENTS AT SATELLITE LOCATIONS (Cont'd)

Date	Location	Measurement period (EDT)		Average ozone concentration (ppm)	Wind speed (mph)	Wind direction	Temperature °F	
		Begin	End				Dry bulb	Wet bulb
September 6	5	1000	1100	0.050	8.0	109	64	55
	6	1200	1300	0.061	12.3	115	69	55
	7	1400	1500	0.055	7.5	118	71	57
	8	1607	1700	0.062	6.3	145	70	57
September 7	2	1000	1100	0.051	4.8	200	66	56
	3	1200	1300	0.058	9.0	258	74	59
	4	1400	1455	0.061	9.0	270	74	60
	1	1600	1700	0.064	2.0	180	77	63
September 9	6	1000	1100	0.020	8.5	350	61	59
	7	1200	1245	0.028	6.3	261	66	60
	8	1409	1555	0.039	7.6	350	69	60
	5	1613	1700	0.051	12.0	350	65	56
September 12	3	1000	1100	0.037	10.8	258	65	65
	4	1200	1300	0.039	11.3	268	65	64
	1	1412	1510	0.047	3.0	203	67	65
	2	1600	1700	0.042	7.0	294	66	65
September 13	7	1000	1100	0.059	6.3	261	72	68
	8	1205	1300	0.062	12.8	275	76	68
	5	1415	1500	0.070	18.0	272	74	68
	6	1600	1700	0.075	18.0	285	75	68
September 16	8	1003	1045	0.047	9.7	290	68	60
	5	1200	1300	0.055	12.3	278	68	58
	6	1400	1500	0.058	10.8	285	72	60
	7	1600	1700	0.059	7.0	265	77	63

C = Calm  
M = Missing data  
E = Equipment malfunction

Table 7. OZONE AND METEOROLOGICAL MEASUREMENTS AT SATELLITE LOCATIONS

Date	Location	Measurement period (EDT)		Average ozone concentration (ppm)	Wind speed (mph)	Wind direction	Temperature °F	
		Begin	End				Dry bulb	Wet bulb
August 23	2	1000	1100	0.058	6.8	280	74	67
	3	1200	1300	0.074	15.0	274	79	71
	4	1400	1500	0.081	12.0	246	80	69
	1	1610	1700	0.084	C	C	80	70
August 25	6	1009		E				
	7	1200		E		304	83	70
	8	1410	1504	0.070	6.8			
	5	1610	1700	0.079	M	292	78	71
August 28	3	1000	1100	0.031	15.3	293	68	63
	4	1200	1300	0.041	9.3	258	67	61
	1	1405	1500	0.049	2.0	263	70	62
	2	1600	1700	0.055	7.8	288	70	62
August 29	7	1000	1100	0.058	2.8	286	71	64
	8	1214	1300	0.073	4.0	334	75	64
	5	1420	1510	0.058	8.3	321	73	64
	6	1600	1700	0.077	6.0	295	72	65
August 31	4	1005	1100	0.069	5.5	157	72	63
	1	1220	1305	0.077	3.0	171	74	64
	2	1400	1500	0.093	7.5	154	73	62
	3	1600	1700	0.082	3.3	153	75	63
September 3	8	1000		E				
	5	1205	1300	0.041	5.8	245	64	62
	6	1400	1500	0.053	8.3	280	64	62
	7	1600	1700	0.068	3.0	268	67	64
September 4	1	1000	1100	0.022	2.5	M	59	56
	2	1200	1300	0.026	4.0	300	64	57
	3	1400	1500	0.044	6.0	310	62	56
	4	1600	1700	0.027	3.3	315	60	55

C = Calm  
M = Missing  
E = Equipment malfunction

### 5.3 Upper Air Measurements

The ozonesonde used for upper air measurements was calibrated with known ozone concentrations immediately before and after tethered balloon flights. For reasons not immediately apparent, the pre- and post-flight calibration curves varied significantly both in scale and slope. Thus, it is questionable whether either the absolute or relative ozone (oxidant) concentrations are valid. Accordingly, only the temperature data are reported.

#### 5.3.1 Tethered Balloon

Thirteen tethered balloon flights were made between September 11 and 22. Flights were made in early morning, at mid-day, near sunset, and near mid-night. The maximum altitudes attained varied from 400 to 900 ft, depending upon weather and balloon conditions.

Surface-based temperature inversions were found in some of the early morning, early evening, and night flights. Distinct temperature inversions aloft were not found within the layer sounded by the tethered flights. Daytime measurements show a nearly adiabatic condition when averaged over the sounding depth. The temperature data obtained are plotted as vertical profiles in Fig. 15.

#### 5.3.2 Free Balloon

Of four free balloon releases, one provided useful data. The temperature and relative humidity profiles from the surface to the 500-mb level (~18,000 ft) for that release are shown in Fig. 16. An inversion based at about the 800-mb level (~6,400 ft) is clearly shown.

Table 8. FIFTEEN-MINUTE AVERAGE OZONE CONCENTRATIONS (PPM) IN THE VICINITY OF 500-KV POWER TRANSMISSION LINES

Date	Study period (EDT)	Begin	End	Location				
				Upwind		Underneath	Downwind	
				140 yards	50 yards	40 feet	50 yards	140 yards
August 24	1300	1725	0.090	0.086	0.080	0.081	0.090	
			0.085	0.086	0.078	0.086	0.085	
			0.088	0.090	0.073	0.078	0.089	
August 30	1310	1748	0.048	0.052	0.049	0.051	0.052	
			0.058	0.056	0.049	0.054	0.057	
			0.064	0.065	0.060	0.065	0.066	
September 5	1230	1731	0.051	0.050	0.049	0.048	0.051	
			0.057	0.057	0.052	0.052	0.058	
			0.050	0.051	0.054	0.056	0.048	
September 8	1255	1722	0.068	0.073	0.068	0.074	0.071	
			0.068	0.067	0.067	0.067	0.068	
			0.072	0.072	0.066	0.069	0.073	
September 14	0900	1157	0.043	0.044	0.038	0.043	0.043	
			0.047	0.046	0.041	0.045	0.046	

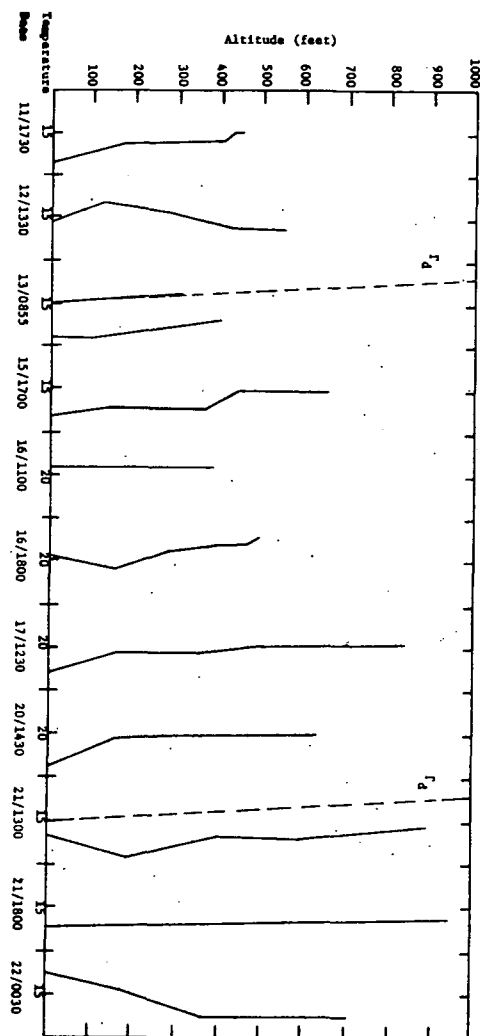


Figure 15. Temperature-altitude profiles during ascent portion of tethered balloon flights. Each horizontal increment is 5°C. Dashed lines ( $T_d$ ) show the dry adiabatic temperature profile.

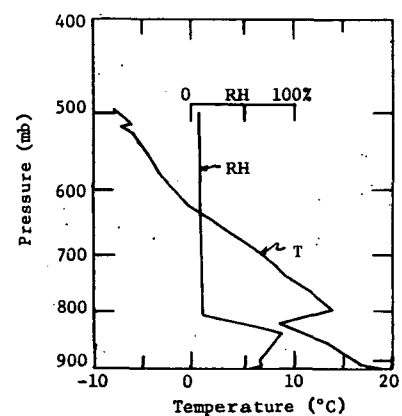


Figure 16. Vertical profiles, temperature (T), and relative humidity (RH) as measured by free balloon release at 1805 EDT, September 15.

## SECTION 6

### OCCURRENCE OF HIGH OZONE CONCENTRATIONS

This section is concerned with the frequency of occurrence of high ozone concentrations, episodes of high concentration and the horizontal and vertical extent of regions of high concentration.

#### 6.1 Frequency of Occurrence

The frequency distribution of hourly ozone concentrations at the Garrett County Maryland Airport during the period August 4-September 25, 1972 was presented in Table 6, above. Examination of that distribution reveals that the National Air Quality Standard for photochemical oxidants of 0.08 ppm was exceeded approximately 11 percent of the time.

The mean and maximum hourly ozone concentrations observed during the present study were 0.057 and 0.119 ppm, respectively. These values are remarkably close to the 0.059 ppm mean and 0.13 ppm maximum seen in the special two-week ozone measurement program conducted in August and September 1970 (Richter, 1970). It is believed that the findings of this study verify the high concentrations of ozone previously found in the Mt. Storm, West Virginia area.

The only time that ozone concentration reached zero at the Garrett County Maryland Airport was between 0530 and 0550 on September 22. This decrease was coincident with a sharp increase in sulfur dioxide and nitrogen dioxide concentrations (Fig. 17). Wind direction at this time was north-northeast. Decreases in ozone concentration associated with increased sulfur dioxide and nitrogen dioxide concentrations were seen on several occasions; however, only on September 22 did ozone concentration fall to zero.

#### 6.2 Episodes

It is of interest to identify extended periods of time, or episodes, of persistent high ozone concentration. For this purpose, episodes were defined as periods in which ozone concentration at the Garrett County Maryland Airport was equal to or greater than 0.08 ppm for more than two hours. Pertinent dates and times and episode durations are given in Table 9. Eleven episodes occurred during the field measurement

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Table 9. EPISODES OF HIGH OZONE CONCENTRATION  
 ( $\geq 0.08$  ppm for more than 2 hours) AT GARRETT  
 COUNTY MARYLAND AIRPORT  
 August 4-September 25, 1972

Begin episode			End episode			
Date		Hour (EDT)	Date		Hour (EDT)	Duration (hours)
August	10	1800	August	10	2200	5
	13	1300		14	0000	12
	14	0500		14	1100	7
		1400			2200	9
	15	0000		15	0700	8
	18	1200		18	1800	7
	31	1100		31	2000	10
September	1	1400	September	1	1800	5
	2	0200		3	0300	26
	11	2200		12	0200	5
	12	2200		13	0800	11

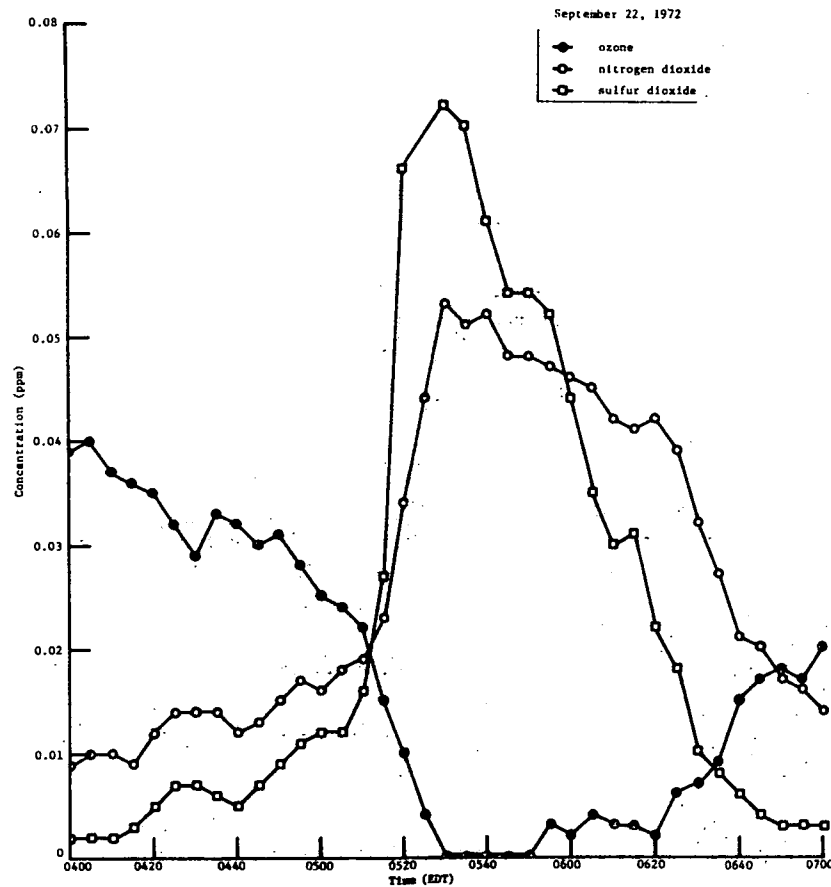


Figure 17. Period of low ozone concentration at  
 Garrett County Maryland Airport.

program, the longest of which persisted for 26 consecutive hours beginning at 0200 EDT on September 2. During the August 31 episode ozone concentration was also measured at satellite locations. At one location the concentration approached 0.08 ppm and it exceeded that value at two others.

The time course of three episodes is graphed in Fig. 18. Corresponding carbon monoxide concentration data are available for two of the episodes; they are also plotted in Fig. 18. The interpretation of the low carbon monoxide concentration data is difficult and the difficulty is compounded by instrument uncertainties (see footnote, p. 21). Recall also that the minimum detectable carbon monoxide concentration is 0.1 ppm.

### 6.3 Horizontal Extent

The mobile ground-level measurement program provided ozone data for eight satellite locations. Hourly ozone concentrations at the satellite locations and the corresponding concentrations at the Garrett County Maryland Airport are given in Table 10. The data shown in Table 10 were not used to test for statistically significant differences between satellite location and airport measurements since hourly ozone measurements within days were tested and found to have high autocorrelation coefficients. Thus, the assumption of statistical independence which underlies the appropriate test procedures, e.g., paired t-test, or Wilcoxon signed-rank test, was violated.

The data of Table 10 were used to prepare the frequency distributions shown in Table 11. Note that the percent of observations equal to or greater than 0.081 ppm was 8.0 and 8.5 for the satellite locations and the airport, respectively.

It is concluded that the region of high ozone concentration extends at least the 12.5 miles from the airport to the several satellite locations. This is not surprising in light of the 1970 oxidant measurements which showed high concentrations at such diverse locations as Stony River farm in Grant County, West Virginia and the Steyer No. 2 and Weise-McDonald farms in Garrett County, Maryland (EPA, 1971).

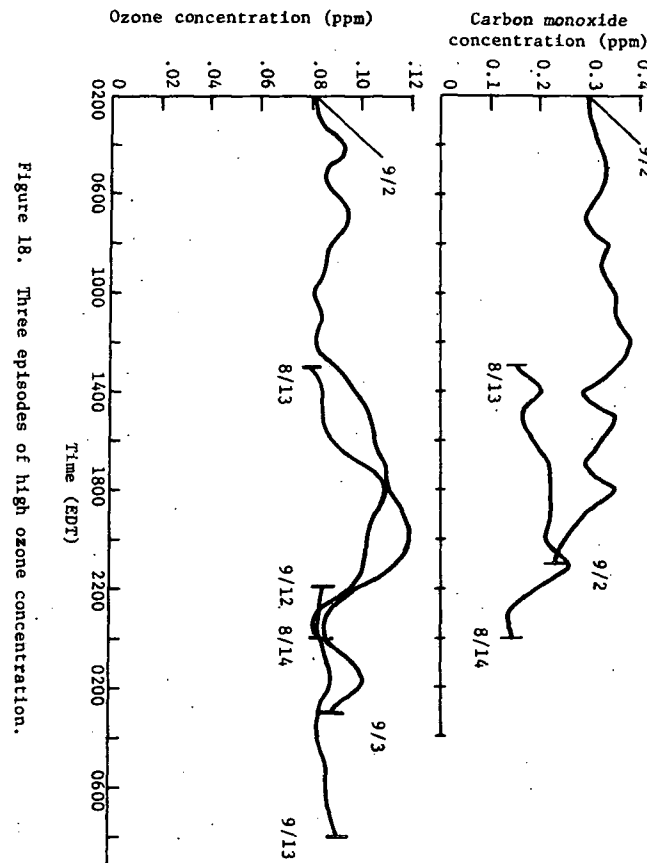


Figure 18. Three episodes of high ozone concentration.

Table 10. HOURLY OZONE CONCENTRATIONS AT SATELLITE LOCATIONS  
AND CORRESPONDING HOURLY OZONE CONCENTRATIONS  
AT GARRETT COUNTY MARYLAND AIRPORT

Satellite locations	Ozone concentration (ppm)		
	Garrett County Maryland Airport	Satellite locations	Garrett County Maryland Airport
0.058	0.050	0.055	0.065
0.074	0.060	0.062	0.068
0.081	0.065	0.051	M
0.084	0.072	0.058	0.057
0.070	0.053	0.061	0.061
0.079	0.049	0.064	0.065
0.031	0.041	0.020	M
0.041	0.046	0.028	0.040
0.049	0.053	0.039	0.047
0.055	0.053	0.051	0.055
0.058	0.054	0.037	0.059
0.073	0.072	0.039	0.059
0.058	0.075	0.047	0.068
0.077	0.081	0.042	0.063
0.069	0.073	0.059	M
0.077	0.091	0.062	0.074
0.093	0.091	0.070	0.073
0.082	0.087	0.075	0.070
0.041	0.064	0.047	0.056
0.053	0.074	0.055	0.062
0.068	0.077	0.058	0.076
0.022	0.033	0.059	0.073
0.026	0.045		
0.044	0.061		
0.027	0.054		
0.050	0.056		
0.061	0.057		

M = Missing

Table 11. FREQUENCY DISTRIBUTIONS OF HOURLY OZONE CONCENTRATION  
AT SATELLITE LOCATIONS AND CORRESPONDING HOURLY OZONE  
CONCENTRATIONS AT GARRETT COUNTY MARYLAND AIRPORT

Ozone concentration (ppm)	Percent of observations ≥ stated concentration	
	Satellite locations	Garrett County Maryland Airport
0.081	8.0	8.5
0.075	16.0	14.8
0.070	24.0	31.9
0.064	30.0	44.6
0.059	42.0	59.5
0.055	58.0	70.2
0.050	66.0	82.9
0.041	80.0	93.6

#### 6.4 Vertical Extent

While it was not possible to define the vertical extent of the region of high ozone concentration, the following can be inferred from meteorological analysis: The lack of well defined nocturnal surface-based temperature inversions, the small diurnal temperature range, and the relatively constant wind speed from day to night suggests that the air masses over the base station were relatively well mixed in the lower levels. As a consequence, the assumption that the high concentrations of ozone are not restricted to a shallow surface layer appears warranted. In fact, higher concentrations of ozone above the surface seem probable since vegetation, soil, and all structures and obstacles on the surface form an ozone sink.

#### SECTION 7

##### RATES OF PHOTOCHEMICAL SYNTHESIS, DESTRUCTION AND TRANSPORT OF OZONE

Due to difficulties not yet resolved, the rate of ozone ( $O_3$ ) synthesis (S) could not be determined from Continuous Stirred Tank Reactor data. Examination of ambient  $O_3$  concentrations, however, indicates that synthesis and sunlight have little to do with maintaining high concentrations such as occurred on September 2. It was possible to determine the rate of destruction (RD); the rate ranged from approximately zero to an isolated high of  $-97 \times 10^{-5}$  ppm min<sup>-1</sup>, with an average of approximately  $-19 \times 10^{-5}$  ppm min<sup>-1</sup> (Table 12). With an ozone concentration of 0.9 ppm, the  $EK_1D_1$  value (average value of rate constant times concentration of  $O_3$ -reactive substance in ppm) is approximately  $2 \times 10^{-3}$  min<sup>-1</sup>. The absolute rate of destruction is approximately twice that observed in rural piedmont North Carolina (Jeffries, 1971), but the  $O_3$  concentration was approximately five times as high. The rate of destruction normalized for ozone concentration was  $-2.1 \times 10^{-3}$  ppm min<sup>-1</sup> per ppm ( $-2.1 \times 10^{-3}$  min<sup>-1</sup>). The normalized rate determined in rural piedmont North Carolina for a period in January 1971 was  $-5.7 \times 10^{-3}$  min<sup>-1</sup> (Jeffries, 1971). Thus, the normalized rate of destruction observed in this study area was well within the range expected for naturally occurring destructive agents of local origin.

With an illustrative rate constant of  $10^4$  l mole<sup>-1</sup> sec<sup>-1</sup> ( $-3 \times 10^{-5}$  ppm<sup>-1</sup> min<sup>-1</sup>), the KD values listed in Table 11 represent concentrations of  $O_3$ -reactive material of 0.01 to 0.08 ppm. The normalized RD values are characteristic of natural rates and do not suggest an "active" pollution system (Jeffries, 1971). The  $O_3$ -destructive material could be of natural origin and recently mixed with  $O_3$ -rich air.

The corresponding rates of change in  $O_3$  concentration due to transport (RT) (for daylight hours, transport plus synthesis) are shown in Table 13. A negative daylight-hour RT value would require the mixing of  $O_3$ -poor air with air previously sampled. For an initial  $O_3$  concentration of 0.08 ppm

Table 13. CALCULATED OZONE TRANSPORT RATES AT GARRETT COUNTY  
MARYLAND AIRPORT FOR SEPTEMBER 2, 1972<sup>a</sup>

Time	O <sub>3</sub> (ppm)	R(T + S) (ppm min <sup>-1</sup> x 10 <sup>1</sup> )	λ (Langley's)	Time	O <sub>3</sub> (ppm)	R(T + S) (ppm min <sup>-1</sup> x 10 <sup>1</sup> )	λ (Langley's)
Daytime							
1305	0.085	-13.3	.50	1310	0.087	+80.9	.50
1320	0.086	+ 3.8	.53	1315	0.095	+37.3	.33
1350	0.093	-18.1	1.00	1345	0.099	+42.1	.86
1730	0.102	+26.4	.46	1725	0.116	+44.8	.44
1750	0.107	-36.3	.30	1745	0.104	+48.8	.32
1800	0.109	+14.0	.29	1755	0.116	+63.7	.32
Nighttime							
0305	0.090	-92.5		0315	0.079	+47.6	
0310	0.080	-100.8		0340	0.087	+237.5	
0355	0.089	-11.0		0345	0.088	+29.7	
2000	0.122	-56.8		2010	0.115	+48.3	
2140	0.106	+19.1		2015	0.123	+11.0	
2150	0.109	+15.2		2030	0.127	+26.6	

Table 12. CALCULATED OZONE DESTRUCTION RATES AT GARRETT COUNTY  
MARYLAND AIRPORT FOR SEPTEMBER 2, 1972<sup>a</sup>

Negative dO <sub>3</sub> /dt						Positive dO <sub>3</sub> /dt					
Time	O <sub>3</sub> (ppm)	dO <sub>3</sub> /dt (ppm/min)	RD (ppm/min)	RD/O <sub>3</sub> =EKD	λ (Langley's)	Time	O <sub>3</sub> (ppm)	dO <sub>3</sub> /dt (ppm/min)	RD (ppm/min)	RD/O <sub>3</sub> =EKD	λ (Langley's)
Daytime											
1305	0.085	-43.2	-30.0	-3.5	.50	1310	0.087	+62.8	-18.0	-2.1	.50
1320	0.086	-23.3	-27.0	-3.2	.53	1315	0.095	+21.5	-15.7	-1.7	.33
1350	0.093	-45.1	-27.0	-2.9	1.00	1345	0.099	+30.8	-11.3	-1.1	.86
1730	0.102	- 3.8	-30.3	-3.0	.46	1725	0.116	+19.4	-25.4	-2.3	.44
1750	0.107	-39.9	- 3.6	-0.3	.30	1745	0.104	+ 6.2	-42.6	-4.1	.32
1800	0.109	-17.2	-31.2	-2.9	.29	1755	0.116	+48.1	-15.7	-1.4	.32
Nighttime											
0305	0.090	-98.3	- 5.6	-0.6		0315	0.079	+38.4	- 9.2	-1.2	
0310	0.080	-120.3	-19.5	-2.4		0340	0.087	+212.7	-24.8	-2.8	
0355	0.089	-19.8	- 8.7	-1.0		0345	0.088	+11.5	-18.3	-2.1	
2000	0.122	-65.7	- 8.9	-0.7		2010	0.115	+ 6.1	-42.2	-3.7	
2140	0.106	-15.8	-34.9	-3.2		2015	0.123	+ 4.5	- 6.5	-0.5	
2150	0.109	- 2.1	-17.3	-1.6		2030	0.127	+ 4.8	-19.8	-1.6	

<sup>a</sup> Multiply dO<sub>3</sub>/dt, RD, and RD/O<sub>3</sub> by 10<sup>-5</sup>.

or greater, any mixing with natural air would result in a negative value of RT. A positive RT value at night is interpreted to mean mixing the previously sampled air with air relatively rich or more concentrated in  $O_3$ . Starting with an  $O_3$  concentration of 0.08 ppm or greater, a positive nighttime RT suggests the presence of an  $O_3$ -rich ( $> 0.08$  ppm) reservoir of air.

Although the daylight synthesis term was not determined, the rate of synthesis at night is obviously zero; thus nighttime transport can be calculated. The average RT value for the above mentioned study in piedmont North Carolina was  $10.1 \times 10^{-5}$  ppm min<sup>-1</sup>. The maximum RT value determined in this study was  $237.5 \times 10^{-5}$  ppm min<sup>-1</sup> - more than an order of magnitude greater than corresponding values for North Carolina.

It is believed that the results of the CSTR experiment provide an independent line of evidence in support of a transport mechanism to account for the observed high concentrations of ozone in the study area.

## SECTION 8

### SOURCE OF HIGH OZONE CONCENTRATIONS

This section considers the contribution of power transmission lines to atmospheric ozone levels, and examines the evidence for local photochemical synthesis of ozone and for atmospheric transport of ozone into the study area.

As a preface to the discussion that follows, it will be helpful to recall the research hypothesis set forth in Section 1: Ozone precursors are released into the troposphere at a location remote from the study area. Given appropriate meteorological conditions, the precursors are transported to the study area. During transport and in the presence of sunlight, ozone is synthesized. The hypothesis further assumes that by sundown the precursors (which are also destructive agents) are consumed, leaving high residual ozone concentrations which are transported to the surface by mechanical turbulence.

#### 8.1 Contribution of Power Transmission Lines

If corona discharge from 500-KV power transmission lines contributes significantly to ambient ozone levels, the ozone concentrations at locations downwind of the power transmission lines should be greater than those upwind or underneath the lines. To evaluate this possibility, a two-way analysis of variance (ANOVA) procedure (Dixon and Massey, 1957) was used to test the null hypothesis; i.e., ozone concentration means for each of the five locations indicated in Table 8 above, are equal. The analysis of variance table is shown in Table 14 where it can be seen that both days and location are significant sources of variation. Accordingly, the hypothesis of equal means is rejected. The mean ozone concentrations were 0.064, 0.064, 0.059, 0.062, and 0.064 ppm for locations 140 yards upwind of, 50 yards upwind of, underneath, 50 yards downwind of, and 140 yards downwind of the power lines, respectively. The fact that the quadratic effect was highly significant while the linear effect was of negligible significance suggests that the variation due to location is primarily attributable to the observations made underneath the power lines. However, no physical explanation for the lower ozone concentrations



Table 14. ANOVA TABLE FOR POWER TRANSMISSION LINE STUDIES

Source of variation	Sum of squares	df	Mean square	F ratio
Days	0.013592	4	0.003398	212.4 <sup>a</sup>
Location	0.000266	4	0.000067	4.19 <sup>a</sup>
Linear	—	1	—	—
Quadratic	0.000130	1	0.000130	8.13 <sup>a</sup>
Remainder	0.000136	2	0.000068	4.25 <sup>b</sup>
Residual	0.001004	61	0.000016	
Total	0.014862	69		

<sup>a</sup> Significant at 0.01 level.<sup>b</sup> Significant at 0.05 level.

occurring underneath the power lines is immediately apparent. In light of this anomalous finding, no conclusions were reached regarding the contribution of power transmission lines to the high ozone concentrations observed at ground-level in the study area.

## 8.2 Ozone Synthesis

### 8.2.1 Local Photochemical Synthesis

The most startling fact that emerges from this study is that ozone concentrations at the Garrett County Maryland Airport exceed the 0.08 ppm National Air Quality Standard approximately 11 percent of the time. In an urban area this would not be remarkable and would be readily attributed to local photochemical synthesis from nitrogen dioxide and hydrocarbon precursors. At Garrett County, however, nitrogen dioxide and non-methane hydrocarbon concentrations were at or near background levels throughout the study period. Also, neither natural nor manmade sources in the study area appear capable of producing the precursor quantities required for synthesis of high ozone concentrations. Ozone synthesis from naturally occurring precursors has been demonstrated (Ripperton, et al., 1971); however, it is considered unlikely that it could account for concentrations exceeding the standard. The persistence of high ozone concentrations at night reflects the low precursor (and destructive agent) concentrations and obviously cannot be the result of ongoing photochemical processes. Thus, an evaluation of air quality measurements suggests that local photochemical synthesis cannot account for the observed high concentrations of ozone.

### 8.2.2 Remote Area Synthesis

Another possibility is that ozone was generated from precursors of urban origin and transported into the study area aloft--aloft, because contact with soil and vegetation probably would destroy most of the ozone. This would be the case particularly at night when there is no possibility of replacement through ozone synthesis. That layers of high ozone concentration can be transported aloft from urban areas is shown by various ozonograms, particularly those for Bedford, Massachusetts (near Boston), and at Point Mugu, California (north of Los Angeles on the coast) (Hering and Borden, 1967). A Pt. Mugu sounding prepared by Lea (Lea, 1968) and shown in Fig. 19 shows a layer of ozone about 0.5 kilometer aloft with a partial pressure of 300  $\mu$ mb ( $\sim$ 0.30 ppm).

It is known from chamber studies that once ozone precursors have been fully utilized, i.e. are no longer detectable, measurable ozone often remains in the chamber air. Since no nitric oxide, nitrogen dioxide, or olefins remain to react with ozone, it tends to persist, reacting slowly with chamber walls and other reaction products. This situation is approximated in the atmosphere when air leaves an urban area; ozone-generating reactions tend to go to completion and there are no additional large injections of nitric oxide or olefins which would destroy the ozone.

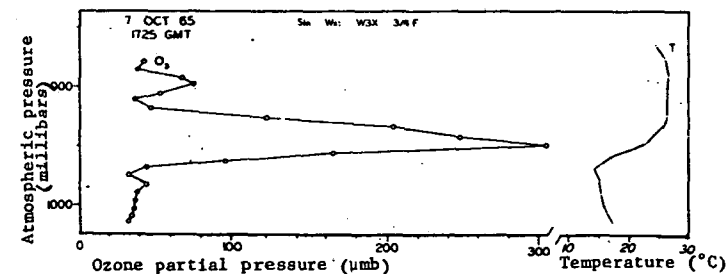


Figure 19. Vertical ozone and temperature profile at Point Mugu, California. (Source: D.A. Lea, 1968)

If the concept of a "high" concentration of ozone and low nitrogen oxide and hydrocarbon concentrations in a "spent" air pollution system drifting to another area is correct, the phenomenon should be observable in a number of areas. This is the case, although the characteristics of such systems need not be, and indeed are not, identical.

Two such cases are Indio and the Mineral King Valley, both in California. Ozone concentrations at Indio, a city of about 15,000 residents located east of the Los Angeles Basin and the intermediate valleys of southern California, have exceeded the California Air Quality Standard (0.10 ppm for 1 hour) more frequently than any other sampling station in California (Pitts, 1972). Carbon monoxide values at Indio were described by Pitts as "low; 1 or 2 ppm."

A situation in the Mineral King Valley of California (Miller, 1972) is analogous to, but not identical with the situation in the present study area. Figure 20 shows a slight diurnal trend with an oxidant peak approaching 0.10 ppm between 1700 and 1800 PST and nighttime concentrations of approximately 0.06 ppm which are unusually high. Oxides of nitrogen were reported to be "very low". Wind and other meteorological data

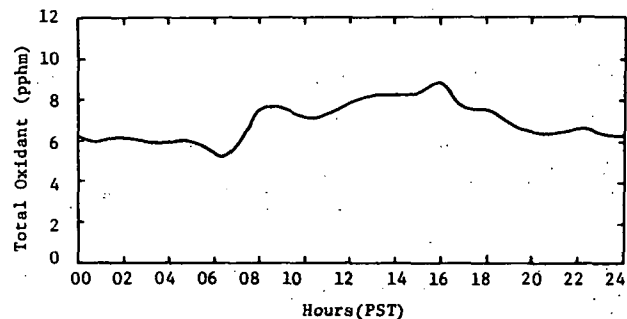


Figure 20. Mean diurnal oxidant concentration at Mineral King Valley, California. (Source: P.R. Miller, et al., 1972)

were interpreted as showing that some of the air sampled at the Mineral King Valley had been advected from Fresno.

From these considerations a picture emerges of a "spent" photochemical system with depleted ozone precursors, low carbon monoxide and sulfur dioxide concentrations, and ozone concentrations lower than those found in urban areas, but higher than could be accounted for by synthesis from naturally occurring precursors or by transport from the stratosphere.

In order to maintain high ozone levels, especially at night, the pollution system would have to travel aloft out of contact with the ground and large pollution sources. Alternatively, if the pollution systems travels in contact with the ground--where ozone destruction occurs--the system must have sufficient vertical extent to provide a reservoir of ozone-rich air to be mixed with the depleted air near the ground. When local turbulence occurs, bringing ozone to the ground and mixing additional precursors in the air, destruction can begin anew (day and night), as can synthesis (day). In a truly rural area, however, these processes would be limited by the quantities of precursors being emitted to the air.

To reiterate, the picture presented by the measurements is one of ozone values in what was thought to be an unpolluted area which exceed the National Air Quality Standard. The rates of change of ozone concentration due to synthesis and destruction during the study period are consistent with a "spent" photochemical system model. Calculated destruction rates approximate those of naturally occurring precursors (destructive agents). Transport (here meaning all air movement) was the dominant process producing change in ozone concentration. The picture is consistent with transport of ozone-rich air from a source of precursors remote from the study area. A question naturally arises as to where the pollution system originates and how long it has been aloft. As to the latter, the air quality measurements, the lack of real diurnal differences, and the comparison with the California experience suggest that the system has been traveling a minimum of two days. Transport mechanisms are examined in the following paragraphs.

### 8.3 Ozone Transport

The preceding discussion indicated that atmospheric transport would account for the high ozone concentrations. A consideration of atmospheric diffusion processes (Paetzold, 1961) and perusal of a thousand or more ozonograms (Hering and Borden, 1967), furnish strong evidence that  $O_3$  concentrations of 0.08 ppm and greater have not been advected from the stratosphere. Accordingly, the discussion that follows concerns itself with tropospheric transport.

#### 8.3.1 Ozone and Wind Direction

If the ozone source is confined to a particular area, or areas, within 100 mi. of the Garrett County Maryland Airport, some dependency of ozone concentration upon the wind direction should be evident, especially high ozone concentrations. To examine this possibility, the frequencies of occurrence of the average hourly wind direction associated with each of six categories of average hourly ozone concentration were computed. The limits selected for the ozone concentration categories were the upper 98, 85, 50, 13, and 2 percentile of observed concentrations. The 13 percentile corresponds to the 0.08 ppm standard. These limits were used to construct the ozone windrose in Fig. 21. Preferred directions for high ozone concentrations appear to be the west-northwest and northwest; however, the latter is also a preferred direction for low ozone concentrations. Ozone concentrations above 0.08 ppm occur most frequently with west and west-southwest winds which also are frequently observed. Other directions, such as north through east are infrequently observed and thus a preference for either high or low ozone concentrations is indistinguishable in the figure.

The data of Fig. 21 were normalized by the frequency of occurrence of each wind direction to eliminate the bias of prevailing or infrequent wind direction. The ozone windrose with bias removed is shown in Fig. 22. The normalized windrose indicates that the categories of high ozone concentration ( $>0.08$  ppm) are reasonably evenly distributed in all directions, whereas the two low concentration categories occur most frequently when winds are from the northeastern semicircle. A comparison

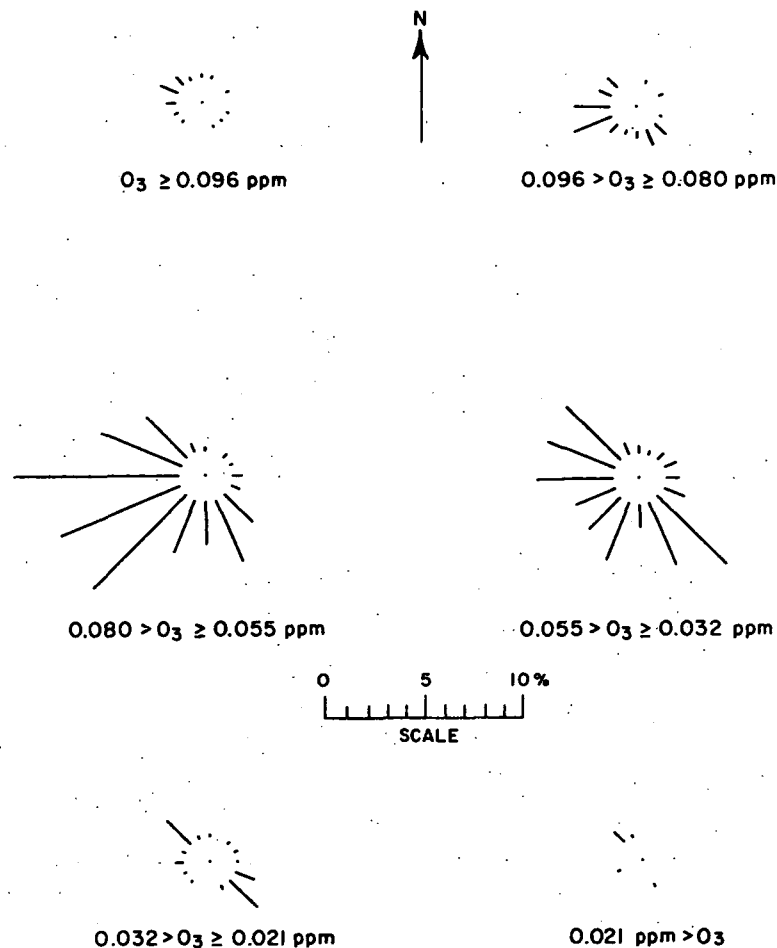


Figure 21. Frequency of occurrence of wind direction with indicated ozone ( $O_3$ ) concentrations.

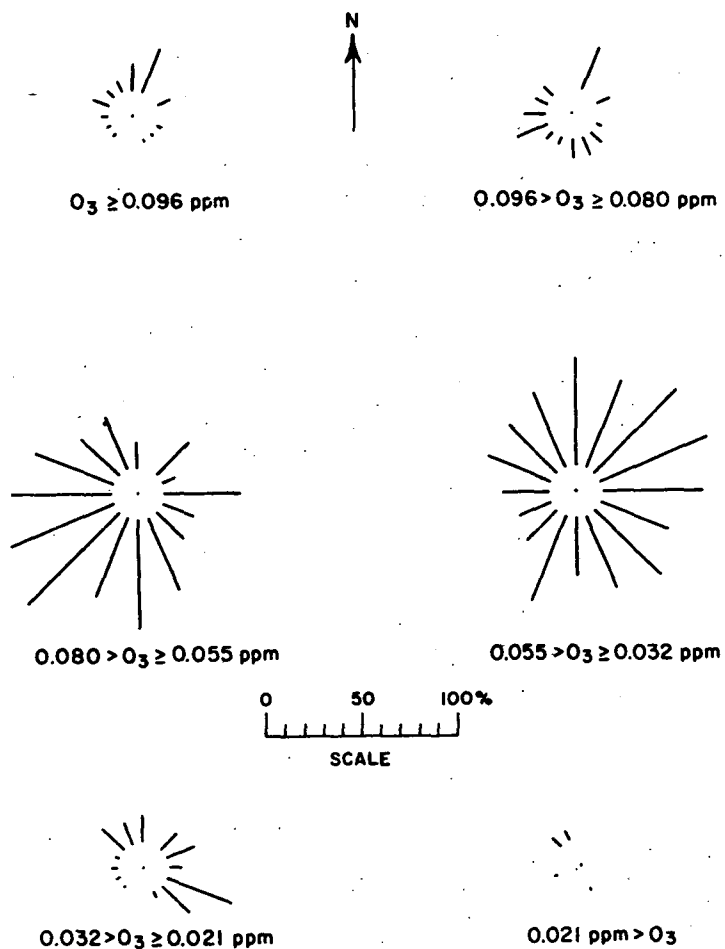


Figure 22. Frequency of occurrence of wind direction with indicated ozone ( $O_3$ ) concentration, normalized by the frequency of occurrence of a wind direction.

of the occurrence of greater than mean concentration to the lower than mean concentration is shown in Fig. 23. This figure shows a preference of ozone concentrations above the mean to occur with winds from south-southeast through southwest to west-northwest and for concentrations below the mean with wind from the remaining directions, although those directions occur less frequently.

The fact that this analysis did not show a definite source-receptor relationship combined with the results of the mobile sampling program suggests non-local sources and a larger time and space scale for ozone transport.

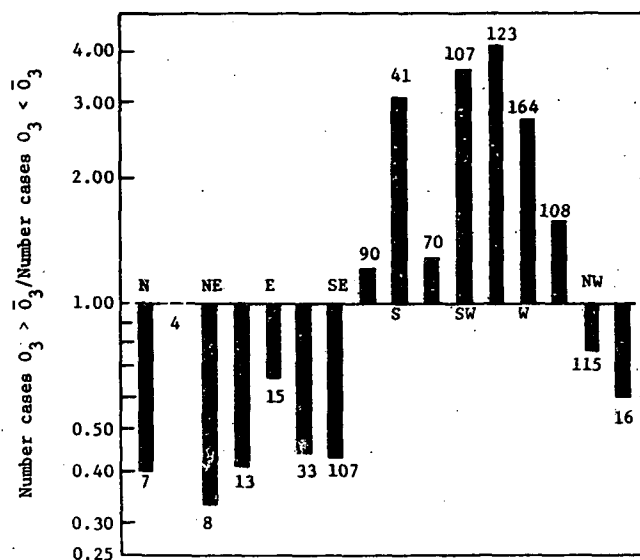


Figure 23. Ratio of occurrences of ozone concentration greater than mean (0.055 ppm) to occurrences of ozone concentration less than mean by wind direction. August 22-September 25, 1972. (Total number of occurrences given at extremity of bar.)

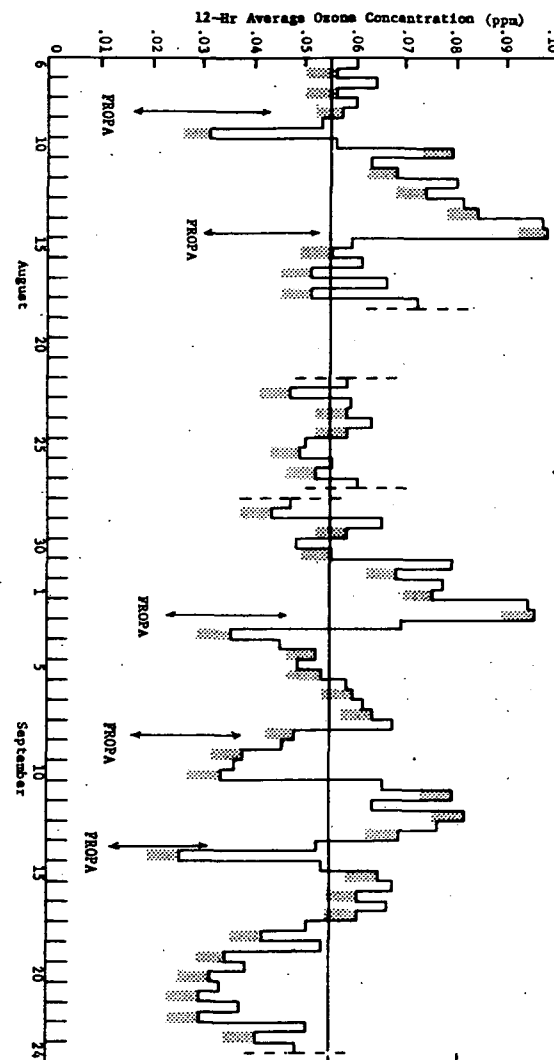
### 8.2.2 Ozone Concentration Changes in Air Masses

The next larger time and space scale meteorological data that are readily available are the twelve-hourly synoptic upper air observations. To correspond with this data, average concentrations of ozone over the 12-hour period 0700 to 1855 EDT (daytime) and over the 12-hour period 1900 to 0655 EDT (nighttime) were computed. These are shown in Fig. 24 for the entire period of observations.

A striking feature of the data presented in Fig. 24 is the repeated occurrence of a gradual increase of ozone concentration to a peak value, followed by a sharp decrease in concentration to approximately half the peak value. Particularly apparent is the sequence of ozone concentration increase over the period from the daytime of 10 August through the night of 14-15 August and the sharp decrease for the daytime period of 15 August. Similarly, the increase of ozone concentration from the daytime of 29 August through the night of 2-3 September and the decrease which continued through the daytime period of 3 September and the night of 3-4 September is quite marked. From the minimum reached on the night of 3-4 September ozone concentration again increased to a peak value during the daytime period of 8 September. This peak, which was only 0.067 ppm, is followed by a sharp decrease in concentration for the next 12-hour period and a continued decrease until a minimum is reached during the night of 10-11 September. A rapid increase in ozone concentration followed this minimum value and a maximum value was reached during the 12-13 September nighttime period. A gradual decrease in concentration occurred over the next 24 hours followed by a sharp decrease to a new minimum concentration value during the night of 14-15 September.

The rates and magnitudes of increase and decrease of ozone concentration during the periods discussed vary considerably. However, there is a remarkable similarity in the patterns indicated by the concentration changes. More significant though, is the fact that the passage of an air mass front occurred either immediately preceding, or during, the 12-hour period characterized by the low ozone concentration following the sudden decrease. The approximate times of passage

Figure 24. Time sequence of 12-hour average ozone concentrations at Garrett County Maryland Airport. The 12-hour periods begin at 0700 EDT (daytime) and 1900 EDT (nighttime). Nighttime periods are shaded and run from 1900 EDT on one day to 0800 EDT on the following day. Double arrow marked FROPA indicates the time of an air mass frontal passage.



of these fronts have been indicated on Fig. 24.\* Since the air masses on either side of a front have different origins and histories, trajectory analysis using the 12-hourly synoptic meteorological data was used to investigate the marked changes in ozone concentrations accompanying the frontal passage.

### 8.3.3 Air Trajectory Analysis

Air trajectories at the 850-mb pressure level (approximately 5000 ft MSL) were prepared for periods preceding and following the frontal passages indicated in Fig. 24. The arrival time at the Garrett County Maryland Airport for air following a particular trajectory is 0800 EDT (approximately the beginning of the averaging period for the daytime ozone concentration) and 2000 EDT (approximately the beginning of the nighttime averaging period). These times coincide to the times at which the meteorological measurements are made.

The air trajectories prepared are only approximations. Even the care taken in their preparation cannot eliminate a decrease in accuracy as time and distance from the terminus increase. Further, it must be recognized that air parcels normally follow isentropic rather than isobaric surfaces. Thus these trajectories represent estimates of the flow along the 850 mb constant pressure surface and inferences concerning sources should not be attempted because a particular trajectory passes over a specific geographic point.

Selected trajectories associated with period of increase followed by rapid decreases in ozone concentrations are presented below.

#### Case 1 - Frontal Passage of 0500 EDT 15 August

Trajectories for four days preceding this frontal passage and two and a half days following are shown in Fig. 25. It should be noted that trajectories A through F, prior to the frontal passage, and thus during the period of increasing ozone concentrations, tend to show decreasing speed for air parcel movement, especially during the 24-hour period immediately prior to arrival at Garrett County. Trajectories G through K for air parcels arriving after the frontal passage indicate quite rapid air movement.

\* These frontal passages were determined independently of the ozone data as part of the documentation of the meteorological conditions occurring during the period of observation. A discussion of the meteorological conditions associated with ozone concentrations greater than 0.08 ppm is given in Appendix E.

Figure 25. Trajectories of air arriving at Garrett County Maryland Airport at the indicated time during Case 1. Dashed portions indicate an estimated trajectory. Open circles (O) and crosses (X) show the 0800 and 2000 EDT positions of the air.

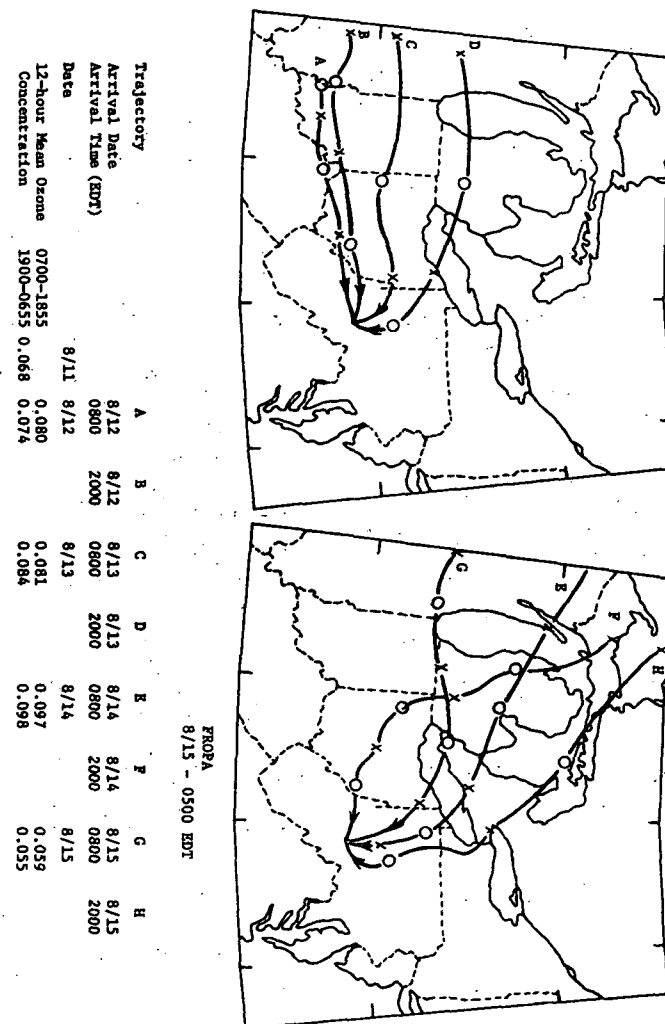
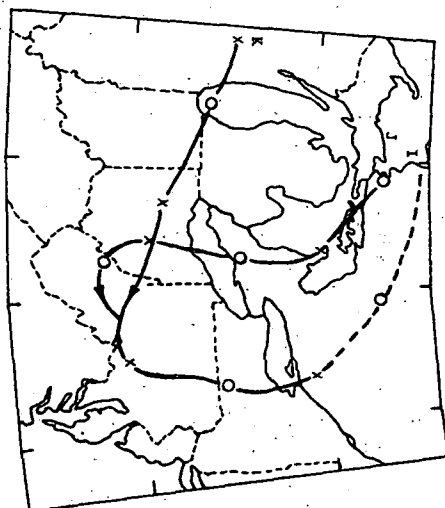


Figure 25. Trajectories of air arriving at Garrett County Maryland Airport at the indicated time during Case 1. (Cont'd)

Trajectory	Arrival Date	Arrival Time (EDT)	Date	12-hour Mean Ozone Concentration
I	8/16	0800	8/16	0.061
J	8/16	2000	8/16	0.051
K	8/17	0800	8/17	0.066



#### Case 2 - Frontal Passage of 0400 EDT 3 September 1972

The period of buildup of ozone concentration from 29 August through 2 September is characterized by air arriving at Garrett County after passing over eastern coastal areas as shown by trajectories A through E in Fig. 26. A definite change in the path of air and the speed of movement is indicated by trajectories F through H, which are post frontal and include the nighttime period of minimum ozone concentration on 3-4 September.

#### Case 3 - Frontal Passage of 0300 EDT 9 September 1972

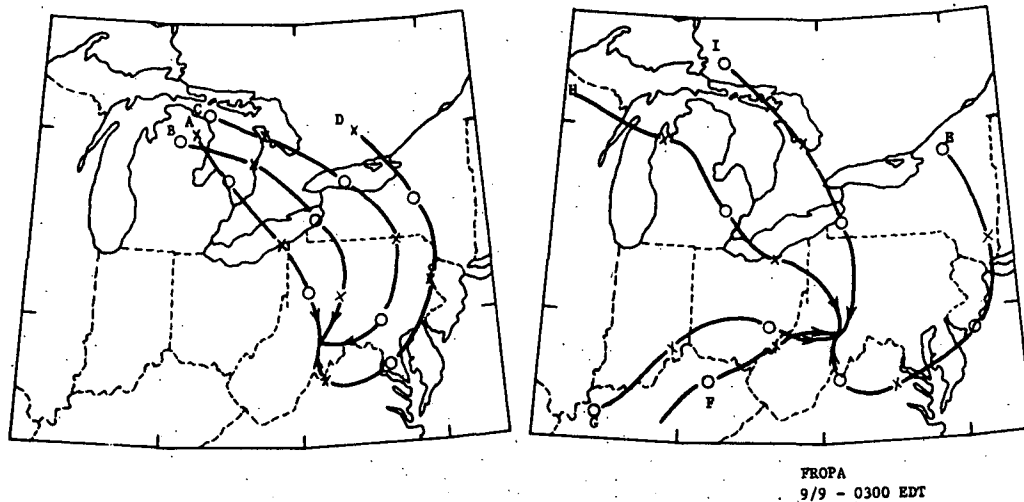
In spite of a rather uniform rate of increase in ozone concentrations during the period from 5 September through 8 September 1900 EDT there are significant differences in the trajectories for the same period (Fig. 27). It should be noted, however, that the movement for all of these is relatively uniform and rapid. The ozone concentration during this period increased to a maximum of only 0.067 ppm (12-hour average), which is less by about 0.03 ppm than the maximum reached in cases 1 and 2.

The marked change in trajectories occurs after the frontal passage as shown by trajectories H and I.

#### 8.4 Interpretation

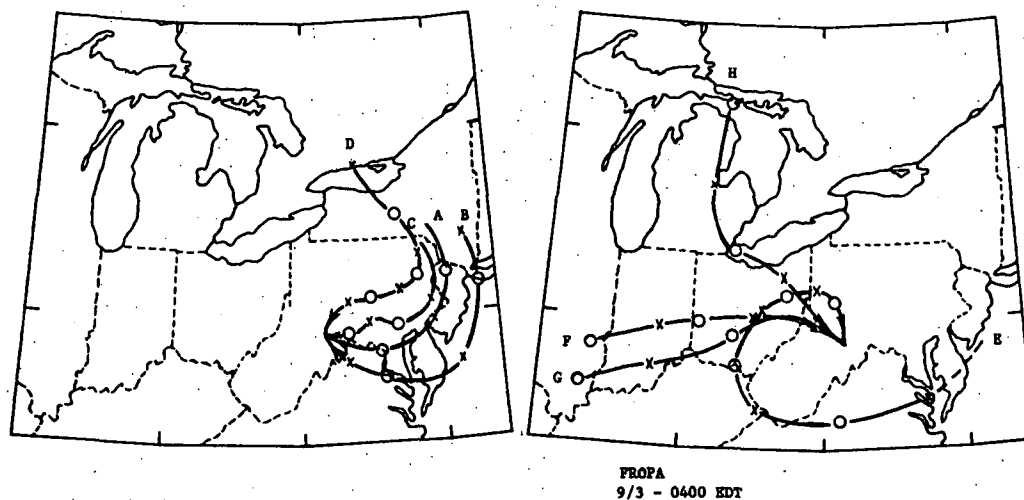
The discussion of a possible chemical model (Section 8.2) and the transport of air parcels to a receptor area (Section 8.3) suggests that the following conditions may exist over a large (multi-state) urban-industrial area:

- 1) Ozone precursors and destructive agents, i.e. nitrogen oxides and reactive hydrocarbons, are emitted by the numerous recognized stationary and mobile sources.
- 2) In the presence of solar radiation, reaction of the precursors produce ozone throughout the surface-based mixing layer.
- 3) Concurrently, destruction of ozone takes place, but over a sufficiently long period (perhaps 48 hours) the destructive agents are depleted as a result of their entering into the ozone production reaction.



Trajectory		A	B	C	D	E	F	G	H	I
Arrival Date		9/5	9/6	9/6	9/7	9/7	9/8	9/8	9/9	9/9
Arrival Time (EDT)		2000	0800	2000	0800	2000	0800	2000	0800	2000
Date		9/5	9/6		9/7		9/8		9/9	
12-hour Mean Ozone	0700-1855	0.048	0.058		0.061		0.067		0.045	
Concentration	1900-0655	0.053	0.059		0.063		0.047		0.037	

Figure 27. Trajectories of air arriving at Garrett County Maryland Airport at the indicated time during Case 3. Dashed portions indicate an estimated trajectory. Open circles (O) and crosses (X) show the 0800 and 2000 EDT positions of the air.



Trajectory		A	B	C	D	E	F	G	H
Arrival Date		8/31	9/1	9/1	9/2	9/2	9/3	9/3	9/4
Arrival Time (EDT)		2000	0800	2000	0800	2000	0800	2000	0800
Date		8/31	9/1		9/2		9/3		9/4
12-hour Mean Ozone	0700-1855	0.079	0.077		0.094		0.069		0.045
Concentration	1900-0655	0.068	0.075		0.095		0.035		

Figure 26. Trajectories of air arriving at Garrett County Maryland Airport at the indicated time during Case 2. Dashed portions indicate an estimated trajectory. Open circles (O) and crosses (X) show the 0800 and 2000 EDT positions of the air.



- 4) A receptor, appropriately located at some presently unspecified distance and travel time from sources of ozone destructive agents, will experience an ozone-rich atmosphere containing insignificant concentrations of ozone precursors or destructive agents.
- 5) Ozone destruction will take place at the air-ground interface, but turbulent mixing will maintain high ozone concentration throughout the mixing layer.
- 6) High ozone concentrations will be the "normal" condition in air masses originating or modified over extensive urban-industrial areas.
- 7) Low ozone concentrations will occur over extensive urban-industrial areas only during the period immediately following the arrival of a relatively rapidly moving air mass having its origin in an extensive non-urban-industrial area.

## SECTION 9

### CONCLUSIONS

The principal conclusions arising from this research are enumerated below:

- 1) The research reported herein verifies the high concentrations of ozone previously found in the Mt. Storm, West Virginia area. The maximum hourly concentration for the study period was 0.119 ppm, while the average hourly concentration for the study period was 0.057 ppm. Approximately 11 percent of the one-hour samples exceeded the 0.08 ppm National Air Quality Standard.
- 2) The occurrence of high ozone concentrations is not restricted to a single location. Rather it appears to be the case for most of Garrett County, Maryland and that portion of Preston County, West Virginia in which ozone measurements were made.
- 3) The lack of well-defined nocturnal surface-based temperature inversions, the small diurnal temperature range, and the relatively constant wind speed from day to night suggests that the air masses over the base station were relatively well mixed in the lower levels. As a consequence, the assumption that the high concentrations of ozone are not restricted to a shallow surface layer appears warranted. In fact, higher concentrations of ozone above the surface seem probable since vegetation, soil, and all structures and obstacles on the surface form an ozone sink.
- 4) High ozone concentrations at the Garrett County Maryland Airport result from ozone transport and not from in situ photochemical synthesis.
- 5) The observed high ozone concentrations cannot be explained in terms of air flow from a specific point source or a single urban-industrial area source. However, episodes of

- high concentration do appear to be associated with air masses arriving in the study area after passing over urban-industrial regions. No clear pattern of air mass trajectory, speed, or time of day of precursor injection is apparent from the available data. This meteorological interpretation is compatible with current concepts of atmospheric chemistry.
- 6) The results of this research provide substantive support for a hypothesis which is as follows: Ozone precursors are released into the troposphere at a location remote from the study area. Given appropriate meteorological conditions, the air mass containing the precursors is transported to the study area. During transport and in the presence of sunlight, ozone is synthesized. The hypothesis further assumes that the precursors (which are also destructive agents) are consumed, leaving high residual ozone concentrations which are transported to the surface by mechanical turbulence.

## SECTION 10

### RECOMMENDATIONS FOR FURTHER RESEARCH

During the course of this study a number of research needs were identified. The most pressing among them are enumerated below:

- 1) The frequency of occurrence of high ozone concentrations ( $>0.08$  ppm) in the study area should be determined over an extended period of time, ideally one year.
- 2) A study to further delineate the horizontal extent of the region of high ozone concentration is indicated. Such a study should involve continuous ozone monitoring at the Garrett County Maryland Airport as well as at several sites approximately 100 miles distant.
- 3) As part of 1) and 2), in-depth synoptic-scale meteorological analysis should be performed. The analysis would identify an air mass according to source region, characterize its thermal structure, and plot its trajectory as a basis for interpreting variations in ozone concentration at monitoring sites.
- 4) The vertical distribution of ozone, ozone precursors, ambient temperature, and dewpoint temperature in the study area should be determined. An instrumented aircraft would be required for these determinations.
- 5) A reaction chamber simulation to model the chemical processes suggested in this report should be undertaken.
- 6) A long-term study of the contribution of corona discharge from high voltage power transmission lines to atmospheric ozone levels is needed. Such a study should examine power lines of various voltages in a number of locations with different terrain features and under a variety of meteorological conditions.

APPENDIX A  
CALIBRATION PROCEDURES

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APPENDIX A  
CALIBRATION PROCEDURES

Dynamic calibration procedures were used to calibrate all instrumentation during the field measurement period. The procedures used and the frequency of use by pollutants were specified in Table 1, Section 4. The validity of the procedures was established in earlier studies (Decker, et al., 1972). Those procedures are described in the following paragraphs.

A-1 Ozone

A dynamic calibration system using an ultraviolet ozone generator (Hodgeson, et al. 1970) was used to calibrate the solid-phase chemiluminescent ozone meter. Briefly, the generator consists of an 8-in ultraviolet mercury vapor lamp which irradiates a 5/8-in quartz tube through which clean, compressed air flows at 5 lpm. Ozone concentrations from 0 to approximately 1.0 ppm can be generated using this technique. Although the ultraviolet ozone generator has been shown to be quite stable and reproducible, the neutral-buffered potassium iodide technique was used as a reference method (Public Health Service, 1965). A permanent calibration assembly consisting of a zero air source, calibrated rotameter, ozone generator, and glass manifold with sampling ports was set up in the RTI Environmental Monitoring Laboratory for calibration of all ozone meters. A schematic diagram of the ozone calibration systems is shown in Fig. A-1.

A-2 Nitric Oxide/Nitrogen Dioxide

Calibration of the Bendix Model 8101-B Chemiluminescent NO-NO<sub>x</sub>-NO<sub>2</sub> Analyzer was accomplished using a nitric oxide-ozone conversion unit developed by EPA. Nitric oxide in nitrogen (=50 ppm) was purchased from Scott Research Laboratories with a certificate of analysis. The desired concentration range for calibration (0-1.0 ppm) was achieved by dilution with compressed air. Nitrogen dioxide concentrations were produced by mixing ozone with nitric oxide in a conversion chamber. An ozone to nitric oxide ratio of 1.2 was required for 100 percent conversion of nitric oxide to nitrogen dioxide. The nitrogen dioxide produced is diluted to the desired concentration with diluent air. A drawing of this calibration system is shown in Fig. A-2.

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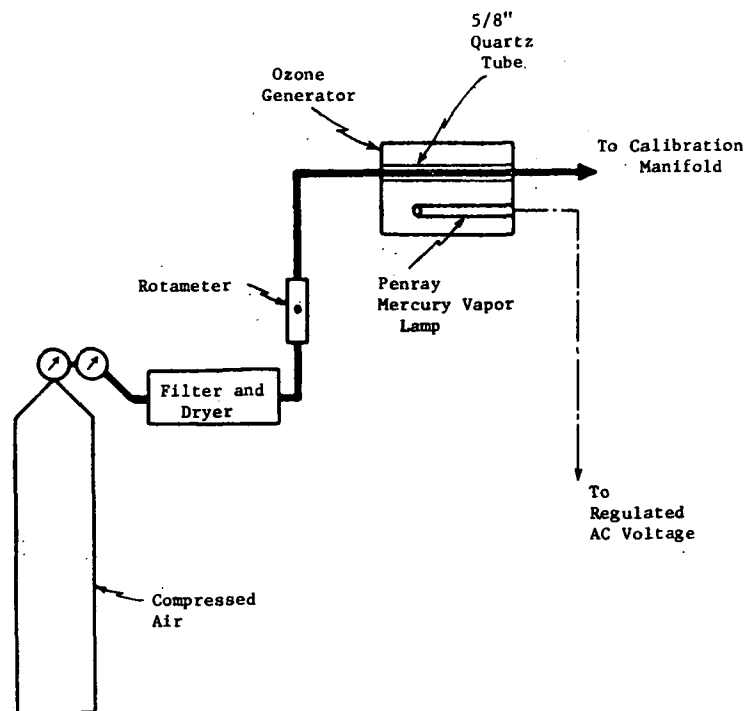


Figure A-1. Ozone calibration system.

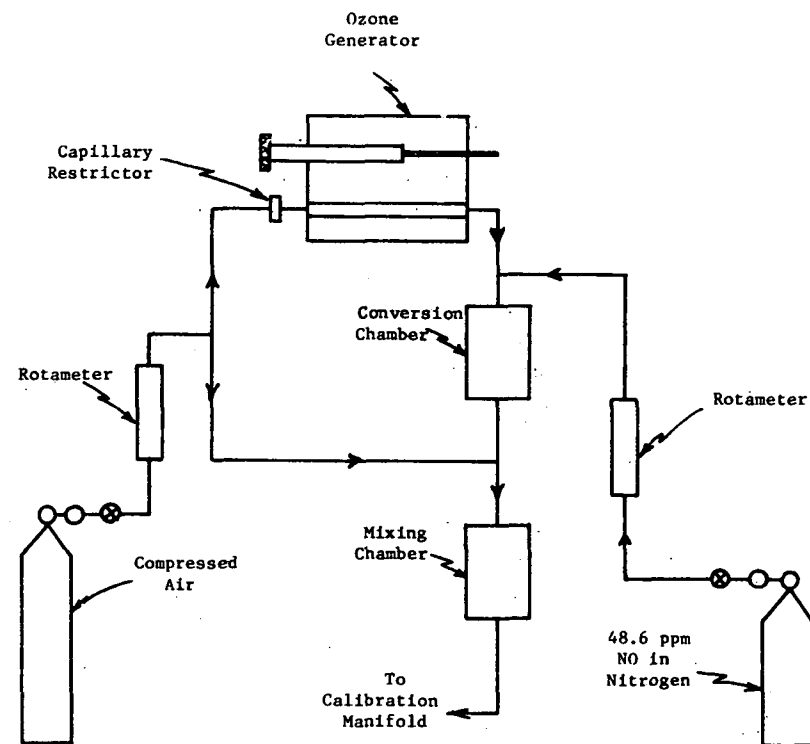


Figure A-2. Nitric oxide and nitrogen dioxide calibration system.

### A-3 Sulfur Dioxide

A dynamic calibration system using a gravimetrically calibrated sulfur dioxide permeation tube (O'Keeffe and Ortman, 1966; Scaringelli, 1966) as a primary standard and zero air as a diluent was used to provide known concentrations of sulfur dioxide to calibrate the Bendix flame photometric analyzer. A schematic diagram of the system is shown in Fig. A-3.

### A-4 Total Hydrocarbon, Methane, Carbon Monoxide

Calibration of the Beckman Model 6800 GC-FID was accomplished using standard calibration gases certified as to component concentrations. These gases were purchased from Scott Research Laboratories. Zero air certified to contain less than 0.1 ppm total hydrocarbon and carbon monoxide was used to zero the instrument. Span concentrations of methane and carbon monoxide in zero air up to 5 ppm were used for calibration purposes.

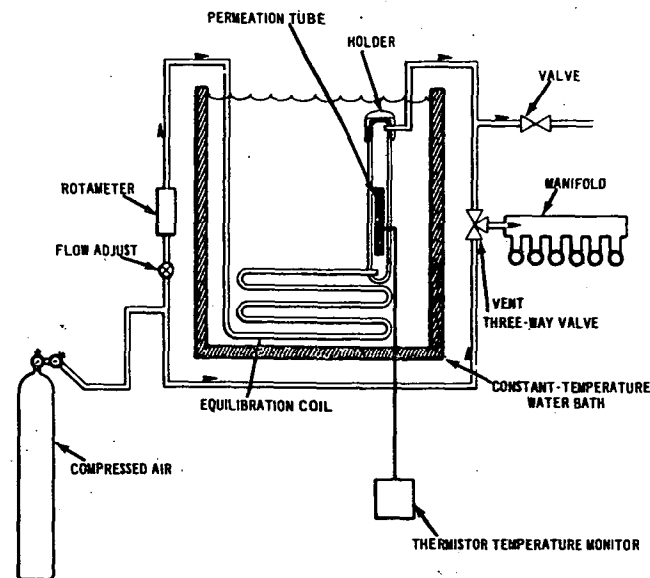


Figure A-3. Permeation tube calibration system.

APPENDIX B  
PERFORMANCE CHARACTERISTICS AND OPERATIONAL  
SUMMARIES FOR AIR QUALITY MONITORING INSTRUMENTS

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APPENDIX B  
PERFORMANCE CHARACTERISTICS AND OPERATIONAL  
SUMMARIES FOR AIR QUALITY MONITORING INSTRUMENTS

B-1 Instrument Performance Characteristics

Minimum detectable concentration, range and precision of the air quality monitoring instruments used in the Mt. Storm study are summarized in Table B-1.

B-2 Operational Summaries

A summary for each air quality monitoring instrument used in the Mt. Storm study is presented below.

Table B-1. INSTRUMENT PERFORMANCE CHARACTERISTICS

Instrument	Parameter	Minimum detectable concentration (ppm)	Range (ppm)	Precision (%)
Solid-phase chemiluminescent ozone meter	O <sub>3</sub>	0.002	0.2	± 1.0
Bendix model 8101-B chemiluminescent NO-NO <sub>x</sub> analyzer	NO	0.005	0.5	± 0.5
	NO <sub>x</sub>	0.005	0.5	± 0.5
	NO <sub>2</sub>	0.010	0.5	± 1.0
Bendix Model 8300 flame photometric analyzer	SO <sub>2</sub>	0.005	0.2	± 1.0
Beckman model 6800 gas chromatographic flame ionization detector	THC	0.100	10.0, 5.0	± 1.0
	CH <sub>4</sub>	0.100	10.0, 5.0	± 1.0
	CO	0.100	10.0, 5.0	± 1.0
	NMHC	0.150		± 2.0

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#### B-2.1 Chemiluminescent Ozone Meter

During the period August 4 to September 25, 1972, two solid-phase chemiluminescent ozone meters were used for ambient monitoring at the Garrett County Maryland Airport. Intermittent problems (i.e. shutter failure, timer failure, electronic problems) necessitated replacement of a meter borrowed from the University of North Carolina which had been online from August 4 to August 22, 1972 with a solid-phase chemiluminescent ozone meter obtained from the Division of Atmospheric Surveillance, EPA.\* The meter obtained from EPA operated from August 22 to September 5, 1972 virtually trouble free. Less than 18 hours of data were invalidated due to failures which were mechanical rather than electronic. Minimal calibration drift (both zero and span) were encountered during this period of time.

#### B-2.2 Bendix Model 8101-B Chemiluminescent NO-NO<sub>x</sub>-NO<sub>2</sub> Analyzer

During the period August 4 to September 24, 1972, the instrument operated with no failure periods. The analyzer exhibited good zero and span stability throughout the measurement program. Negative concentration were frequently encountered for NO<sub>x</sub> and NO values. It is believed that zeroing the instrument with dry compressed air and then monitoring ambient air with humidities greater than 60-70 percent depressed instrument zero to some point below that previously defined as zero. Since the instrument output is linear and both NO<sub>x</sub> and NO were similarly affected, it is reasonable to assume that the relative difference between NO<sub>x</sub> and NO, i.e. NO<sub>2</sub> is valid.

#### B-2.3 Bendix Model 8300 Flame Photometric Analyzer

During the period August 4 to September 24, 1972, this analyzer experienced three failures. Two of the three failures were electronic and required readjustment of the gain on the photomultiplier tube. The other failure was a flow regulation problem that resulted in the invalidation of approximately 4 days of data. Excellent zero and span stability was exhibited by the unit while it was operating.

#### B-2.4 Beckman Model 6800 Gas Chromatographic Flame Ionization Detector

Several failures and malfunctions occurred which severely affected the performance of this instrument. Some problems resulted from electronic failure of integrated circuits. Diffusion of moisture through the hydrogen regulator diaphragm contaminated the analytical column which in turn caused a shift in the elution time of methane and carbon monoxide from the column. Intermittent switching on and off of the calibrate solenoid valve resulted in a loss of sample and thus invalidated a considerable amount of data. Negative non-methane hydrocarbon values were obtained when methane concentrations were greater than indicated total hydrocarbon concentrations.

During the period August 4 to August 11, 1972 the instrument performed satisfactorily. During the period August 11 to September 24, 1972 the problems cited above were encountered. The carbon monoxide data are considered to be the most valid of three measurements. Methane and total hydrocarbon data are less reliable.

\* Obtained from EPA warehouse on August 18, 1972.

## APPENDIX C

### THE CONTINUOUS STIRRED TANK REACTOR

In order to determine the synthesis, destruction and transport of ozone near the surface of the earth (Jeffries, 1971) used an experimental technique consisting of two non-steady-state continuous stirred tank reactors (CSTR) which use ambient air as the reacting medium. Figure C-1 shows this experimental set-up.

Behavior of a reactive substance in a CSTR is represented by

$$\frac{dO_3}{dt} (\text{outlet}) = f \cdot O_3 (\text{inlet}) - f \cdot O_3 (\text{outlet}) - vr \quad (1)$$

where

$f$  = flow rate through the reactor,

$O_3$  = appropriate  $O_3$  concentration,

$v$  = volume of reactor, and

$r$  = rate of reaction affecting  $O_3$  concentration per unit volume and time.

Equation (1) is a mass balance equation for the reactor. Letting

$Q = f/v$  and rearranging (1) gives

$$r = Q O_3 (\text{outlet}) - Q O_3 (\text{inlet}) + \frac{dO_3}{dt} (\text{outlet}) \quad (2)$$

Only  $O_3$  concentrations as a function of time at the inlet and outlet to the CSTR are needed.  $dO_3 (\text{outlet})/dt$  can then be computed numerically. The rate,  $r$ , depends on how the reactor is operated. If light is excluded from the reactor, only  $O_3$  destruction can occur and  $r = r_d$ . If light is allowed in the reactor, both synthesis and destruction of  $O_3$  may occur and  $r = r_d + r_s$ . Knowing  $r_d$ ,  $r_s$  and

## APPENDIX C

### THE CONTINUOUS STIRRED TANK REACTOR

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the concentration of  $O_3$  in the ambient air, the rate of transport of  $O_3$ ,  $r_t$ , necessary to maintain the ambient  $O_3$  concentration can be computed.

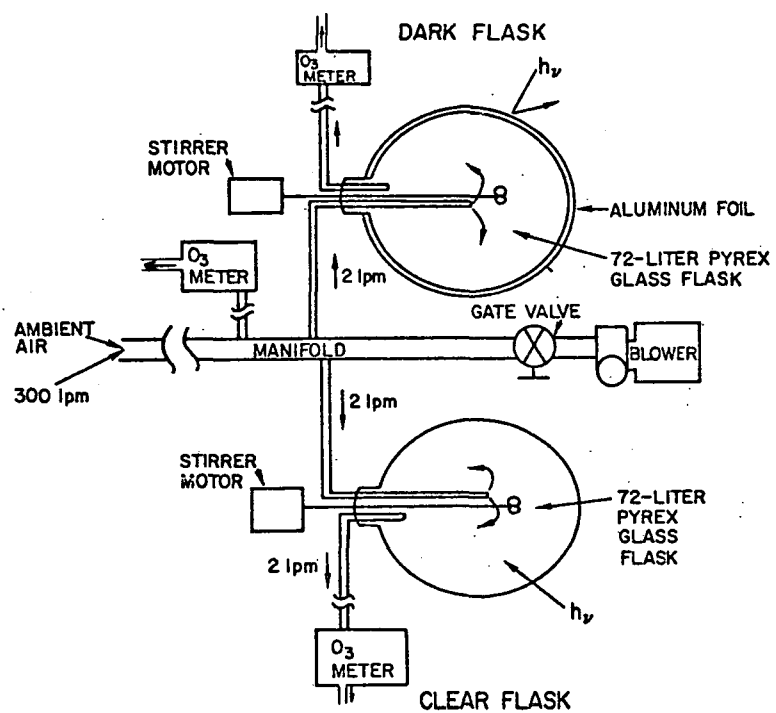


Figure C-1. CSTR system for rate measurements.

#### APPENDIX D

##### TETHERED BALLOON PROCEDURES

Preflight checkout of the system consisted of the standard radiosonde baseline measurements. The ozone sensor was calibrated with zero air and air containing 0.05, 0.10, and 0.15 ppm of ozone before each flight. The strip chart ordinate corresponding to each ozone concentration was recorded and subsequently a calibration curve was prepared. A final check of reference signals, temperature, and ozone concentration was made immediately prior to launching. All launchings were made with prior approval of the airport manager.

Initially, the balloon was allowed to rise until 200 ft of tether line was out. A five- to eight-minute sample of ozone and temperature or humidity was taken at this height. This procedure was carried out at increments of 200 ft of tether line, until 1000 ft of line were out. Two-hundred ft increments were used during the balloon descent as well. Measurements of the elevation angle between the tether line and the horizontal at the tether point were made and recorded for each significant change of angle during a flight. Comments on the flight characteristics of the balloon and/or meteorological conditions were recorded on the flight log as necessary. The duration of a flight was approximately 90 minutes.

A post-flight calibration of the instrument package was performed for each flight in which the radiosonde transmitter battery was still functional after approximately two-and-one-half hours of operation. The procedure was identical to the preflight checkout except that zero air and 0.10 ppm ozone were used.

The ozonesonde transmissions were received, demodulated and recorded on a strip chart. Figure D-1 is a segment of strip chart record. For each sample, the ozone signal was averaged over two-minute intervals, and the drift of the  $I_o$  and  $I_c$  signals was carefully noted. The ozone partial pressure was determined from the preflight calibration of the

#### APPENDIX D

##### TETHERED BALLOON PROCEDURES

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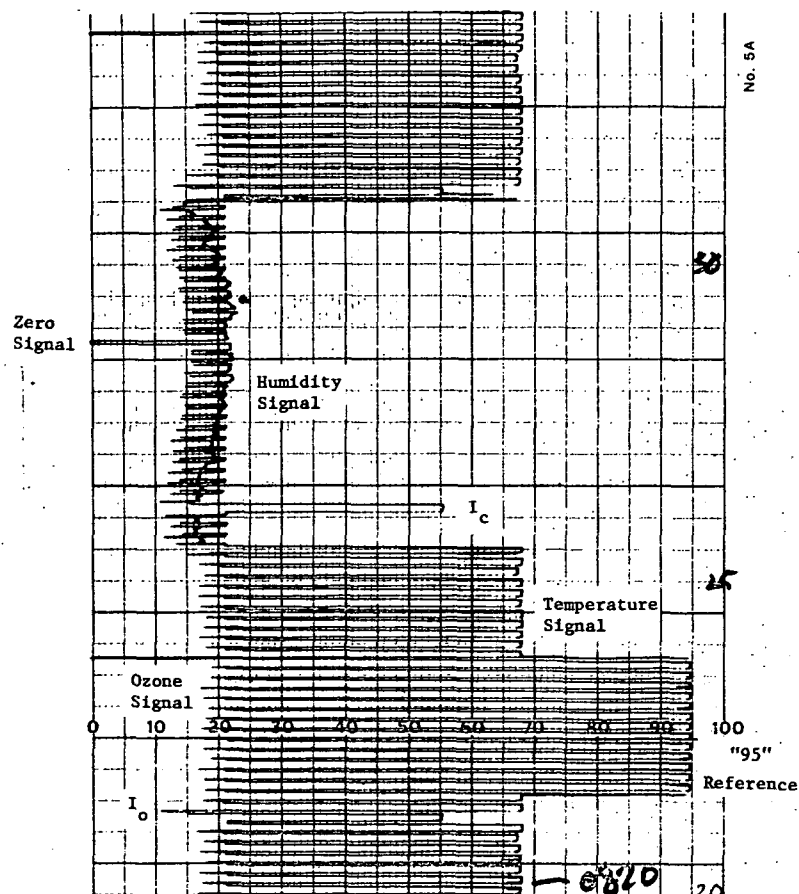


Figure D-1. Segment of ozonesonde strip chart record showing ozone signal, ozone calibration signals ( $I_c$ ,  $I_o$ ), temperature, relative humidity, and reference signals.

sensor, adjusted as necessary for any  $I_c$  and  $I_o$  drift, and converted to concentration units using the estimated pressure at altitude. An average value of temperature or relative humidity was obtained by applying standard radiosonde procedures to each strip chart sample period.

The approximate altitude of the instrument package was estimated using two independent techniques. The first of these used the measured station pressure, the baroswitch calibration chart and the switching sequence of the baroswitch, to estimate the pressure at the sampling altitude. The hypsometric equation, with measured temperature and humidity, gave the altitude. At temperatures and pressures encountered at the study site, a one millibar change of pressure corresponded to an approximate 30 ft altitude change.

The second technique assumed that the tether line formed a catenary. This being the case, the altitude of the balloon could be determined when 1) the free plus aerodynamic lift of the balloon, 2) the weight per unit length of the tether line, and 3) the angle that line makes with the horizontal at the tether point are known. The latter two requirements were measured. The free lift of the balloon is equal to the buoyancy of the helium within the balloon less the weight of the balloon and the instrument package. It varies from flight to flight due to leakage in flight and during storage of the balloon. The roof of the hangar used for balloon storage was not high enough to permit measurements of the actual free lift of the balloon in static air; however, outside the hangar in nearly calm air, a free lift of 1.5 lb was measured. The aerodynamic lift, a function of the wind speed and angle of attack, was not known. Observation of the balloon flight characteristics indicate that this additional lift significantly affects the flight altitude.

Sets of curves of altitude versus elevation angle for different arc lengths were prepared for several values of lift. These curves were used to estimate the altitude of the balloon from the measurements taken. Subtracting 25 ft from that altitude gives the altitude of the instrument package. The estimated error in altitude estimates is  $\pm 40$  ft. Final altitude estimates were made by insuring that the two methods gave comparable results.

#### APPENDIX E

##### DISCUSSION OF SYNOPTIC WEATHER FEATURES ACCOMPANYING EPISODES OF HIGH OZONE CONCENTRATION

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#### APPENDIX E

##### DISCUSSION OF SYNOPTIC WEATHER FEATURES ACCOMPANYING EPISODES OF HIGH OZONE CONCENTRATION

The following discussion is based on the 0800 EDT weather maps as they appeared in the Daily Weather Map Series produced by the National Weather Service.

##### August 10 - 1800 EDT to 2200 EDT

An occluded front passed through the central and northeastern states on August 9. A large high pressure system behind the front moved out of central Canada over the Great Plains, then moved eastward. On the morning of August 10, the center of the system was located over the Indiana-Ohio-Michigan border. The system had moved to the New Jersey coast by the next morning, with the center moving over the Garrett County Maryland Airport during the episode.

##### August 13 - 1300 EDT to August 15 - 0700 EDT

The surface high which moved across the northeastern United States in the previous episode had migrated slowly eastward. At 0800 12 August, the high (1027 mb) was centered over the New Jersey coast and continued to move eastward at about 20 kt while maintaining a ridge extending over the southeast United States. As the high receded a weak cold front moved southeastward, but little contrast of temperature or dewpoint temperature. The front passed the Garrett County Maryland Airport at approximately 0400 EDT August 13. No substantial change of air mass seems to have occurred. A trough through the upper Great Lakes developed pinching the ridge between Canadian air and stagnant maritime air. By the 14th at 0800 a weak high pressure center (~ 1022 mb) established itself over West Virginia, and a cooler, stronger high (~ 1025 mb) was developing west of James Bay, with a stationary front (the "pinching" trough) separating them. The West Virginia high was the surface evidence of a strong ridge aloft over the central USA. The Canadian high intensified and began to push southward, transforming the stationary front into a cold front, passing the field site near 0500 EDT, August 15. From the 15th, 0800 EDT map, temperatures and moisture ahead of the front were similar to those about

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100 miles behind, indicating mixing across the frontal zone. By the 16th, the cold front had pushed southward and westward Charleston, S. C. and the ridge line lay about 120 miles inland of the Atlantic seaboard with the high center (1028 mb) near Albany, New York.

August 18 - 1200 EDT to 1800 EDT

By August 17, 0800 EDT the Canadian high of the previous series had moved offshore, with an extension over the southeast United States and with ridging into the Great Plains. Maritime air, originating in the Gulf of Mexico pushed across as far eastward as Ohio and Michigan behind a warm front across Lake Huron to very near the Garrett County Airport. By the next morning the airport remained in the maritime air, which showed little movement. A cool front moved across New England, leaving a stationary front along an arc from Flint, Michigan to Buffalo to Washington, D. C. by the next morning. The airport remained in the original maritime air. Aloft an east-west ridge over the southeastern United States persisted throughout the period.

29 August - 0200 to 3 September - 1200 EDT

In the few days previous to this episode, a maritime polar air mass moving across the Rocky Mountains and central plains gradually was transformed into a maritime tropical air mass from the Rocky Mountains to the east coast. At 0800 on the 28th a cool front lay along a line from Boston through Richmond to Tallahassee and was moving out to sea. A second cool front moving out of Canada lay along the Minnesota-Canada border. On the 29th the situation was changed little except that the Canadian front had penetrated eastward to a central New York-Michigan line and showed some upper air support. By the morning of the 30th, Canadian air pushed south-eastward behind a front on an arc from Chicago to Cincinnati and through south central Virginia. A cool high pressure center was located over New York-Pennsylvania border. The surface ridge line extended from San Antonio to Evansville, Pittsburgh and north northeastward. Aloft, ridging over Illinois and Indiana was increasing.

Over the next 24 hours, the front dissipated but the ridge line remained on the southwest-northeast axis to a high over southwest New England. Morning temperatures were cooler over mountain areas. The ridge aloft formed into a high over the Philadelphia-Washington, D. C. area. The coolest and driest air on the morning of the 31st was found through New England,

central Maryland, and east of the mountains to Indiana but not Illinois. Flow from the ocean modified the coastal air. For the next 24 hours the ridge line followed the Appalachians, keeping them relatively dry. Tropical storm Carrie began approaching the mid-Atlantic coast, from the southeast and cold front was crossing the midwestern states. By September 2 at 0800, Carrie was advancing northward, 200 miles east of Wallops Island, Virginia. Moisture remained east of the mountains. The progress of the frontal system had slowly moved to Buffalo to Evansville line. Post-frontal precipitation covered an extensive area. The ridge line, squeezed between Carrie and the front along the Appalachians, although weakened, persisted and remained dry.

By September 3, Carrie, approaching Cape Cod from the south, lay east of New York City. The front progressed slowly eastward with its rain as the ridge line dissipated. The front passed the airport 0400 EDT.

11 September - 2200 EDT to 13 September - 0800 EDT

On September 9, a continental polar air mass pushed south southeast across the United States from central Canada. On the 10th, the high pressure center (~ 1030 mb) was located over southwest Ontario bringing cool air and clear skies to the eastern United States. Aloft, high pressure centers were scattered across the southeastern states. Tropical Storm Dawn was moving east and southeast away from the North Carolina coast. By the morning of the 11th, the surface high drifted to the North Carolina-Virginia border, with the continental polar air from New York City to Atlanta. West of the Appalachians, air mass modification to maritime tropical air was underway. A system of Pacific was moving eastward across Northern Plains. Within 24 hours the air over the eastern United States was fully modified to maritime tropical air, and in a southwest flow. The Pacific front was stationary from Kansas to the St. Lawrence River valley. Another Canadian high pressure center (~ 1022 mb) north of stationary front was moving east northeast, but not pushing southeastward. By the morning of the 13th, warm, moist air extended up to the Great Lakes, with rain and showers for 150 miles south of a warm front through Michigan to Buffalo to New York City.

# REFERENCES

- Decker, C. E., T. M. Royal, and J. B. Tommerdahl, Field Evaluation of New Air Pollution Monitoring System, Research Triangle Park, N. C.: Research Triangle Institute, May 1972.
- Dixon, W. J. and F. J. Massey, Jr. Introduction to Statistical Analysis, New York, N. Y.: McGraw-Hill Book Company, Inc., 1957.
- Environmental Protection Agency. Mount Storm, West Virginia-Gorman, Maryland, and Luke, Maryland-Keyser, West Virginia, Air Pollution Abatement Activity, Air Pollution Control Office Publ. No. APTD-0656, Research Triangle Park, N. C., April 1971.
- Hering, W. S. and T. R. Borden, Jr. Ozonesonde Observations Over North America, Vol. 4, Bedford, Massachusetts: Air Force Cambridge Research Laboratories, 1967.
- Hodgeson, J. A., B. E. Martin, and R. E. Baumgardner. "Laboratory Evaluation of Alternate Chemiluminescent Approaches for the Detection of Atmospheric Ozone," Presented at the American Chemical Society Meeting, September 1970.
- Jeffries, H. E. An Experimental Method for Measuring the Rate of Synthesis, Destruction, and Transport of Ozone in the Lower Atmosphere, ESE Publication No. 285, Chapel Hill, North Carolina: University of North Carolina, 1971.
- Lea, D. A. "Vertical Ozone Distribution in the Lower Troposphere Near an Urban Pollution Center," J. Appl. Meteor. 7, 252-267, 1968.
- Miller, P. R., M. H. McCutchan, and H. P. Milligan. "Oxidant Air Pollution in the Central Valley, Sierra Nevada Foothills, and Mineral King Valley of California," Atmos. Environ. 6, 623-633, 1972.
- O'Keefe, A. E. and G. C. Ortman. "Primary Standards for Trace Gas Analysis," Anal. Chem. 38, 760-763, 1966.
- Paetzold, H. K. "The Photochemistry of the Atmospheric Ozone Layer," In Chemical Reactions in the Lower and Upper Atmosphere, New York, N. Y.: Interscience, 1961.
- Pitts, J. N., Jr. Personal communication to L. A. Ripperton, 1972.
- Public Health Service. Selected Methods for the Measurement of Air Pollutants, Cincinnati, Ohio: R. A. Taft Sanitary Engineering Center, 1965.
- Richter, H. G. "Special Ozone and Oxidant Measurements in Vicinity of Mount Storm, West Virginia," Research Triangle Park, N. C.: Research Triangle Institute, October 1970.

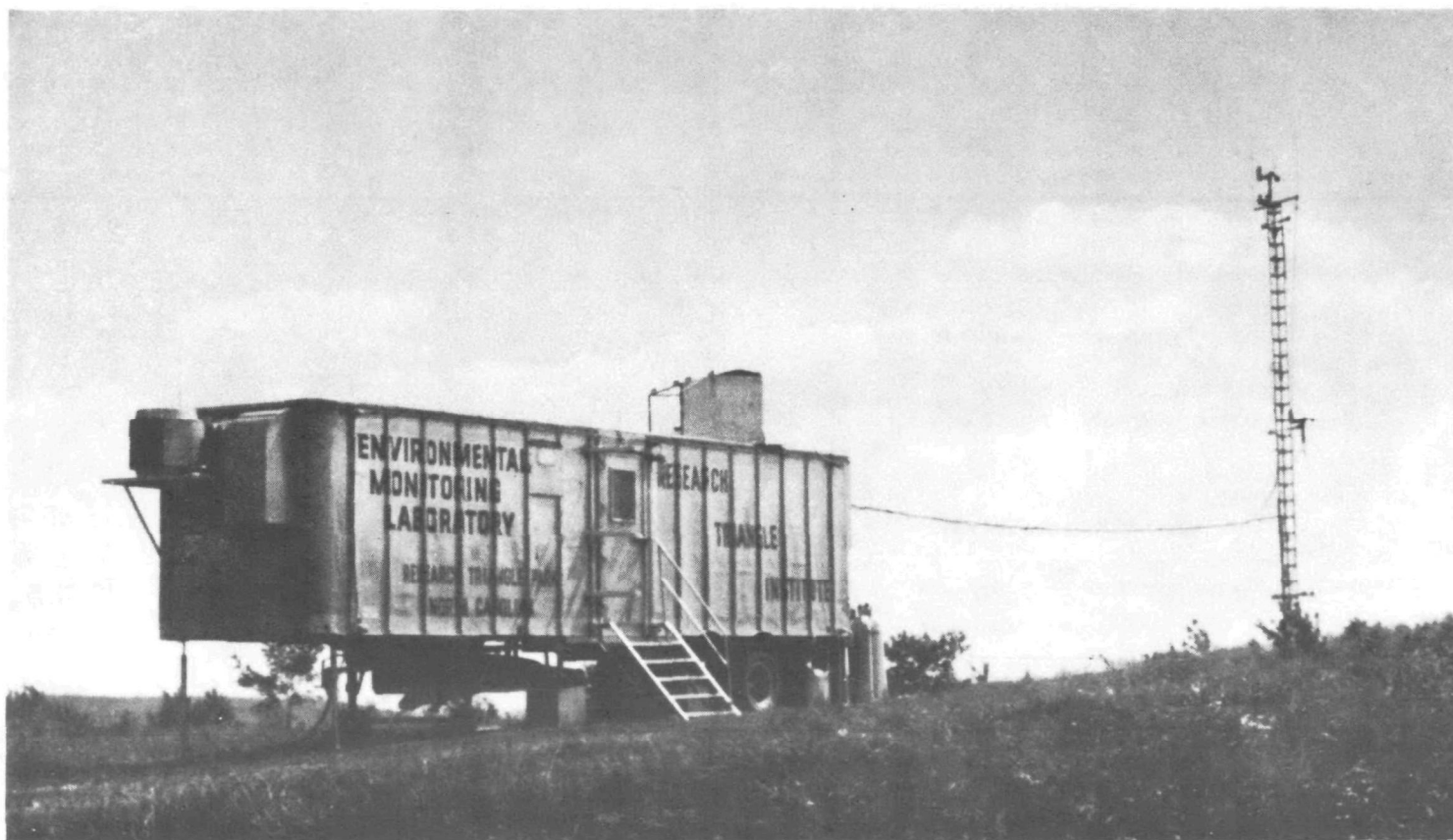
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REFERENCES (Cont'd)

Ripperton, L. A., H. Jeffries, and J. J. B. Worth. "Natural Synthesis of Ozone in the Troposphere," Environ. Sci. and Tech. 5, 246-248, 1971.

Scaringelli, F. P., et al. "Evaluation of Teflon Permeation Tubes for Use with Sulfur Dioxide," Presented in part at the American Industrial Hygiene Association Annual Meeting, May 1966.

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