United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450/4-81-011
March 1981

Air

Philadelphia Oxidant Data Enhancement Study

Analysis and Interpretation of Measured Data

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by

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Contract No. 68-02-3332

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

March 1981

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SUMMARY

The objectives of this study were twofold:

1. To obtain air quality and meteorological data of sufficient extent and quality to apply the Systems Application, Incorporated (SAI) photochemical model to the Philadelphia area.

2. To recommend days suitable for model validation through analysis of field data.

Sixteen surface air quality sites, eighteen surface meteorological sites, and three upper-air meteorological sites contributed data to the study during the summer of 1979. In addition, helicopter-based measurements of air quality and meteorology and measurements of hydrocarbon species were performed.

Based upon analysis of all data, the following days were recommended for model validation:

July 12	August 4	August 10
July 13	August 5	August 22
July 16	August 6	
July 19	August 7	

ACKNOWLEDGEMENTS

Many people at AeroVironment Inc., besides the authors, contributed significantly to this study. Other primary participants and their areas of responsibility are:

Mr. Robert Baxter, Field Manager
Mr. Don Gonzales, Data Processing
Ms. Diane Barker, Report Editing
Mrs. Darlene Asamura, Technical Typing
Ms. Gloria Best, Technical Illustrating
Mr. Timothy Press, Data Analysis
Mr. Howard Hammeren, Field Calibration
Mr. David Pankrantz, Senior Field Technician
Mr. Steven Fisher, Field Technician
Mr. David Emery, Field Technician
Mr. Stan Krzywonos, Field Technician

A number of other organizations were also involved in this study. The U.S. EPA's Environmental Monitoring Systems Laboratory, Las Vegas, Nevada (EMSL-LV), supplied an instrumented helicopter. Mr. Charles Fitzsimmons was responsible for EMSL-LV field operations. The helicopter measurements were made by Northrop Services' Environmental Science Center under the supervision of Mr. Calvin Hancock. Mr. Barry Martin, EPA Environmental Monitoring and Support Laboratory, Research Triangle Park, North Carolina, and his staff gave invaluable assistance with instrumentation problems. Finally, the contribution of Mr. Norm Possiel, EPA Project Officer, to the technical direction of the project is certainly one of the most appreciated.

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1. INTRODUCTION

The Clean Air Act Amendments of 1977 require states to submit State Implementation Plans (SIPs) that demonstrate the attainment of the National Ambient Air Quality Standard (NAAQS) for ozone (and certain other pollutants) by 1982. If such attainment is shown to be impossible using reasonably available control measures, an extension to 1987 can be granted. To assist the states in developing their SIPs, the U.S. Environmental Protection Agency (EPA) is conducting a program to provide technical information and guidance on available procedures for estimating control requirements needed to attain the NAAQS for ozone.

Photochemical models, particularly the Systems Applications, Incorporated (SAI), Airshed Model (Reynolds et al., 1978) can be used to quantify control requirements. The EPA plans to verify this model for several urban areas which typify different photochemical and meteorological regimes. When this model is verified, the EPA will be in a position to establish the range of the model's applicability and to issue guidance on its application.

One of the urban areas under study is Philadelphia, Pennsylvania. Considerable information on the transport of ozone and precursors into the Philadelphia area was obtained in a study conducted in 1978 (Chan et al., 1979), even though the primary emphasis of that study was to evaluate and demonstrate different approaches to measure such transport. To enhance the data base for verifying the Airshed Model, another study was conducted in Philadelphia in the summer of 1979. Besides gathering data for model verification, another objective of that study was to increase our knowledge of the photochemical and meteorological processes which lead to peak ozone and NO_2 concentrations in Philadelphia.

This report documents the data collection efforts of the 1979 study, characterizes the air quality and meteorology during the monitoring period, investigates periods of high ozone and NO_2 with modeling potential, and provides recommendations for model verification.

2. FIELD MEASUREMENT PROGRAM

Data were collected from July 2, 1979 through September 18, 1979. These data included continuous surface air quality measurements at fifteen locations, surface meteorological measurements at seventeen locations, aircraft measurement of air quality and meteorological parameters in the vertical, upper air meteorology at three locations, and hydrocarbon species measurements.

2.1 OBJECTIVES OF THE FIELD PROGRAM

The primary objective of the field program was to obtain air quality and meteorological data of sufficient extent and quality to apply the Systems Application, Incorporated (SAI), photochemical model to the Philadelphia area. A secondary objective was to collect data which would increase the EPA's knowledge of the photochemical and meteorological processes which lead to peak ozone and NO_2 concentrations in a portion of the Northeast Corridor. Philadelphia was selected because it is a large city within the Northeast Corridor capable of generating high ozone levels while remaining subject to significant inter-urban ozone/precursor transport.

2.2 PROGRAM DESIGN

To achieve the objectives of the field program, measurements were taken in the vicinity of Philadelphia, Pennsylvania, to assess:

- the levels of ozone and precursors transported into the study area;
- the levels of precursors produced from emissions within the study area;
- the highest levels of NO_2 and ozone downwind of the Philadelphia urban area.

The field monitoring program had four components:

1. Surface measurements of air quality and meteorology at fixed sites;
2. Aircraft measurements of air quality and meteorology;

3. Balloon measurements of upper air meteorology;
4. Hydrocarbon species measurements.

Table 1 shows the periods during which each of these field components contributed data to the study and the organizations responsible for each component's operation.

2.3 SURFACE MEASUREMENTS AT FIXED SITES

The fixed surface station component consisted of:

1. Five stations set up specifically for the study (special study sites);
2. Eleven existing air quality meteorological monitoring stations;
3. Supplemental meteorological sites;
4. Special PAN/nitric acid/NO_x monitoring.

2.3.1 Special Study Sites

Figure 1 shows the locations of the five stations set up specifically for the study. Table 2 lists the parameters monitored at each of these AeroVironment-operated sites. Table 3 lists the instruments used, their precision, lower detection limit, and lower limit of data validity. All monitoring equipment at these sites, with the exception of the acoustic sounder used to measure mixing height at Site 1, was provided by the EPA's Environmental Monitoring and Support Laboratory in Research Triangle Park, North Carolina.

Sites 1 and 2 were upwind of Philadelphia under prevailing flow which was from the south-southwest to west. Site 1 was near Summit Bridge, Delaware, approximately 60 km southwest of the Philadelphia urban core. Site 2 was near Downingtown, Pennsylvania, approximately 50 km west of Philadelphia. Site 2 was at the same position as one of the sites in the 1978 Philadelphia Oxidant Study, thus providing some year-to-year data comparison.

Sites 1 and 2 were to monitor ozone and precursors transported into the city, both along the surface and aloft, when the prevailing flow was southwesterly. Surface stations

Table 1. RESPONSIBLE ORGANIZATIONS AND PERIODS OF OPERATION OF FIELD MONITORING PROGRAM COMPONENTS.

Program Component	Dates	Responsible Organization
Surface Measurements of Air Quality and Meteorological Data at Fixed Sites		
Special study sites	July 2-September 18	AeroVironment Inc./U.S. Environmental Protection Agency
Existing sites	July 2-September 18	Philadelphia Department of Health (Air Management Services) Pennsylvania Department of Environmental Resources New Jersey Department of Environmental Protection
Supplemental meteorological sites	July 2-September 18	National Weather Service Federal Aviation Administration U.S. Air Force, U.S. Navy
Special PAN/nitric acid NO_x monitoring	July 15-August 22	Washington State University Battelle Columbus Laboratories
Aircraft Measurements of Air Quality and Meteorological Data		
Bell UH-1H helicopter	July 18-August 16	Northrop Services/U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas
Balloon Measurements of Upper Air Meteorological Data		
Pibal	July 16-August 16	U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas
Radiosonde	July 18-August 26	Beukers Laboratories, Inc.
Hydrocarbon Species Measurements		
	July 15-August 15	Washington State University

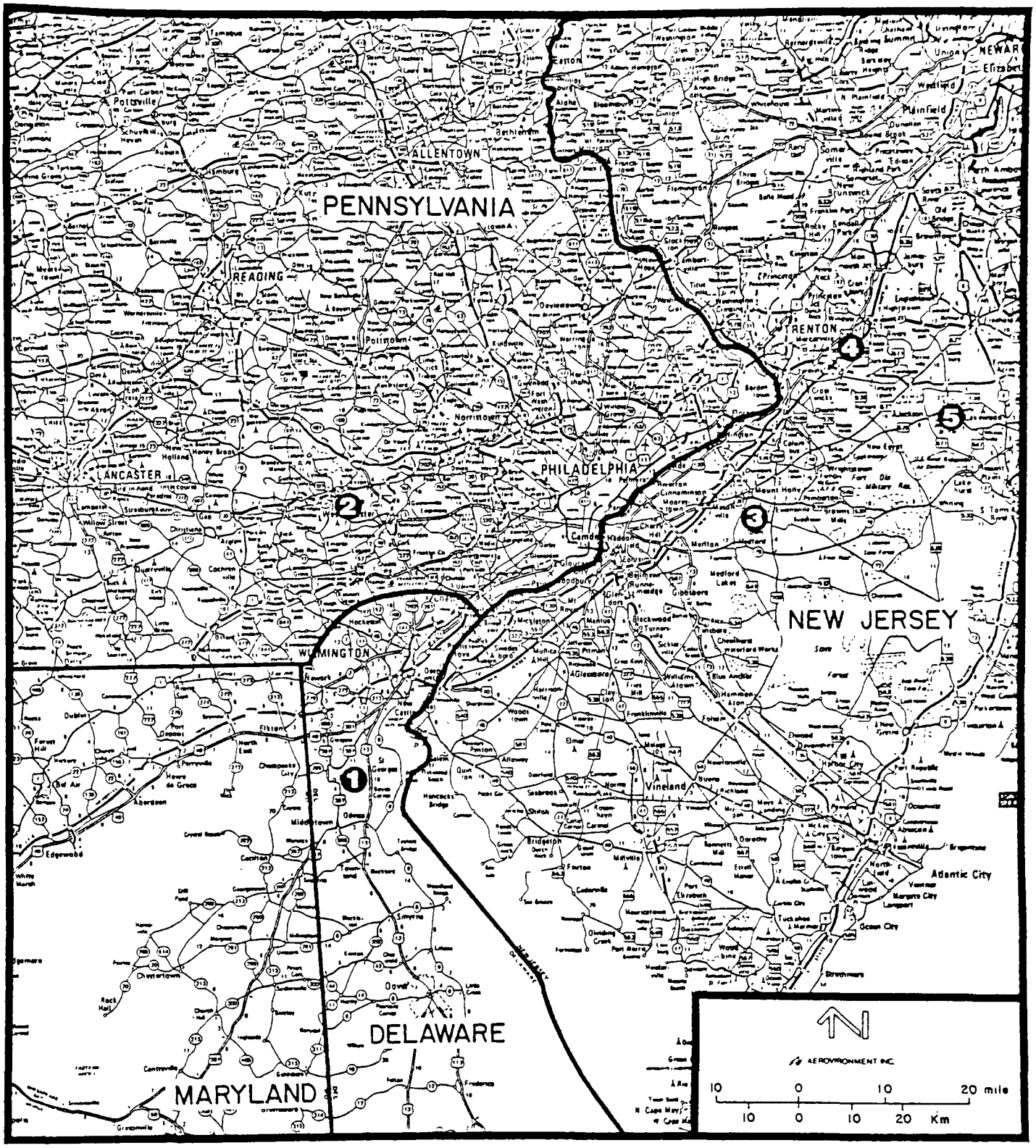


FIGURE 1. Locations of monitoring sites set up specifically for the study.

Table 2. METEOROLOGICAL AND AIR QUALITY PARAMETERS MONITORED AT THE FIVE SITES SET UP SPECIFICALLY FOR THE STUDY.

Component	Site				
	1	2	3	4	5
	Summit Bridge, DE	Downing-town, PA	Lumber-ton, NJ	Robbins-ville, NJ	Van Hise-ville, NJ
Ozone	X	X	X	X	X
Nitrogen Dioxide	X	X	X	X	X
Oxides of Nitrogen	X	X	X	X	X
Nitric Oxide	X	X	X	X	X
Non-Methane Hydrocarbon	X	X	X		
Total Hydrocarbon	X	X	X		
Methane	X	X	X		
Carbon Monoxide			X		
Wind Speed	X	X	X	X	X
Wind Direction	X	X	X	X	X
Temperature	X		X	X	
Solar Radiation	X		X		
Mixing Height	X				

Table 3. MONITORING INSTRUMENTS WITH THEIR LOWER DETECTION LIMITS, DATA PRECISION, AND LOWER LIMITS OF DATA VALIDITY.

Parameter	Instrument	Instrument Lower Detection Limit	Data Precision	Lower Limit of Data Validity
Air Quality				
O_3	Bendix 8002	0.001 ppm	0.005 ppm	0.005 ppm
NO	Bendix 8101	0.005 ppm	0.010 ppm	0.010 ppm
NO_2	Bendix 8101	0.005 ppm	0.010 ppm	0.010 ppm
NO_x	Bendix 8101	0.005 ppm	0.010 ppm	0.010 ppm
THC	Beckman 6800	0.100 ppm	0.100 ppm	0.100 ppm
CH_4	Beckman 6800	0.100 ppm	0.100 ppm	0.100 ppm
NMHC	Beckman 6800	0.200 ppm	0.200 ppm	0.200 ppm
CO	Bendix 8501	0.500 ppm	0.500 ppm	0.500 ppm
Meteorology				
Wind Speed	Climatronics	0.2 m/s	0.2 m/s	0.2 m/s
Wind Direction	Climatronics	N/A	5°	N/A
Temperature	Climatronics	N/A	0.5^{o} C	N/A
Solar Radiation	Eppley (Model 2)	0.05 $cal/cm^2/min$	0.05 $cal/cm^2/min$	0.05 $cal/cm^2/min$
Mixing Height	AeroVironment 300C	30 m	10 m	30 m

can provide an indication of transport aloft, since ozone and precursors trapped aloft overnight are brought to the ground through turbulent vertical mixing after the breakup of the nocturnal radiation inversion. Placing the acoustic sounder at Site 1 provided the time of inversion breakup.

Sites 3, 4, and 5 were downwind of Philadelphia under prevailing flow. Site 3 was near Lumberton, New Jersey, approximately 35 km east-northeast of the Philadelphia urban core. Site 4 was near Robbinsville, New Jersey, approximately 60 km northeast of Philadelphia. Site 5 was near Van Hiseville, New Jersey, approximately 75 km east-northeast of Philadelphia. These sites were established to monitor peak ozone and NO_2 concentrations resulting from ozone and precursors transported into Philadelphia and precursors emitted in the urban core under southwesterly flow. Figure 2 shows an exterior view of the monitoring station at Site 5, which was identical to the monitoring stations at Sites 1, 2, 3, and 4.

2.3.2 Existing Air Quality/Meteorology Monitoring Stations

Figure 3 shows the locations of the eleven existing air quality/meteorology monitoring stations which contributed data to the study, and Table 4 lists the parameters monitored at each. The state and local agencies operating these sites are named in Table 5. The operating agencies themselves supplied most of the air quality and meteorological instruments. The EPA's Environmental Monitoring and Support Laboratory in Research Triangle Park, North Carolina, supplied some additional instrumentation. Information on the accuracy, precision, and ranges of the instruments can be obtained from the agencies themselves.

The EPA selected the stations to be included in the study based primarily upon location and instrumentation available. Sites 6, 11, and 15 were included as upwind stations for south to southwest flow and monitored transport of ozone and precursors into the study area under these flows. Sites 9, 12, 13, and 14 were urban sites for monitoring both urban generated precursors and urban ozone peaks or, in the case of Site 9, urban wind flow. Site 10 provided a near-urban monitor. Sites 7, 8, and 16 served as downwind ozone and/or NO_2 stations under southwesterly flow. Table 6 gives the distances and bearings from the urban core for these stations.

FIGURE 2. Exterior view of the monitoring station at Site 5.

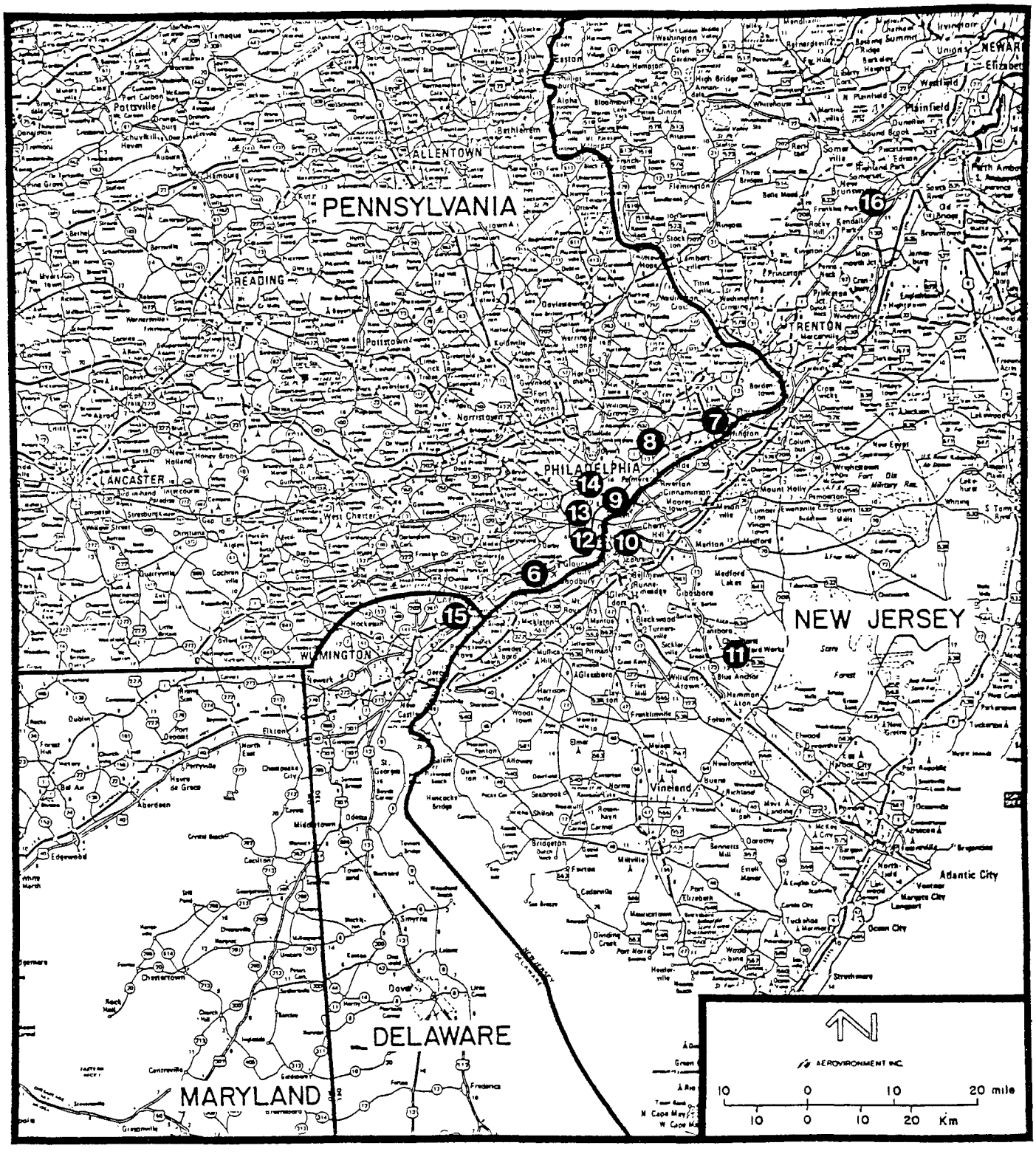


FIGURE 3. Existing air quality/meteorological monitoring stations used in the study.

Table 4. METEOROLOGY AND AIR QUALITY PARAMETERS MONITORED AT EXISTING STATIONS.

Component	Site										
	6	7	8	9	10	11	12	13	14	15	16
Ozone	X	X	X		X	X	X	X	X	X	X
Nitrogen Dioxide	X	X	X		X		X	X	X	X	
Oxides of Nitrogen											
Nitric Oxide			X		X		X	X	X		
Non-Methane Hydrocarbon	X	X					X	X	X		
Carbon Monoxide					X	X	X	X	X		
Wind Speed	X	X		X						X	
Wind Direction	X	X		X						X	
Temperature	X	X						X			

Table 5. SITE LOCATIONS AND OPERATING AGENCIES OF THE EXISTING AIR QUALITY/METEOROLOGY STATIONS.

Site Number	Location	Operating Agency
6	Chester, Pennsylvania	Pennsylvania Department of Environmental Resources
7	Bristol, Pennsylvania	Pennsylvania Department of Environmental Resources
8	North Philadelphia Airport Philadelphia, Pennsylvania	Air Management Services (Philadelphia Department of Health)
9	Allegheny Philadelphia, Pennsylvania	Air Management Services (Philadelphia Department of Health)
10	Camden, New Jersey	New Jersey Department of Environmental Protection
11	Ancora, New Jersey	New Jersey Department of Environmental Protection
12	South Broad and Spruce Streets Philadelphia, Pennsylvania	Air Management Services (Philadelphia Department of Health)
13	Franklin Institute Philadelphia, Pennsylvania	Air Management Services (Philadelphia Department of Health)
14	Air Management Services Laboratory Philadelphia, Pennsylvania	Air Management Services (Philadelphia Department of Health)
15	Claymont, Delaware	Delaware Department of Natural Resources and Environmental Control
16	New Brunswick, New Jersey	New Jersey Department of Environmental Protection

Table 6. LOCATIONS OF EXISTING AIR QUALITY/METEOROLOGY MONITORING SITES WITH RESPECT TO PHILADELPHIA URBAN CORE.

Site Number	Location	Position with Respect to Philadelphia Urban Core	
		Distance (km)	Bearing Direction
6	Chester, Pennsylvania	20.3	WSW
7	Bristol, Pennsylvania	30.5	NE
8	North Philadelphia Airport Philadelphia, Pennsylvania	16.0	NNE
9	Allegheny, Pennsylvania	6.2	NE
10	Camden, New Jersey	4.8	E
11	Ancora, New Jersey	38.9	SE
12	South Broad and Spruce Streets, Philadelphia, Pennsylvania	CBD*	CBD*
13	Franklin Institute, Philadelphia, Pennsylvania	2.5	NNW
14	Air Management Services Lab, Philadelphia, Pennsylvania	9.0	N
15	Claymont, Delaware	28.1	WSW
16	New Brunswick, New Jersey	85.0	NE

*CBD = central business district

2.3.3 Supplemental Meteorological Sites

Data were also obtained from eight existing meteorological monitoring stations operated by the National Weather Service, the Federal Aviation Administration, the U.S. Air Force, and the U.S. Navy. Figure 4 shows the locations of these stations. All sites recorded one-minute averages of wind speed, wind direction, and temperature once an hour. These data were included to better define the study area wind field. Table 7 gives the distance and bearing from the urban core for these stations.

2.3.4 Special PAN/Nitric Acid/NO_x Monitoring

Special PAN, nitric acid, and oxides of nitrogen monitoring was conducted by Washington State University and Battelle Columbus Laboratories during July 15 through August 22, 1979, at Downingtown, PA (Site 2), and Van Hiseville, NJ (Site 5). Washington State University monitored NO, NO_x and PAN at Downingtown, and Battelle monitored nitric acid at Downingtown, and NO, NO_x, PAN, and nitric acid at Van Hiseville. Information regarding measurement methods can be obtained directly from these organizations.

2.4 AIRCRAFT MEASUREMENTS OF AIR QUALITY AND METEOROLOGY

The primary objective of the aircraft measurements was to obtain vertical profiles and cross-sections of ozone and precursors to quantify pollutant transport aloft. That is, from these profiles and cross-sections, we could find the levels of ozone and precursors transported into the city in layers aloft over various periods during days of high photochemical activity. Such measurements would also provide boundary and initial conditions for verifying of the SAI model.

Aircraft measurements were taken by the EPA's Environmental Monitoring Systems Laboratory in Las Vegas, and Northrop Services, Inc., between July 18 and August 16, 1979, using a Bell UH-1H helicopter (Figure 5). Parameters measured included O_3, NO, NO_x, visible light scattering, temperature, and dew point versus location and time. In addition, hydrocarbon grab samples were taken for species analysis. The hydrocarbon sampling will be discussed in more detail later in this chapter. Table 8 lists the

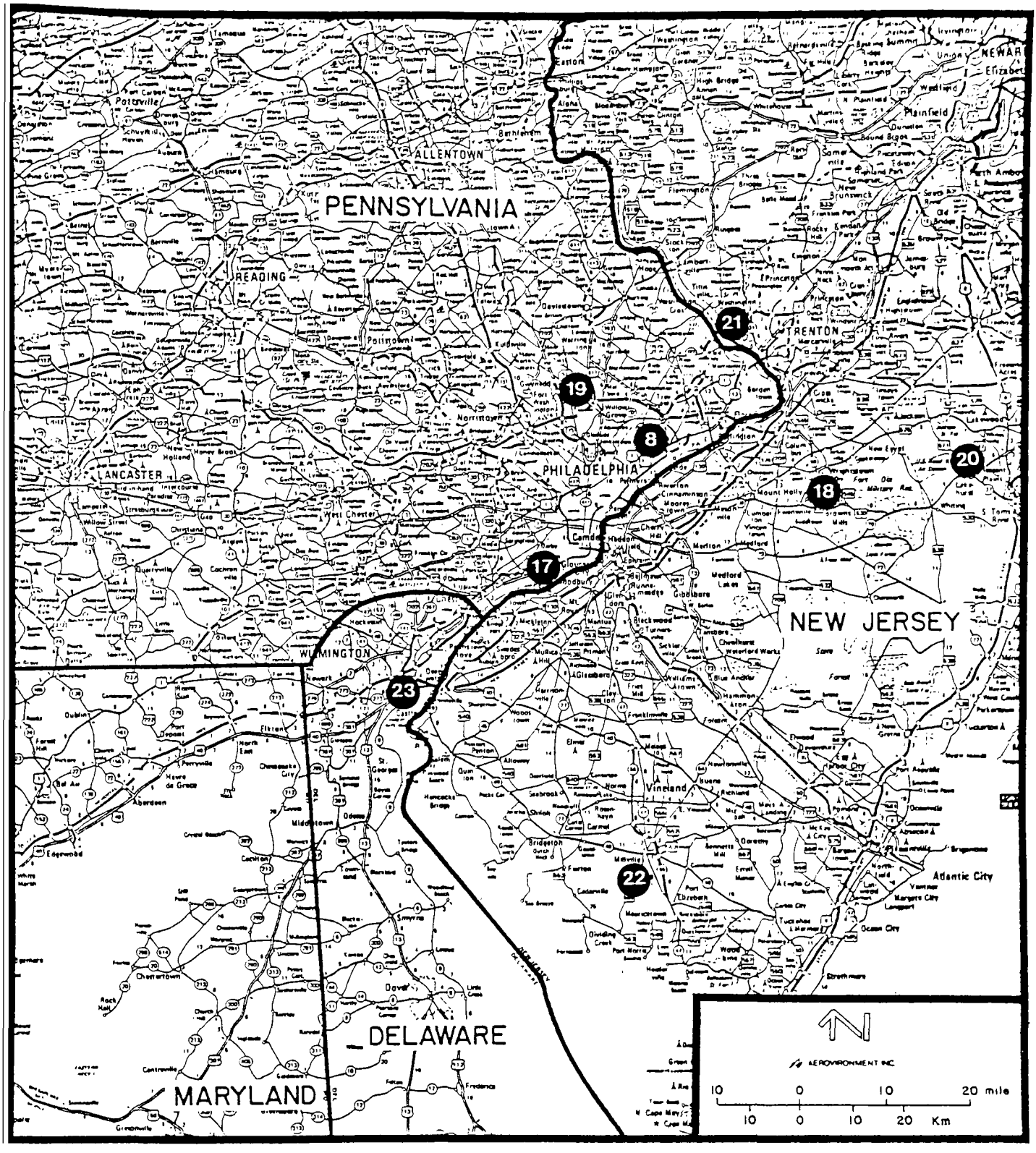


FIGURE 4. Locations of supplemental meteorological monitoring sites used in the study.

Table 7. LOCATIONS OF SUPPLEMENTAL METEOROLOGICAL MONITORING SITES WITH RESPECT TO PHILADELPHIA URBAN CORE.

Site Number	Location	Position with Respect to Philadelphia Urban Core	
		Distance (km)	Bearing Direction
8	North Philadelphia Airport, PA	16.0	NNE
17	Philadelphia International Airport, PA	9.1	SW
18	McGuire Air Force Base, NJ	49.2	E
19	Willow Grove Naval Air Station, PA	28.6	N
20	Lakehurst Naval Air Station, NJ	75.8	E
21	Trenton-Mercer County Airport, NJ	48.2	NE
22	Millville Airport, NJ	64.3	S
23	Greater Wilmington Airport, DE	47.6	SW

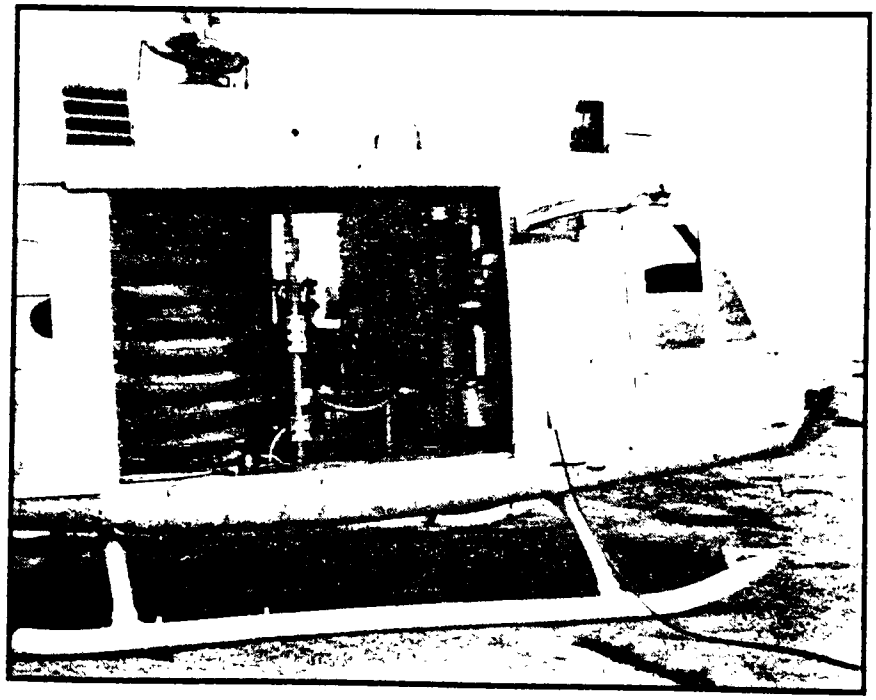


FIGURE 5. EPA-Las Vegas instrumented UH-1H helicopter.

Table 8. PARAMETERS MEASURED BY HELICOPTER AND INSTRUMENTS USED.

Parameter	Instrument
Hydrocarbons	Grab samples using evacuated stainless steel canisters
Ozone	REM 612 B chemiluminescent analyzer
$NO/NO_2/NO_x$	Monitor Labs 8440 chemiluminescent analyzer
Light Scattering	Meteorology Research Inc. Model 1550 nephelometer
Temperature/Dew Point	EG&G 137-C1
Static Pressure (altitude)	National Semiconductor LX3702A
Position	Two Collins DME 40

instruments used. The accuracy, precision, and ranges of these instruments have been previously documented (Hancock, 1980).

The aircraft (helicopter) measurement program consisted of 10 days of intensive vertical soundings and transects upwind, over, and downwind of the study city. The choice of these 10 days was based on forecasts predicting meteorological conditions favorable for significant photochemical activity.

On each measurement day, three flights were generally made: one in the early morning (takeoff at 0500 EST), one at mid-morning (takeoff at 0900 EST), and one in the early afternoon (takeoff at 1300 EST).

Each flight consisted of vertical soundings over three surface monitoring stations from as close to the ground surface as possible up to 2 km above ground level (AGL), and a horizontal traverse between the stations at the elevation where maximum ozone levels were observed. Figure 6 shows the locations of these stations. Spirals were performed at two upwind and one downwind sites during the early morning; one upwind, one downtown, and one downwind site during the late morning; and one downtown and two downwind sites during the afternoon. The specific sites over which sampling was performed varied depending upon the wind direction. The exact flight paths taken on each sampling day have been documented elsewhere (Hancock, 1980).

The mission of each day was to obtain information about ozone and precursor concentrations aloft being transported into the study area, concentrations present aloft near the central business district, and peak ozone concentrations downwind. Table 9 summarizes the aircraft sampling missions actually flown.

2.5 BALLOON MEASUREMENTS OF UPPER AIR METEOROLOGY

2.5.1 Radiosonde Releases

Beukers Laboratories, Inc. was responsible for releasing five radiosondes per day from July 18 through August 26, 1979, from 315 East Chelten Avenue, Philadelphia (about 10 miles west-southwest of North Philadelphia Airport). These five releases provided

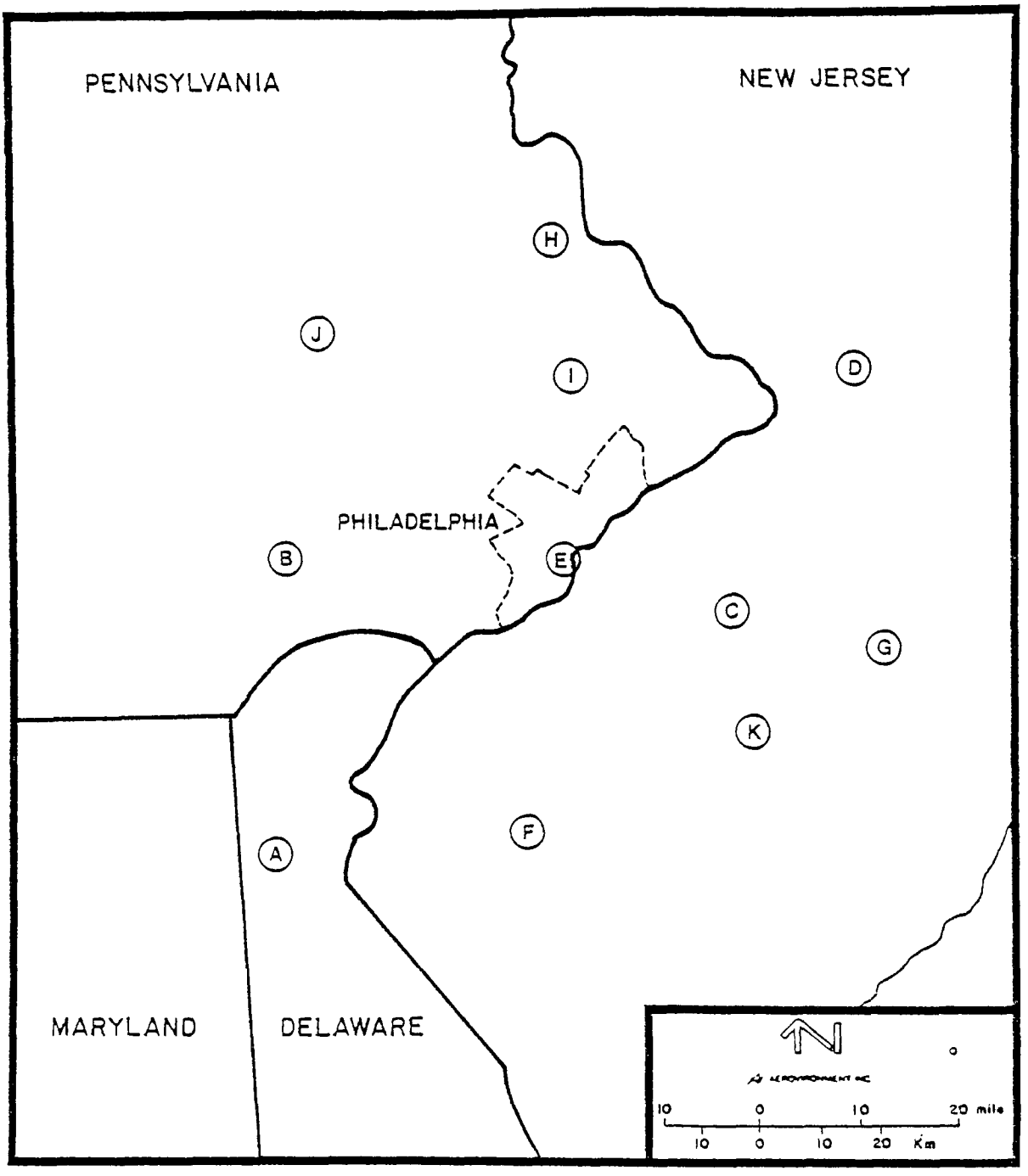


FIGURE 6. Locations of helicopter sounding and sampling sites.

Table 9. SUMMARY OF AIRCRAFT SAMPLING MISSIONS ACTUALLY FLOWN.

Date	Flight Time (EST)	Pattern*
July 23	1044-1243	Southwesterly
	1432-1658	Southwesterly
July 25	0532-0737	Westerly
	0854-1052	Westerly
	1314-1530	Westerly
August 4	0919-1124	Westerly
	1308-1536	Westerly
August 5	0738-0938	Westerly
	1305-1530	Westerly
August 6	0517-0741	Northwesterly
	0907-1057	Northwesterly
	1316-1525	Northwesterly
August 7	0517-0723	Northwesterly
	0844-1050	Northwesterly
	1301-1507	Northwesterly
August 10	0519-0724	Southwesterly
	0832-1045	Northwesterly
	1258-1527	Northwesterly
August 14	0522-0723	Southwesterly
	0851-1043	Southwesterly
	1300-1530	Southwesterly
August 15	0519-0732	Northwesterly
	0848-1126	Northwesterly
	1317-1515	Northwesterly
August 16	0510-0715	Northwesterly
	0835-0927	Northwesterly

*The exact sounding locations for each flight pattern varied.

vertical profiles of wind speed, wind direction, temperature, and dew point for the hours 0500, 0700, 0900, 1200, and 1500 EST. The 0700 and 1200 EST releases provided data at "mandatory" levels (surface, 1000 mb, 850 mb, 700 mb, and 500 mb), while the 0500, 0900, and 1500 EST releases provided data at other significant levels (based upon temperature lapse rate).

2.5.2 Pibal Releases

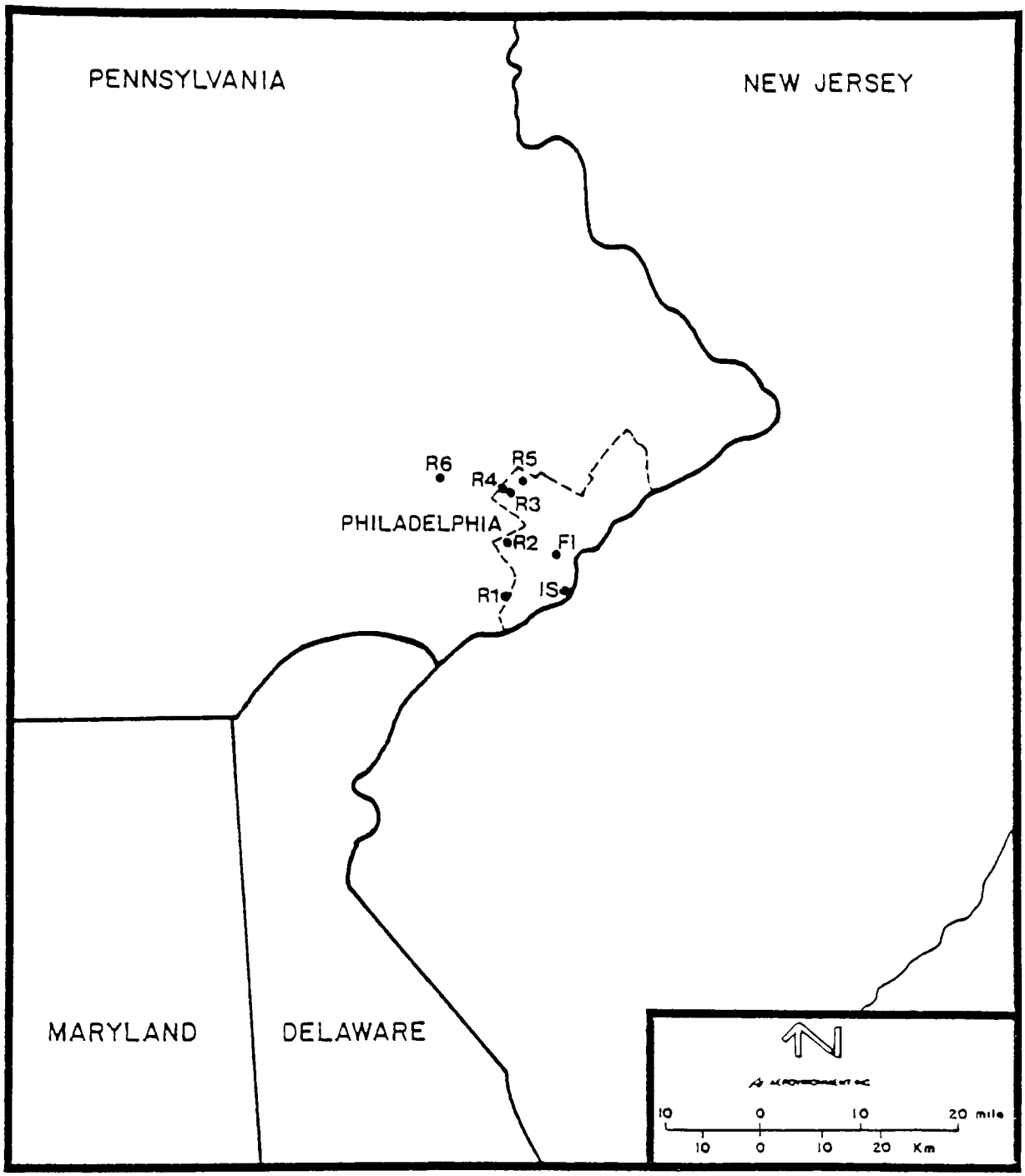
The EPA Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (EMSL-Las Vegas), was responsible for releasing and tracking approximately 12 pilot balloons per weekday from July 16 through August 16, 1979, from Robbinsville Airport, New Jersey (Site 4), and from Greater Wilmington Airport, Delaware (Site 23). These releases provided vertical profiles of wind speed and direction for 0500 EST through 1600 EST.

2.6 HYDROCARBON SPECIES MEASUREMENTS

This component of the program, which was the responsibility of Washington State University, provided information on the hydrocarbon species as they were transported into and emitted within the urban area.

There were three parts to the sampling program: (1) integrated samples were collected at ground level; (2) grab samples were collected at ground level; and (3) grab samples were collected aloft. Samples were collected between July 15 and August 15, 1979.

Figure 7 shows the ground level sampling locations. One-hour integrated samples were taken at the Franklin Institute (Site 13) and at a site near an industrial area in south Philadelphia along the Delaware River. Eighty-five of these samples were collected from 0600 to 0700 EST and 0800 to 0900 EST. On selected days, a surface grab sample was collected at each of two roving sites, the location of which varied from day to day. Fourteen of this type of samples were collected. Four grab samples were collected by the EPA-EMSL helicopter during each flight day for a total of forty. Nine samples were collected for intercomparison purposes. A grand total of 148 samples were analyzed.



FI = Franklin Institute
IS = Industrial Site
R1-6 = Roving Sites

FIGURE 7. Locations of ground-level sampling sites.

All samples were analyzed within 24 hours of collection. The gas chromatography procedures used to analyze these samples are documented elsewhere (Westberg and Sweany, 1980).

2.7 QUALITY ASSURANCE

This section summarizes the procedures used to assure data quality for AeroVironment's portion of the field program, and specifically describes the calibration methods and frequency, station check methods and frequency, and audit and interlaboratory tests.

2.7.1 Surface Monitoring Program

The equipment listed in Table 3, except for the acoustic radar, was tested and furnished to AeroVironment by the EPA. Both EPA and AV extensively bench-tested all equipment to assure proper operation. To meet the manufacturers' specifications, the equipment and recording devices were installed in environmentally controlled shelters at each of the five stations. Additional air conditioners were installed at all sites to insure that stations were operating within the specified temperature range.

o Calibration of Air Quality Instruments

AV personnel performed multipoint calibrations of all air quality instruments at each station at least monthly throughout the measurement program. In addition, an instrument was calibrated whenever any of the following conditions occurred: (a) the control limit for the span check as specified in the Station Check List Log was exceeded; (b) after repair of a malfunctioning analyzer; (c) after replacement of major components of an analyzer; and (d) when the audit results exceeded the limits established (see discussion of audits, Section 2.7.2). Zero plus a minimum of four calibration points equally spaced over the analyzer range were used to generate a calibration curve. A "master" calibrator was used for all of the multipoint calibrations to ensure data comparability. The purpose of the multipoint calibrations was twofold: (a) to check the instrument linearity; and (b) to assign the values of the on-site calibration sources used for daily station checks so that they would be traceable.

Dynamic calibration of the $NO-NO_2-NO_x$ and O_3 analyzers was performed using a Monitor Labs calibrator. For NO and NO_x channels, a National Bureau of Standards Standard Reference Material (NBS SRM) gas cylinder containing approximately 50 ppm NO in N_2 was diluted to ambient levels for the calibration. For the NO_2 channel, AV used gas phase titration (GPT) of NO and O_3 prescribed by the EPA (40 CFR, Part 50, Appendix F).

For the O_3 analyzers, the calibrator's O_3 output was determined on site by the ultraviolet (UV) photometry method (44 Federal Register 8221-8233, February 8, 1978). A modified Dasibi Model 1003-AH ozone monitor served as a transfer standard. Gas cylinders containing approximately 100 ppm NO in N_2 were used for the NO/NO_x spans.

To calibrate the THC/CH_4 instruments, two compressed gas cylinders containing zero ppm and approximately 8 ppm of CH_4 in an ultrapure air were used. Two compressed gas cylinders containing zero ppm and approximately 50 ppm of CO in an ultrapure air with about 350 ppm CO_2 were used to calibrate the CO analyzer. In both cases, multipoint calibrations were performed using an AeroVironment Model BB-100 dilution system. All gas cylinders were NBS-traceable.

The NO flow rate and dilution system of the calibrator and the flow rate for the AeroVironment Model BB-100 dilution system were calibrated with a bubble flowmeter at the beginning, mid-way through, and at the end of the measurement program.

o Calibration of Meteorological Equipment

Calibration checks of the meteorological equipment were done on site. The wind cups were turned to make sure that the bearings were in normal condition. The wind vanes were aligned to the true north, true south, and true north again to calibrate the recorder output. The local magnetic north declination of $+10^{\circ}$ was accounted for. The temperature output from each station was checked using an NBS-traceable mercury thermometer.

o Station Checks

AV personnel checked stations daily using the Station Check List Log prepared for the project. Their primary concerns were to ensure that the analyzers and the supporting equipment were in proper working order.

Zero and span were checked for all gaseous analyzers during the station check. For the NO/NO_x and O_3 instruments, this was done by using the on-site Monitor Labs Model 8500 calibrator. For the hydrocarbon analyzer, a zero cylinder containing hydrocarbon-free air and a span cylinder containing approximately 2 ppm of CH_4 in ultrapure air were used. A similar procedure for CO was used, with the span cylinder containing approximately 50 ppm CO in ultrapure air.

The zero and span values for each instrument were used to determine control limits. The control limits were a useful tool to detect early instrument problems.

Hydrocarbon analyzers were precision-checked three times a week using EPA-furnished gas cylinders containing known concentrations of hydrocarbon. The results of these checks were recorded and forwarded to the EPA.

The station check personnel reported any instrument problems to the Field Manager on the same day so that corrective action could be initiated as soon as possible. In addition, the Field Manager provided a weekly instrument status report to AV's Program Manager in Pasadena, California, to update him on the field program status and to enable him to provide direction when needed.

2.7.2 Audits

Quality assurance verification of the O_3, $NO-NO_2-NO_x$, $THC-CH_4$, and CO systems used for calibrating was done at Research Triangle Park, North Carolina, at the start of the measurement program. The agreements for all systems were within 5%.

During the monitoring phase, the project was further audited by Research Triangle Institute (RTI) under contract to the EPA. Each of the five surface monitoring stations were audited twice. RTI also audited other study participants.

The acceptable criteria for all audits were set at $\pm 15\%$ agreement for the slope of regression analysis of the audit data. Any audit results indicating that these limits were exceeded resulted in prompt recalibration or repair/recalibration of the instrument(s) in question.

2.8 DATA REDUCTION AND COMPILATION PROCEDURES

The continuous air quality and meteorological data AV collected on chart recorders were reduced at AV's main office in Pasadena, CA. The data were digitized, tabulated, and spot-checked for obvious instrument malfunctions and unusual data points. Site logs, field personnel, and project scientists were consulted concerning the validity of unusual data points. Calibration factors were applied to the data, as appropriate, using the monthly multi-point calibration data supplemented by the daily zero and span check values.

The air quality and meteorological data collected by federal, state, and local agencies were provided to AV by EPA in tabulated form. These data were merged with data collected by AV to form a data set with consistent units and time reference (Eastern Standard Time -- EST). AV prepared data volumes containing hourly averages of all these data for all the sites.

AV also obtained hard copy printouts of supplemental meteorological data collected by the National Weather Service, Federal Aviation Administration, U.S. Navy, and U.S. Air Force. AV entered these data into the computer, error checked them, and produced a magnetic tape.

Special PAN/nitric acid/NO_x data collected by Washington University and Battelle Columbus Labs were provided to AV by EPA in hard copy and magnetic tape format. These data were entered in a form consistent with the rest of the data base, error checked, and a magnetic tape produced.

In addition, EPA provided AV with data recorded by the EPA EMSL-Las Vegas aircraft. These data were sent in hard copy and magnetic tape format along with hard copies of pollutant profiles measured during soundings. These data were used during the analysis.

Hard copy printouts of pibal data from Trenton, New Jersey, and Wilmington, Delaware, collected by EPA EMSL-Las Vegas were provided by EPA for use in the analysis. Upper air radiosonde data collected by Beukers Labs were provided to AV by EPA on magnetic tape for use in the analysis.

Finally, hydrocarbon species data collected by Washington State University were provided to AV by EPA in hard copy format for use in the analysis.

3. OZONE AND PRECURSOR CONCENTRATIONS IN THE STUDY AREA

3.1 DATA SUMMARIES

This section summarizes the data collected during the 1979 field program. It also briefly compares data collected during the study with data collected during recent years and, when possible, with long-term means to determine how representative the study period was with respect to characteristic ozone concentrations.

3.1.1 Representativeness of the 1979 Summer Months

Table 10 compares some meteorological parameters recorded in each of the summer months of 1979 with the corresponding long-term means at the Philadelphia International Airport. The average maximum monthly temperatures were lower than the long-term mean during July, August, and September of 1979, whereas the average minimum monthly temperature was higher than the long-term mean during each of those months. Moreover, the mean monthly temperature (which is the average of the minimum and maximum temperatures) indicates that July was slightly cooler and August and September slightly warmer than the long-term mean. Another useful statistic for relating long-term meteorological data to ozone climatology is the number of days in each month with temperatures greater than or equal to 90° F. From Table 10, we can see that even though the mean temperature for July 1979 was lower than the long-term mean, July 1979 had a normal number of days during which the temperature reached or exceeded 90° F. August 1979 had two days more and September 1979 had two days less than the corresponding long-term means. Also, July had less precipitation and August and September had more precipitation than normal, and each of the three months had less sunshine than normal.

Table 11 summarizes the number of high ozone days and the number of episode periods (three or more consecutive high ozone days) from July 2 through September 18 for the study year and the previous four years at Bristol, Pennsylvania. At this site, peak ozone concentrations were generally lower in the study year than in the four previous

Table 10. COMPARISON OF METEOROLOGICAL PARAMETERS RECORDED DURING EACH SUMMER MONTH OF 1979 WITH CORRESPONDING LONG-TERM MEANS.

Meteorological Parameter	Number of Years in Long-Term Average	July		August		September	
		1979	Long-Term	1979	Long-Term	1979	Long-Term
Average Maximum Monthly Temperature (^{o}C)	30	29.3	30.4	28.8	29.3	24.8	25.8
Average Minimum Monthly Temperature (^{o}C)	30	19.7	19.3	19.5	18.2	15.7	14.3
Mean Monthly Temperature (^{o}C)	30	24.6	24.9	24.2	23.8	20.3	20.1
Number of Days with Maximum Temperature ($\geq 90^{o}$ F)	17	7	7	7	5	0	2
Total Precipitation (cm)	30	10.0	10.4	15.1	10.4	12.4	7.7
Average Station Pressure (mb)	4	1,015.9	1,014.4	1,015.9	1,016.9	1,017.3	1,017.1
Average Wind Speed (m/sec)	36	3.3	3.6	3.6	3.5	3.9	3.7
Percent of Possible Sunshine	34	46	63	52	63	52	60

Table 11. SUMMARY OF HIGH OZONE DAYS (greater than 0.100 ppm and 0.120 ppm) FROM JULY 2 THROUGH SEPTEMBER 18, 1979, FOR THE STUDY YEAR AND THE PREVIOUS FOUR YEARS AT BRISTOL, PENNSYLVANIA (the national ambient air quality standard for ozone is 0.120 ppm).

Year	Number of Days with Peak O_3 (ppm)		Number of Episode* Cases	Total Number of Observations (maximum possible 79)	Percent of Days with O_3 (ppm)	
	>0.100	>0.120			>0.100	>0.120
1979	14	4	0(0)	71	19.7	5.6
1978	21	13	3(5)	63	33.3	20.6
1977	23	11	3(4)	68	33.8	16.2
1976	14	6	0(0)	45	31.1	13.3
1975	24	10	1(4)	67	35.8	14.9

*An episode is defined as three or more consecutive days with O_3 measurements greater than 0.100 ppm. Numbers in parentheses indicate the number of days in the longest episode.

years. For the study period, less than 20% of the daily maximum concentrations were greater than 0.100 ppm, whereas during each of the previous four years more than 30% of the days exceeded this value. A similar reduction in the number of days exceeding 0.120 ppm was noted.

While one might infer from the above discussion that maximum ozone levels were lower in 1979, conditions at Bristol, Pennsylvania may not be indicative of the entire study area. A field program similar to the one for this study was performed in the summer of 1978 to evaluate measurement approaches for studying ozone and precursor transport into an urban area (Chan et al., 1979). Four of the sites contributing data to that study were also used in this study. Table 12 summarizes data collected at these sites during the two summers. From this table, we can see that ozone levels were generally not substantially different between the two years.

3.1.2 Average and Maximum Levels of Pollutants

Table 13 gives peak and average daily maximum ozone concentrations as well as peak and average morning (0500 through 0800 EST) precursor concentrations observed at all monitoring locations during the study period. Site locations were shown in Figures 3 and 4. Ozone levels were similarly high even at some stations located predominantly upwind. Precursor concentrations were generally quite low except at downtown locations.

Table 14 is a frequency distribution of ozone levels observed at various sites in and around Philadelphia. The greatest frequency of concentrations in excess of 0.12 ppm occurred at outlying stations. Downingtown, PA (Site 2), to the west of Philadelphia, and Lumberton, NJ (Site 3), to the east, each had relatively high frequencies of observations (>.85%) greater than 0.12 ppm compared to downtown Philadelphia (<.15%). This pattern is also true for frequency of ozone values greater than 0.08 ppm. Sites 1 through 5 had concentrations greater than 0.08 ppm for more than 3.5% of the observations, whereas in downtown Philadelphia (Site 12) the frequency is less than 1.0%. The high frequency of low ozone concentrations at Site 12 was expected due to the higher levels of ozone-scavenging NO in urban areas. Surprisingly, the frequency of high ozone levels at outlying sites is somewhat independent of the direction from Philadelphia. Sites to the west or southwest have roughly the same frequency of concentration levels in excess of

Table 12. SUMMARY OF OZONE DATA COLLECTED DURING THE SUMMER OF 1978 AND 1979 AT THE SAME LOCATION.

Location	Site Number	Peak		Number of Days with Peak O_3 (ppm)				Daytime Monthly Averages					
				>0.100		>0.120							
		1978	1979	1978	1979	1978	1979	Jul 1978	Jul 1979	Aug 1978	Aug 1979	Sep 1978	Sep 1979
Downingtown, Pennsylvania	2	0.142	0.146	11	11	3	6	--	0.057	0.055	0.044	0.041	0.042
Ancora, New Jersey	11	0.142	0.147	15	15	4	6	0.049	0.051	0.052	0.047	0.034	0.039
South Broad and Spruce Streets (Philadelphia)	12	0.180	0.140	7	4	2	1	0.028	0.030	0.024	0.020	0.018	0.013
Franklin Institute (Philadelphia)	13	0.250	0.150	6	4	5	1	0.036	0.031	0.030	0.029	0.024	0.020

TABLE 13. PEAK AND AVERAGE OZONE PRECURSOR CONCENTRATIONS (in ppm) FOR THE STUDY PERIOD AT ALL AIR QUALITY MONITORING SITES.

Site No.	Location	Ozone				Oxides of Nitrogen				Non-Methane Hydrocarbons			
		Maximum Hourly Average	Mean Daily Maximum			Maximum Hourly Average	Morning Average (0500-0800 EST)			Maximum Hourly Average	Morning Average (0500-0800 EST)		
			Jul	Aug	Sep		Jul	Aug	Sep		Jul	Aug	Sep
1	Summit Bridge, DE	0.137	0.080	0.072	0.058	0.063	0.010	0.006	0.012	1.0	0.1	0.2	0.3
2	Downingtown, PA	0.157	0.087	0.068	0.064	0.083	0.019	0.013	0.022	1.1	0.1	0.1	0.1
3	Lumberton, NJ	0.146	0.079	0.078	0.052	0.131	0.025	0.022	0.024	1.5	0.1	0.1	0.1
4	Robbinsville, NJ	0.144	--	0.072	0.052	0.207	--	0.028	0.048	--	--	--	--
5	Van Hiseville, NJ	0.161	0.078	0.072	0.054	0.082	0.012	0.007	0.010	--	--	--	--
6	Chester, PA	0.183	0.077	0.071	0.061	--	--	--	--	6.6	1.1	1.0	1.3
7	Bristol, PA	0.135	0.073	0.080	0.060	--	--	--	--	1.7	0.5	--	--
8	North Philadelphia Airport, PA	0.160	0.077	0.079	0.053	--	0.042	0.031	0.037	--	--	--	--
10	Camden, NJ	0.161	0.078	0.076	0.055	--	0.068	0.052	0.080	--	--	--	--
11	Ancora, NJ	0.147	0.079	0.078	0.060	--	--	--	--	--	--	--	--
12	South Broad & Spruce Sts. Philadelphia, PA	0.140	0.057	0.041	0.026	--	0.069	0.059	0.035	2.9	0.6	0.3	0.3
13	Franklin Institute, Philadelphia, PA	0.150	0.061	0.058	0.041	--	0.068	0.060	0.067	1.7	0.8	0.3	0.3
14	Air Management Services Lab, Philadelphia, PA	0.160	0.071	0.059	0.056	--	0.055	0.057	0.059	3.1	0.6	0.4	0.5
15	Claymont, DE	0.170	0.070	0.062	0.033	--	--	--	--	--	--	--	--
16	New Brunswick, NJ	0.105	--	0.056	0.038	--	--	--	--	--	--	--	--

Table 14. OZONE FREQUENCY DISTRIBUTION FOR THE STUDY PERIOD AT SEVERAL SITES IN AND AROUND PHILADELPHIA.

Site Name	Total Hours Observed with Specified Ozone Concentration (ppm)						
	Site	.000-.039	.040-.079	.080-.099	.100-.120	>.120	Total
Summit, DE	1	990	541	97	15	8	1,651
Downingtown, PA	2	994	689	81	27	17	1,808
Lumberton, NJ	3	1,194	480	70	30	16	1,790
Robbinsville, NJ	4	807	202	38	9	4	1,060
Van Hiseville, NJ	5	1,111	487	69	19	8	1,694
South Broad Street, PA	12	1,430	224	11	9	2	1,676

0.08 ppm as do sites to the east and northeast. This suggests the importance of ozone transport within the Northeast Corridor.

3.1.3 Ozone Wind Roses

Ozone wind roses for Sites 1 through 5, shown in Figures 8 through 12, give some information concerning the general source areas of these high concentrations. These depict simultaneously the frequency distribution of ozone concentrations and wind direction. The wind directions associated with high ozone concentrations are easily identified from these figures. Some data are not included in Figures 8 through 10 since coincident wind direction and ozone data were not available. It is not expected that these data would significantly alter the wind direction frequency distribution.

Site 1 is southwest of the Philadelphia urban area. However, at this site ozone concentrations greater than 0.12 ppm generally occurred with winds from the west or west of southwest and concentrations greater than 0.10 ppm generally occurred with winds from the northwest, west or southwest. This indicates that high ozone levels at this site are associated with surface transport from source regions (such as Baltimore or Washington D.C.) other than Philadelphia.

Site 2 is west of the Philadelphia area. During the field study, ozone concentrations greater than 0.12 ppm at this site generally occurred with winds from the east, southeast or south which suggests that the Philadelphia urban plume affects this site. This differs from the case during the summer of 1978 when winds from the southeast were only associated with ozone concentrations lower than 0.08 ppm (Chan et al., 1979). However, winds from the southeast were much less frequent during the summer of 1978 than during the summer of 1979 and, as can be seen from Figure 9, the ozone concentrations with the greatest frequency associated with southeast winds in 1979 were less than 0.08 ppm.

Site 3 is east of the Philadelphia urban area. From Figure 10 we can see that ozone concentrations higher than 0.12 ppm at this site occur with winds ranging from the west to south to east. Only winds from the north or northwest are not associated with high ozone levels at this site.

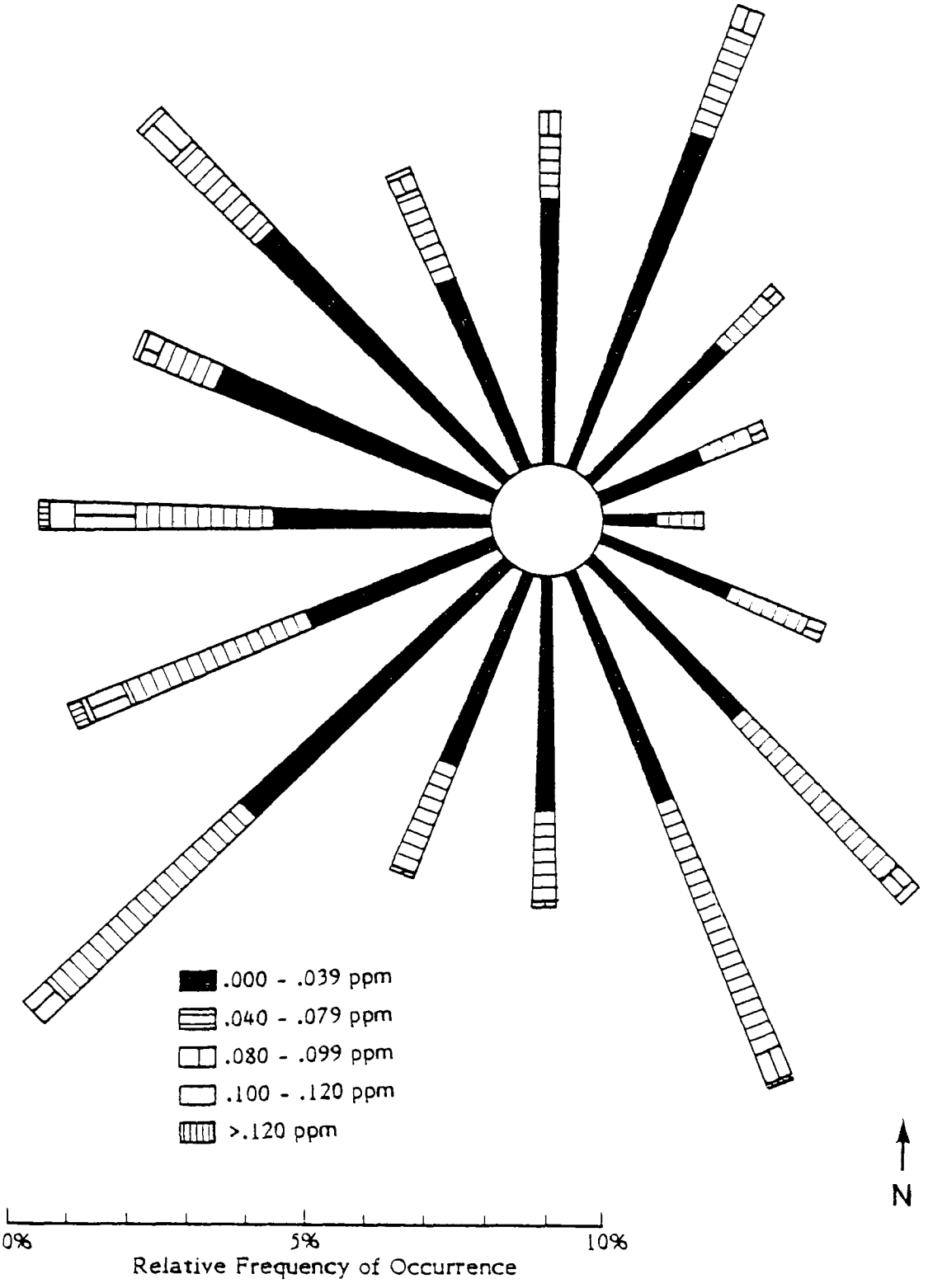


FIGURE 8. Ozone wind rose for Summit Bridge, DE (Site 1).

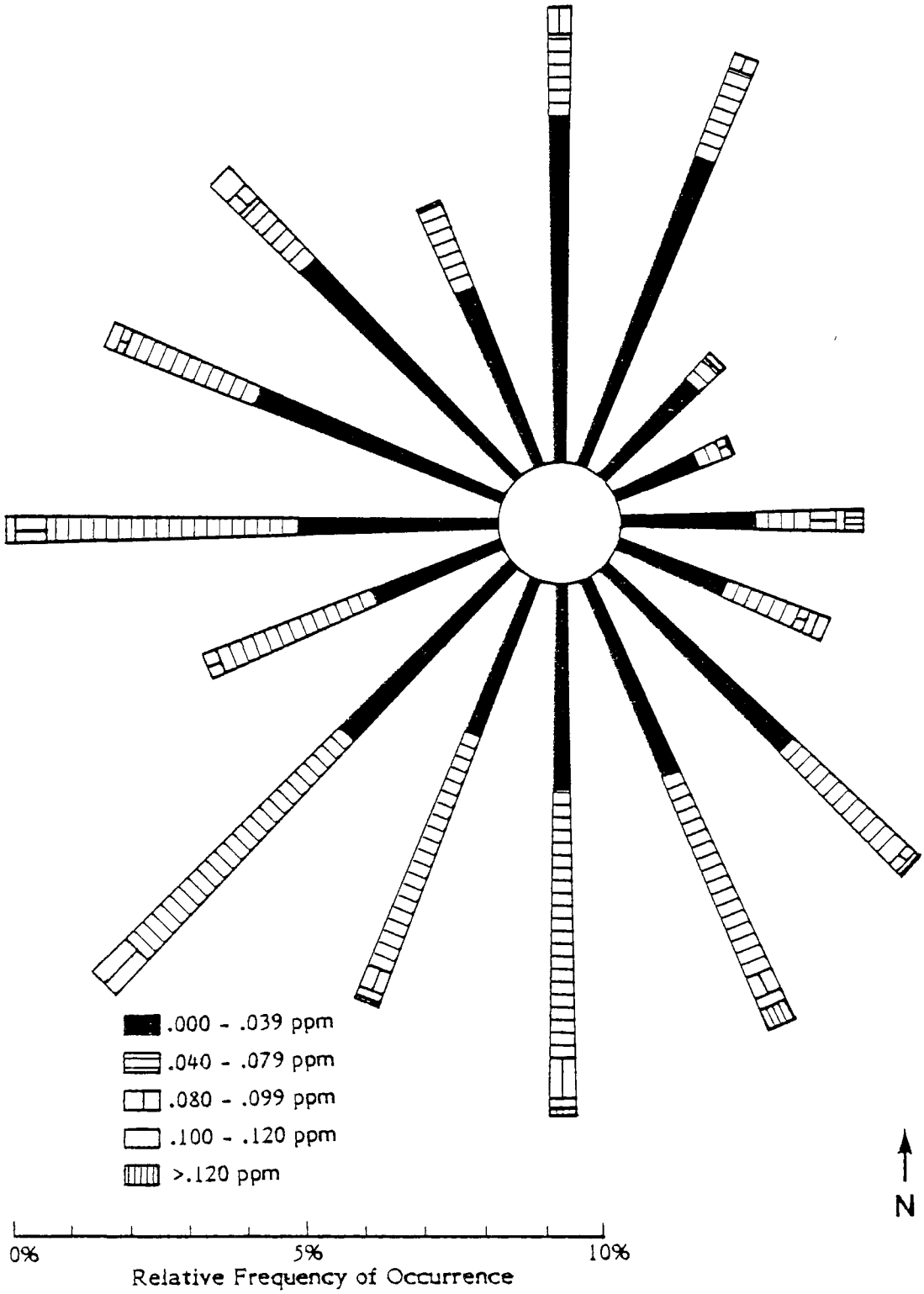


FIGURE 9. Ozone wind rose for Downingtown, PA (Site 2).

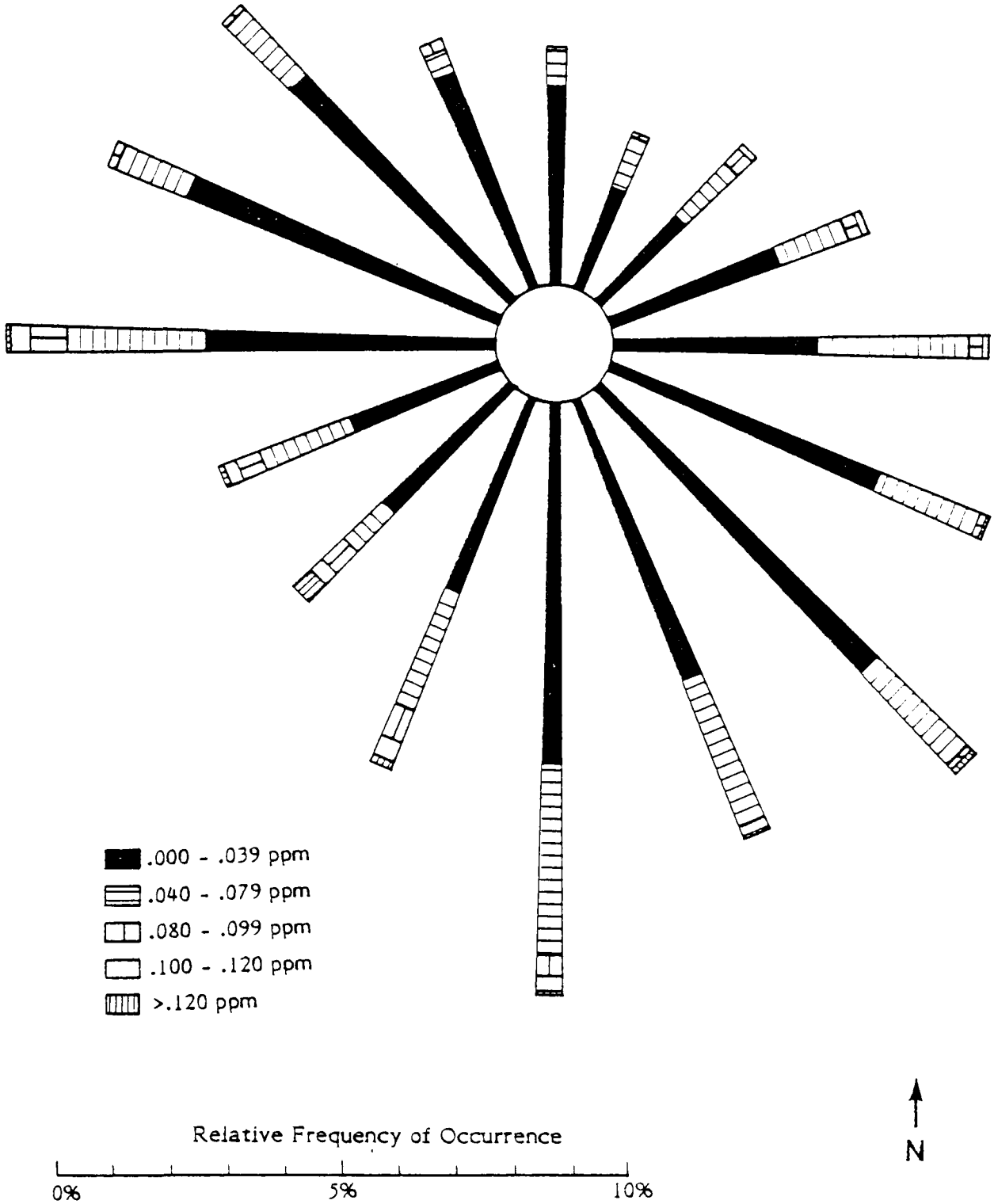


FIGURE 10. Ozone wind rose for Lumberton, NJ (Site 3).

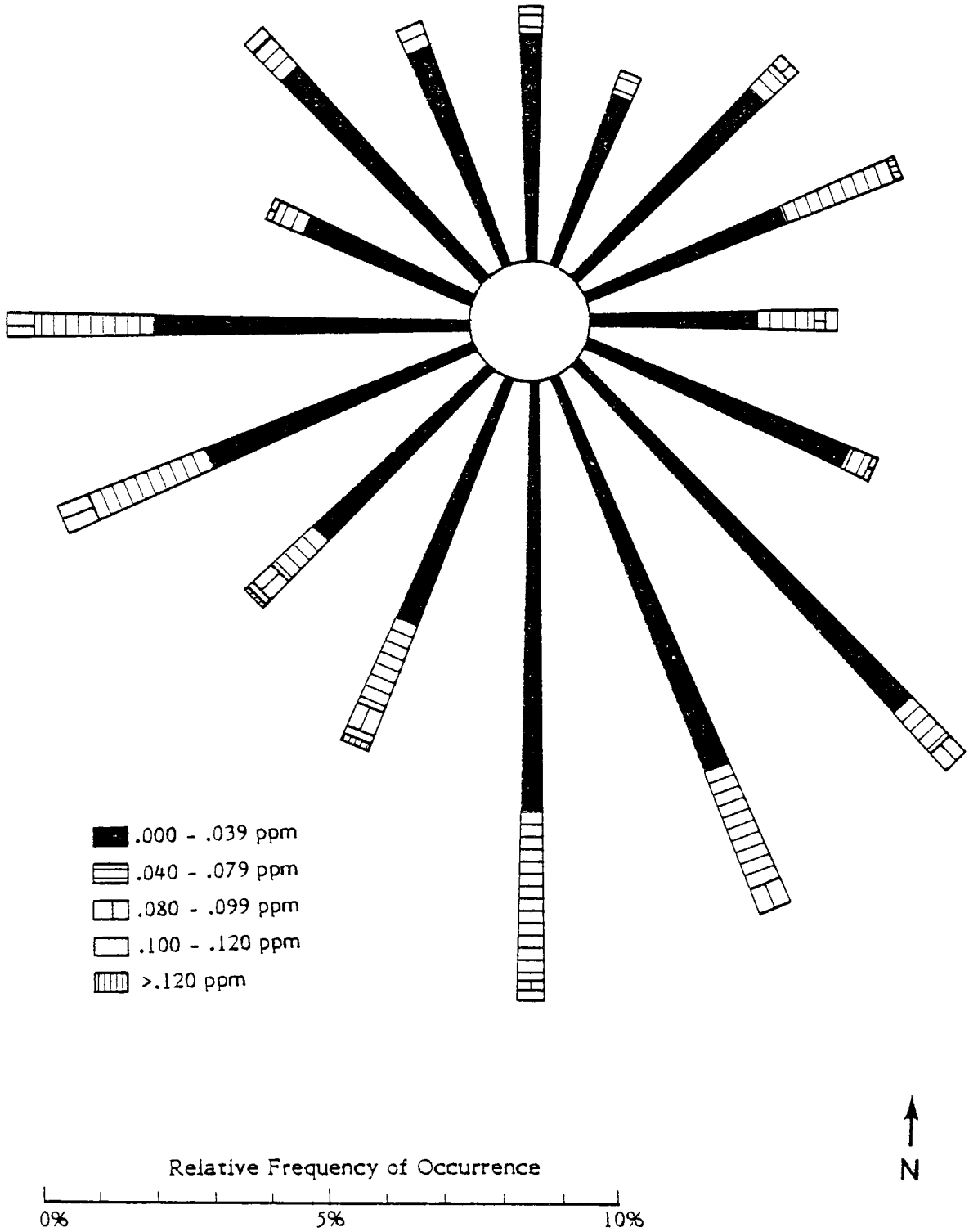


FIGURE 11: Ozone wind rose for Robbinsville, NJ (Site 4).

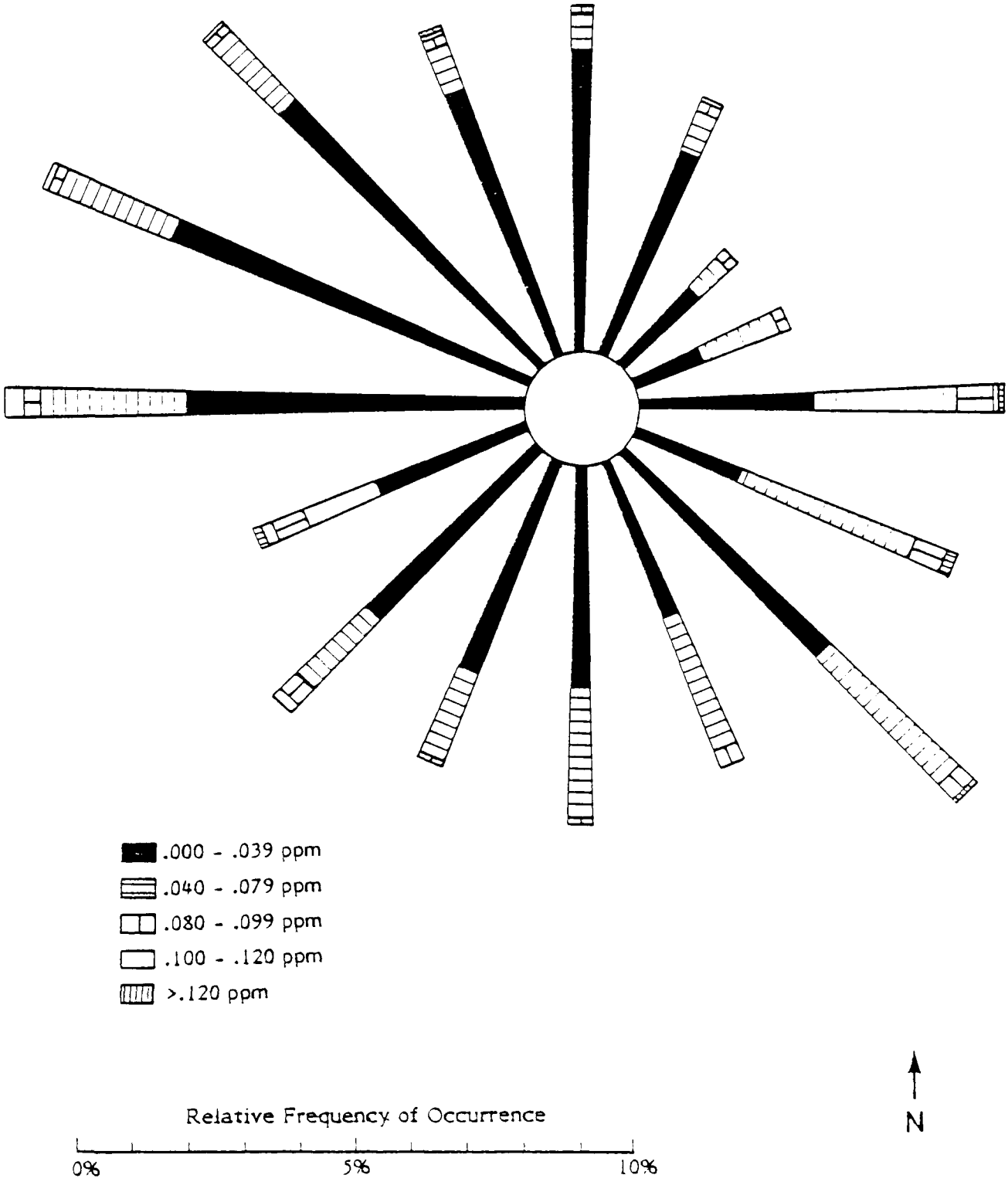


FIGURE 12. Ozone wind rose for Van Hiseville, NJ (Site 5).

Sites 4 and 5, northeast of Philadelphia, record high ozone levels with winds from the southwest indicating the effects of the Philadelphia urban plume. Moreover, as with Site 3, Site 5 also measures high ozone levels with winds from the southeast. This finding is unexpected since flow from this direction is usually associated with high pressure off the coast to the northeast. Sites 4 and 5 also show some ozone levels higher than 0.10 ppm with winds from the northwest, indicating some long-range transport.

3.2 HYDROCARBON SPECIES ANALYSIS

The 148 samples analyzed between mid-July and mid-August by Washington State University (WSU) fall into several different categories.

1. Over half (85) of the samples were taken in the morning either at the Franklin Institute site (Site 13) near center city or at the "industrial site" in south Philadelphia (see Figure 7 for sampling locations). Of these, half were taken at each site between 0500 and 0600 EST and the other half between 0700 and 0800 EST. This forms the most uniform data set in the study and includes data from six of the ten case study days to be discussed in Chapter 4.

2. Five afternoon samples were taken at the industrial site between 1300 and 1400 EST.

3. A set of 35 samples was taken by EPA/Las Vegas at various locations. Fifteen of these were taken on five of the case study days.

4. A group of fourteen roving samples was taken at various points in the Philadelphia area.

5. Another set of nine samples was taken for intercomparison purposes at various locations.

3.2.1 Data Summary

Most of the samples were taken between July 17 and August 15, 1979, during a consistent sampling program at the Franklin Institute (Site 13) and at a site in south

Philadelphia near the industrial area along the Delaware River. Franklin Institute is within a few blocks of the City Hall which is in the center of Philadelphia. Integrated samples were taken from 0500 to 0600 EST and from 0700 to 0800 EST at each site for about 20 days during the heart of the study. The distribution by types (%) along with the total identified (known) species and the sum, including unidentified peaks for this block of data, are given in Tables 15 and 16. The averages for each of the two sites and two collection times are also given. The most striking feature of these averages is that there is so little difference between the four sets of data. Paraffins make up about two-thirds of the total, aromatics about one fourth, olefins (omitting ethylene) about 6% and acetylene 2%. This distribution is valid at both sites at both hours even though individual samples depart from this average significantly.

It is also noteworthy that the average total NMHC at the Franklin Institute site (Site 13) for the 0700 to 0800 EST samples was slightly higher than for any of the other three sets of data. This provides no support for the idea that industrial emissions are the major source of hydrocarbon pollution in the Philadelphia area. If industrial emissions were the major source of hydrocarbons, the industrial site would be expected to show the higher hydrocarbon concentrations. The higher value at 0700 to 0900 EST at Franklin Institute may reasonably be ascribed to the higher traffic levels at this location at the later hours.

Some departures from the average type distribution can be explained by reviewing the species distribution. Before citing examples of this, it is well to note that these anomalies normally affect only individual samples, not samples taken at different sites on the same day or at different times at the same day. The early Franklin Institute sample of July 20, 1979, showed high paraffins and low aromatics, while the sample taken later at Franklin Institute and the early sample at the industrial site showed just the reverse. Review of the species data reveals very high concentrations of butane and pentanes, suggesting that this sample contained hydrocarbons from a nearby gasoline vapor source. This sample also contained large concentrations of light olefins, especially propene, which are more difficult to explain. On July 24, 1979, all four samples contained the highest levels of NMHC in the entire set. The industrial site samples were nearly average in type composition while the Franklin Institute samples were both high in paraffins and low in aromatics. Again, referral to the species distribution reveals high levels of light

Table 15. SPECIES BREAKDOWN OF FRANKLIN INSTITUTE SAMPLES.

Date	Acetylene (percent)	Olefin (percent)	Aromatic (percent)	Paraffin (percent)	Known (ppbC)	Sum (ppbC)	Acetylene/ n-Butane Ratio
0500 to 0600 EST							
July 17	3	10	28	60	478	670	0.277
July 18	3	2	27	69	305	411	0.227
July 19*+	2	2	16	71	460	575	0.356
July 20	1	7	12	80	1095	1211	0.035
July 23*	2	5	31	63	307	377	0.173
July 24	—	3	7	90	1612	1740	—
July 25*	1	10	17	71	719	815	0.070
July 26	1	5	11	84	892	980	0.023
July 27	2	2	32	65	232	271	0.250
July 30	3	2	30	65	232	271	0.341
July 31	3	2	35	59	392	483	0.391
August 1	1	7	17	75	672	770	0.045
August 2	4	4	23	69	218	266	—
August 3	—	3	24	72	351	407	0.206
August 4*+	—	3	45	52	562	899	—
August 5*+	2	5	26	66	194	205	0.258
August 6*+	1	3	29	67	197	227	0.118
August 7*+	—	—	—	—	—	—	—
August 8	—	—	—	—	—	—	—
August 9	—	—	—	—	—	—	—
August 10*+	1	6	14	80	786	930	0.037
August 14*	—	4	34	63	751	1023	—
August 15*	2	4	40	54	141	284	0.250
Average/ Standard Deviation	2/1	4.4/2.5	25.4/10	68.8/9.6		638/407	
0700 to 0800 EST							
July 17	2	6	20	72	871	1051	0.114
July 18	5	9	29	57	475	611	0.511
July 19*+	3	6	30	61	623	756	0.408
July 20	3	5	30	51	692	831	0.321
July 23*	2	7	23	67	774	975	0.180
July 24	1	6	14	80	1144	1337	0.083
July 25*	1	6	19	74	768	885	0.083
July 26	2	6	19	72	709	818	0.148
July 27	3	5	26	65	356	405	0.390
July 30	1	3	30	64	514	622	0.381
August 1	1	5	15	79	1047	1206	0.063
August 2	2	6	25	67	413	546	0.169
August 3	3	5	24	68	829	1160	0.298
August 4*+	2	5	26	68	794	996	0.257
August 5*+	2	2	29	67	209	246	0.257
August 6*+	—	9	25	67	532	614	—
August 7*+	3	6	32	60	737	949	0.242
August 8	—	—	—	—	—	—	—
August 9	—	—	—	—	—	—	—
August 10*+	1	5	16	77	660	777	0.111
August 14*	1	6	27	66	111	1409	0.146
August 15*	3	7	31	59	312	476	0.283
Average/ Standard Deviation	2.2/1	5.7/1.6	24.6/5.5	67.0/7		832/303	

*Helicopter data available
+Case study day

Table 16. SPECIES BREAKDOWN OF INDUSTRIAL SITE SAMPLES.

Date	Acetylene (percent)	Olefin (percent)	Aromatic (percent)	Paraffin (percent)	Known (ppbC)	Sum (ppbC)	Acetylene/ n-Butane Ratio
0500 to 0600 EST							
July 17	3	5	13	79	1034	1511	0.277
July 18	2	6	25	68	434	520	0.156
July 19*+	2	5	32	60	376	448	0.367
July 20	2	4	34	61	480	575	0.281
July 23*	3	9	27	61	392	575	0.268
July 24	0	9	20	71	1419	1700	0.012
July 25*	1	7	25	66	350	493	0.060
July 26	0	8	36	55	860	1130	0.100
July 27	—	—	—	—	—	—	—
July 30	2	2	35	60	288	361	0.326
July 31	2	2	35	60	288	361	0.326
August 1	2	8	18	72	285	345	0.079
August 2	2	2	31	65	189	226	0.146
August 3	2	5	25	69	457	539	0.226
August 4*+	2	6	19	73	282	307	0.141
August 5*+	2	3	27	68	255	290	0.207
August 6*+	3	7	21	71	467	550	0.356
August 7*+	2	4	27	66	273	272	0.113
August 8	1	5	10	84	817	878	0.038
August 9	2	5	31	61	336	418	0.228
August 10*+	0	3	49	48	663	744	0.075
August 14*	1	18	12	69	340	367	0.058
August 15*	3	5	20	73	489	588	0.236
Average/ Standard Deviation	1.9/1	6/3.4	26/9	66/8		603/387	
0700 to 0800 EST							
July 17	3	4	24	69	561	809	0.240
July 18	4	9	24	63	406	558	0.523
July 19*+	3	5	37	56	511	630	0.479
July 20	—	—	—	—	—	—	—
July 23*	1	7	20	73	786	1048	0.073
July 24	1	8	21	69	831	1047	0.131
July 25*	0	4	15	81	824	988	0.030
July 26	1	10	31	58	408	572	0.138
July 27	3	4	50	43	476	666	0.432
July 30	3	5	32	59	330	385	0.389
August 1	1	0	14	75	848	975	0.067
August 2	3	5	28	65	217	278	0.010
August 3	2	5	26	66	568	700	0.195
August 4*+	2	15	16	67	436	532	0.134
August 5*	5	2	30	63	230	255	0.412
August 6*+	4	8	23	65	588	691	0.383
August 7*+	2	5	27	66	330	399	0.127
August 8	2	6	15	67	481	507	0.155
August 9	3	7	24	66	387	452	0.278
August 10*+	—	9	25	66	257	306	—
August 14*	1	7	14	78	375	419	0.102
August 15*	4	4	21	72	302	316	0.377
Average/ Standard Deviation	2.5/1	6.6/2.9	24.9/8.5	65.8/8		592/251	

*Helicopter data available
+Case study day

paraffins. So gasoline vapor is suggested, although the propane is also quite high in both Franklin Institute samples. The industrial site samples on July 24, 1979, were unusually high in olefins, even higher carbon number olefins. The two 2-hexenes totaled 39 ppbC in the early sample. This source signature is not recognizable. One-hexene was high also on August 10, 1979, at the industrial site in the later sample, but benzene was unusually high in the early sample that day (185 ppbC).

The type distribution, indeed the individual species distributions, are strongly suggestive of gasoline composition. It would be very useful to know the species composition of the gasoline sold in the Philadelphia area. Even more valuable would be information on the brand-to-brand variations in fuel composition. Lacking this specific information, comparison can be made only with the rather meager open literature on gasoline composition. One of the most complete analyses was reported by the Shell Oil Company, Wood River Laboratory (Sanders, 1968; Maynard, 1969). Two fuels were analyzed with no claim to representativeness. They each contained about 60% paraffin, 30% aromatics, and the balance olefin. This is consistent with the type distribution in the Philadelphia study. The detailed breakdown by species also shows similarities with the fuel analysis.

It is evident from this data set that, while the species distributions are similar in different areas and at different times, some samples show excesses of small groups of hydrocarbons. With more information on signatures it might be possible to identify the sources of these hydrocarbons.

3.2.2 Acetylene/n-Butane Ratios

Acetylene is of interest in studies of this kind, not because it is toxic or photoreactive, but because it is almost exclusively derived from automobile exhaust. It is not present in gasoline (or any other motor fuel) but is formed in the engine. Since it is one of the least reactive of atmospheric hydrocarbons, it serves as a good tracer for engine exhaust.

Normal butane (n-butane) is also of fairly low reactivity but it enters the atmosphere from several sources: automobile exhaust, gasoline vapor, vaporized gasoline,

as well as industrial sources. The ratio of these two hydrocarbons then should give a measure of the contribution of automobile exhaust to any given sample. If each ambient sample represents exhaust emissions from a large number of vehicles, and if the n-butane is all due to exhaust, this ratio should be approximately constant and equal to that found in average automobile exhaust. Mayrsohn et al. (1977) used a ratio of about 2 acetylene to 1 n-butane for their source reconciliation studies. Since air samples showed lower values, substantial contributions of n-butane from other sources were indicated. In fact, Mayrsohn et al. attributed roughly one-half the total hydrocarbon to automobile exhaust based on their source reconciliation procedure.

The acetylene/n-butane ratios from the present study are tabulated in Tables 15 and 16. Most values are much lower than the 2:1 ratio used by Mayrsohn et al. for automobile exhaust. They are even lower than the approximate 1:1 ratio reported by Stephens (1973) for air samples in Riverside, California. The ratios given in Tables 15 and 16 are also quite variable, which suggests a nonuniform air mass with varying contributions of other sources compared to automobile exhaust. No distinctive pattern in these variations could be discerned. If local sources of gasoline vapor are responsible for much of the n-butane, a recognizable pattern is not to be expected.

3.2.3 Hydrocarbon Data Validity

The analytical group at Washington State University presented some data on precision, providing in their report (Westberg and Sweany, 1980) comparisons with two other laboratories on one calibration sample which contained one hydrocarbon (C_4H_{10}; isomer not stated). Agreement was fair. They also reported an exchange sample study done with an EPA field laboratory. Complete species breakdown is not given but the totals and the breakdown by types were in fair agreement.

Another possible comparison is between the sum of individual hydrocarbons indicated by the gas chromatograms and the total measured by an NMHC (non-methane hydrocarbon) analyzer. Data from such an analyzer (Beckman Instruments Model 6800) are available, but the NMHC data are given to only one significant figure so this method hardly provides a useful test. This instrument measures methane and total hydrocarbons separately -- indeed, on separate samples -- and then subtracts to determine NMHC.

Since methane is not small compared to the total hydrocarbon, it is necessary to subtract a large number from a slightly larger number. This magnifies the error.

Hydrocarbon levels in ambient air can be quite variable, so it is necessary to take simultaneous samples if agreement is to be expected. Two such replications were included in the data base; one pair taken in Lancaster, Pennsylvania on August 14, 1979 (time not stated), and a second pair taken in Downingtown, Pennsylvania, at 0700 to 0800 EST on August 17, 1979. The data are shown in Table 17. It should be noted that these two cities are many miles from Philadelphia, yet hydrocarbon concentrations were comparable to those in urban air. Automobile exhaust is probably the main source in these cities. Table 17 follows the format used for the main data table for the Franklin Institute and industrial site samples. The type distribution gives the percent acetylenes, olefins, aromatics, and paraffins while the last two columns give total of identified compounds in ppbC and the sum which includes unidentified compounds. Ethylene is omitted from these olefin totals for two reasons: to keep the data presentation uniform, and because the quite high values are suspect although some sort of local source cannot be ruled out. The two Lancaster samples each showed about 600 ppbC of hydrocarbon with quite similar type distributions. Even though the two Lancaster samples appear very similar, some large differences between individual hydrocarbons are apparent. For example, in Sample 2 the benzene and toluene were about 40% smaller than in Sample 1 but some of the C_9 aromatics were larger. The type distributions are reasonably consistent even though the total hydrocarbon differed by a factor of two between the two Downingtown samples. The second Downingtown sample contained only half as much hydrocarbon as the first: concentrations were lower across the board so the type distribution remained unchanged. There is no ready explanation for the disagreement between these two samples taken at the same time and place. Successive samples taken the same morning were similar in composition except for much lower ethylene concentrations (4 to 6 ppbC instead of 50 to 75 ppbC).

3.2.4 Limitations of Analytical Scheme

The present analytical scheme had some limitations which should be recognized.

Table 17. DISTRIBUTION (%) OF HYDROCARBON SPECIES IN SIMULTANEOUS SAMPLE PAIRS, TAKEN AT LANCASTER AND DOWNINGTOWN, PENNSYLVANIA, RESPECTIVELY.

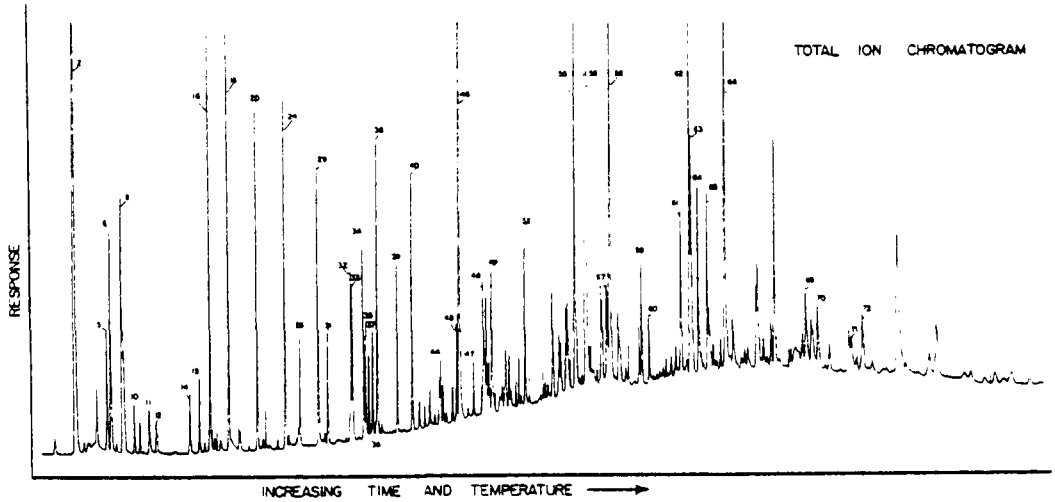
Sample Number	Type Distribution (%)				Total (ppbC)	
	Acetylene	Olefin	Aromatic	Paraffin	Identified Compounds	Including Unidentified Compounds
Lancaster, Pennsylvania (time not stated) August 14, 1979						
1	5	11	23	61	487	592
2	5	8	25	62	447	552
Downingtown, Pennsylvania (0700-0800 EST) August 17, 1979						
1	3	3	32	61	169	205
2	2	2	29	66	84	94

1. Data are limited to hydrocarbons, although oxygenates must be present, some from atmospheric reactions and some from sources.

2. The ethylene values are all suspect. The operators recognized that many samples taken near monitoring stations were contaminated by the effluent from chemiluminescent ozone analyzers. Other samples, not subject to this fault, showed such high ethylene values that they are hardly believable. The data summaries omitted ethylene from the olefin total for the samples subject to contamination samples but not for others. This introduced a bias into the data reports. If distributions are to be compared it is better to omit ethylene for all samples since it cannot be included for all samples. The data have been recalculated on this basis.

3. Qualitatively, all the hydrocarbons can be attributed to auto exhaust. Figure 13 shows a total ion chromatograph used to identify hydrocarbon species seen in field samples. While the chromatograph is not for a sample from the Philadelphia study, it is characteristic of most of the samples analyzed and includes the hydrocarbon species in the C_5-C_{12} molecular weight range observed in the Philadelphia study. The only species listed in Figure 13 with a prominent industrial use is styrene. While information on production and use of styrene in the Philadelphia area is lacking, it would be most helpful. Butadiene 1, 3, another prominent industrial hydrocarbon, was not measured.

4. Isoprene, 2 methyl butadiene 1, 3, is shown on the sample chromatogram (Figure 13) as a well-separated, although very small, peak. However, it was not included in any of the data reports. This hydrocarbon is important because it is the parent of the entire terpene series. Isoprene itself, along with alpha pinene, beta pinene and a host of other terpenes are emitted by vegetation. As olefinic hydrocarbons they are extremely reactive but this must be balanced against quite low emission rates. Because the actual size of these emissions is not accurately known, the role they play in oxidant enhancement is still controversial. A large family of terpenes, including alpha and beta pinene, have the formula $C_{10}H_{16}$. They would probably appear in the chromatogram interspersed among the C_9 aromatics. They were apparently not identified on the chromatogram.



1. 2 Methyl 1 butene
2. 2 - Methylbutane
3. Halocarbon
4. 1 - Pentene
5. 3 - Methyl 1 butene
6. n Pentene
7. Isoprene
8. Carbon disulfide
9. t - 2 - Pentene
10. c - 2 Pentene
11. 2 - Methyl - 2 butene
12. 2,2 - Dimethylbutane
13. Cyclopentene
14. (Cyclopentane
    4 - Methyl 1 Pentene
15. 2,3 - Dimethylbutane
16. (2 Methylpentane
    t 4 - Methyl - 2 pentene
17. c 4 Methyl 2 - pentene
18. 3 - Methylpentane
19. (2 - Methyl 1 - pentene
    1 Hexene
20. n - Hexane
21. t - 2 - Hexene
22. (2 - Methyl 2 - Pentene
    t - 3 - Methyl - 2 - Pentene
23. c - 2 Hexene
24. Methylcyclopentane
25. c - 3 - Methyl - 2 pentene
26. 2,2,3 Trimethylbutane
27. 1,1,1 Trichloroethane
28. 2,4 Dimethylpentane
29. Benzene
30. 1 - Methylcyclopentene
31. Cyclohexane
32. 2 - Methylhexane
33. 2,3 - Dimethylpentane
34. 3 - Methylhexane
35. Dimethylcyclopentane
36. Dimethylcyclopentane
37. Dimethylcyclopentane
38. 2,2,3, - Trimethylpentane
39. n - Heptane
40. Methylcyclohexane
41. Trimethylcyclopentane
42. Ethylcyclopentane
43. 2,5 - Dimethylhexane
44. 2,4 - Dimethylhexane
45. 2,3,4 - Trimethylpentane
46. Toluene
47. 2,3 - Dimethylhexane
48. 2 - Methylheptane
49. (3 - Ethylhexane
    3 - Methylheptane
50. C - 9 Alkane
51. Dimethylcyclohexane
52. n - Octane
53. Ethylcyclohexane
54. C 9 Alkane
55. Ethylbenzene
56. (p - Xylene
    m - Xylene
57. Styrene
58. o - Xylene
59. n - Nonane
60. i - Propylbenzene
61. n - Propylbenzene
62. 3 Ethyltoluene
63. 2 Ethyltoluene
64. 1 Ethyltoluene
65. 1,3,5 Trimethylbenzene
66. 1,2,4 Trimethylbenzene
67. 1,2,3 Trimethylbenzene
68. Methylstyrene
69. 1,3 Diethylbenzene
70. 1,4 - Diethylbenzene
71. C 10 Substandard benzene
72. C 10 Substandard benzene

FIGURE 13. Total ion chromatograph from ambient air sample (source: Westberg and Sweany, 1980).

5. The nature of hydrocarbon isomerism introduces a potential bias into species summation. Thus, there is only one 6-carbon aromatic hydrocarbon (benzene), and 10 ppbC of this will produce an easily measurable chromatographic peak. There are seven 6-carbon saturates (counting cyclohexane and methyl cyclopentane) each of which produces a separate peak in the chromatogram. There are twenty-two 6-carbon olefins each giving a separate peak in the chromatogram. If 10 ppbC of 6-carbon olefins were distributed equally among twenty-two peaks, each would contribute a little less than one-half ppbC. Many would be unmeasurable among the larger peaks. This problem becomes more acute at lower hydrocarbon loading and severe for larger molecules. This "isomer explosion" not only makes the average concentration at each carbon number very small, but it also complicates the problem the analyst has in identifying peaks. It means that the absence of higher olefins from the analytical list is partly an artifact.

6. The sample chromatogram in Figure 13 tapers off at molecular weights above C_{10}, suggesting that not too many hydrocarbons are being overlooked in this range. It is significant that the chromatograms end at the end of the gasoline range.

4. CASE STUDY DAYS

One of the primary objectives of this study was to recommend days for which data could be used for model application and validation. The case study days were chosen to present a variety of situations in which ozone concentrations in excess of 0.12 ppm were observed. Other factors considered in selecting the case study days included NO_2 concentrations, data availability (including EPA-EMSL helicopter data), and wind speed and wind direction at the surface and aloft during early morning (0400 to 0800 EST), late morning (0800 to 1200 EST) and afternoon (1200 to 1800 EST) hours. AV selected ten case study days, with the concurrence of the EPA Project Officer. These days are: July 12, 13, 16, and 19, and August 4, 5, 6, 7, 10, and 22. August 4 through August 7 represents an episode of high ozone levels.

This section discusses and compares the case study days, particularly with respect to meteorology, trajectories, transport of ozone and precursors into and within the study area, pollutant sources, and concentrations aloft.

Synoptic scale trajectories referred to in the following discussions were provided by the EPA. An atmospheric transport and diffusion model was used to compute the latitude and longitude of an air parcel at several time intervals prior to its reaching Philadelphia. The program computes trajectories by taking average winds in the layers of interest from 0000 GMT (1700 EST) and 1200 GMT (0700 EST) wind soundings and, if available, 0600 GMT (0100 EST) and 1800 GMT (1100 EST) soundings. Each observation was weighted by the inverse of the square of the distance between the parcel and the sounding station.

Mesoscale trajectories were derived using surface wind information from all sites in the study area for which data were available. The interpolation scheme uses weighted averages of the wind components. The weighting factors are inversely proportional to the square of the distance between the air parcel and the wind site. More weight was given to wind observations made directly upwind or downwind of the air parcel than when made removed to one side. This feature is included to reflect the tendency of winds to change more rapidly in cross-streamline directions than in the along-streamline direction.

For each case study day, mesoscale trajectories were constructed for the following selected air parcels: (1) an air parcel near downtown Philadelphia at 0600 EST, (2) a control trajectory approximately 10 miles northwest of downtown Philadelphia at 0600 EST (these were constructed to determine the sensitivity of the starting point on the trajectory path), (3) an air parcel at an upwind site at 0600 EST, and (4) an air parcel ending at the site and time of the maximum ozone concentration measured during the day. Other trajectories were constructed when appropriate.

Rural and urban mixing heights were derived for the case study days for which data were available. Urban mixing heights were computed from radiosondes released at Beukers Laboratories in downtown Philadelphia. Detailed temperature profiles were constructed at 0500, 0900, and 1500 EST for the seven case study days that soundings were made. The three hours mentioned above are the only times that sufficient data were available to construct meaningful profiles. From these profiles the height of the base of the first stable layer (i.e., where the variation of temperature with height is less than the dry adiabatic lapse rate: 1° C per 100 m) was taken to be the height of the urban mixed layer. The height of the mixed layer at hours other than 0500, 0900, and 1500 was taken to be the height at which the temperature profile represented by the dry adiabatic lapse rate (or moist adiabatic lapse rate, when the air was near saturation) intersected the detailed profile measured by the temperature sounding. The surface temperature for the hour of interest and the most recent temperature sounding available (0500, 0900, or 1500) were used for this determination. In order to minimize the errors involved in extrapolating the 0900 sounding to 1300 and 1400 in this way, the mixing height determined for 1500 EST was used as an upper bound for mixing heights of earlier hours.

The heights of the mixed layer for 0500 through 1800 EST are presented in Table 18 for the case study days. On all days but one, the mixing height was zero meters above ground level at 0500 EST, signifying a stable layer started at the surface. By 1500 EST the mixed layer height was usually above 1000 m MSL indicating significant mixing in the lower atmosphere. The mixing heights usually reached a maximum between 1300 and 1600 EST. At that time, surface temperatures usually began to decrease, causing a ground-based inversion to form, thus inhibiting mixing from the ground level. The time at which surface temperatures began to decrease after 1500 is indicated by a zero mixing height in Table 18. A ground-based inversion began to form by 1800 EST on all of the days shown.

Table 18. URBAN MIXING HEIGHTS (m MSL) FOR THE CASE STUDY DAYS AS DETERMINED FROM RADIOSONDE RELEASED FROM DOWNTOWN PHILADELPHIA.

Date	Hour (EST)													
	0500	0600	0700	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800
July 19	0	187	407	407	741	741	851	991	1572	1572	2314	2314	0	0
August 4	0	0	0	0	157	157	505	606	698	698	930	1270	1270	0
August 5	0	0	0	147	388	424	606	606	1072	1072	1072	1287	1287	0
August 6	0	0	0	96	345	591*	591	666	666	666	666	1044	0	0
August 7	0	0	181	250	325	620	972	1332	1332	1332	1332	1439	1439	0
August 10	125	221	291	291	339	503*	503	503	1245	1516	1516	0	0	0
August 22	0	0	171	197	411	900	900	1080	1567	1567	1707	0	0	0

*Radiosonde "surface" temperature used instead of Franklin Institute.

Rural mixing height information was obtained from AV's acoustic sounder at Summit Bridge, DE (Site 1). From these data, the time at which surface ozone concentrations were representative of concentrations aloft was determined in the following way: The surface-based inversion layer usually begins eroding shortly after sunrise. Heat transported upward from the surface acts to lift the inversion above the surface at the same time that it is eroded from below. When the bottom of this elevated inversion layer reaches the height of the top of the original morning ground-based inversion, some of the ozone trapped aloft is transported downward. However, the bulk of the ozone reservoir aloft is not mixed downward until the inversion layer, now elevated, is completely destroyed. After the destruction of the inversion layer, mixing usually proceeds upward to the vertical limit of the acoustic sounder (1000 m) in a matter of minutes. The time at which this thorough mixing within the mixed layer occurs is the time at which surface ozone concentrations are most representative of concentrations aloft. For the case study days, the times at which the mixing height first exceeded 1000 m MSL are given in Table 19. From this table, we can see that, for the case study days, thorough mixing had occurred by 1100 EST and that the average time of the rural mixing heights exceeding 1000 m is 1000 EST.

A comparison of ozone concentrations at several stations before and after the time of uninhibited vertical mixing revealed that concentrations were generally low in the study area before the breakup and became higher afterwards due to mixing of ozone from aloft. This is supported by the observation that on days when the helicopter was flown, the surface ozone concentrations just after the inversion breakup were similar to the concentrations measured aloft by the helicopter. For example, Figure 14 shows an ozone profile taken over Summit Bridge, DE (Site 1) on August 10 at 0535 EST. The surface concentration at this site was 0.026 ppm at 0500 EST. The profile indicates concentrations higher than 0.06 ppm in a layer from about 600 to 900 meters MSL. Surface concentrations at this site increased later as the higher concentrations aloft were mixed down. At 1000 EST -- the first hour when the mixing height was above 1000 meters -- this site recorded a surface concentration of 0.079 ppm.

Information on the locations of the major point sources of volatile organic emissions within the study area was provided by Philadelphia's Air Management Services. The majority of these sources are along or close to the Delaware River, with the largest

Table 19. TIME WHEN RURAL MIXING HEIGHTS FIRST EXCEEDED 1000 m AS DETERMINED BY AV ACOUSTIC SOUNDER AT SUMMIT BRIDGE, DELAWARE (Site 1).

Date	Time (EST)
July 19	1000
August 4	0900
August 5	0900
August 6	0930
August 7	0945
August 10	1100
August 22	0915

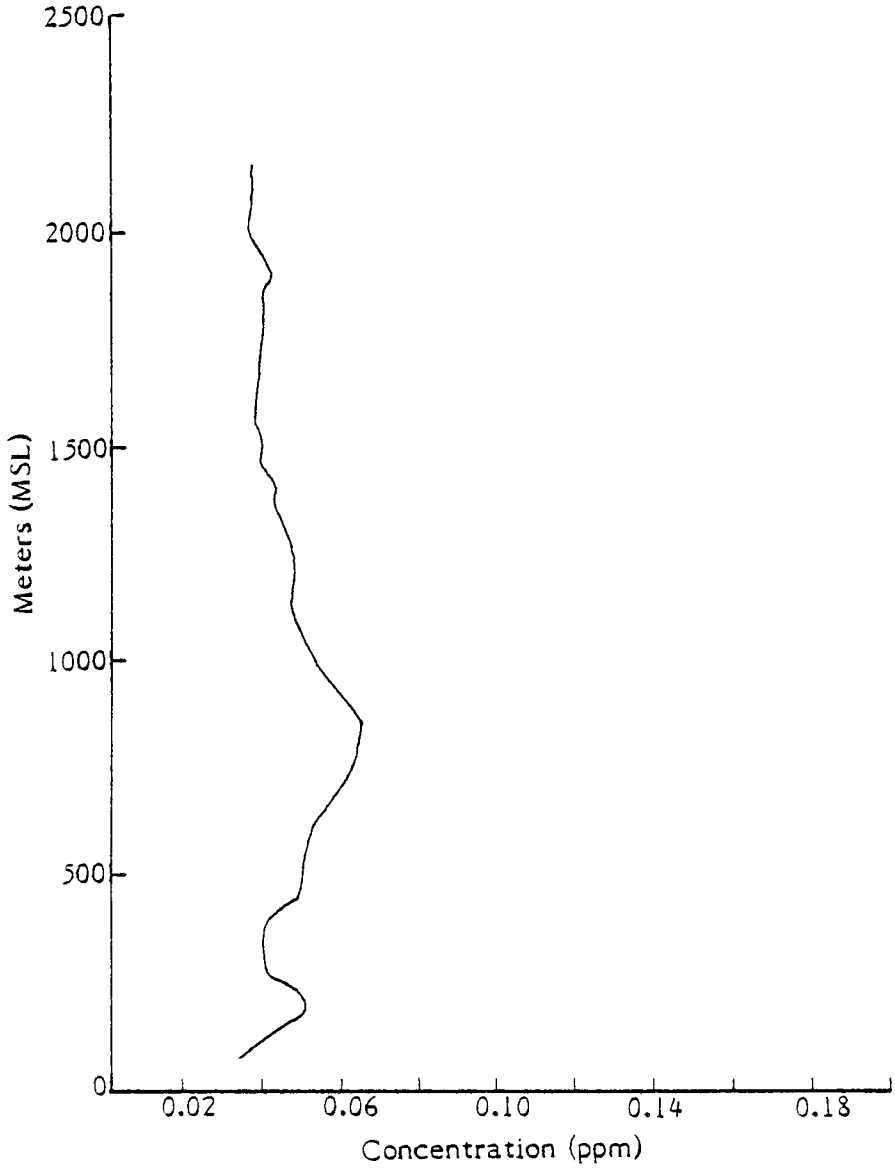


FIGURE 14. Ozone profile over Summit Bridge, DE (Site 1) at 0535 EST on August 10, 1979.

concentration of sources in Philadelphia and Chester. These are also areas with heavy commuter traffic. These sources were considered in the analysis of patterns of high ozone concentrations.

The hydrocarbon species data set from the Franklin Institute/industrial site provides data for six of the ten case study days. Although these days were chosen because of elevated oxidant values, the hydrocarbon species data for these days do not stand out as distinctive with regard to total concentrations or species distributions.

A resultant wind speed and wind direction vector was derived for each station in the study area for each of the time periods (early morning, late morning, and afternoon) on each case study day. From these resultant vectors for each station, then, resultant wind speed and wind direction vectors were approximated for the entire study area. Table 20 gives, along with peak ozone (O_3) and nitrogen dioxide (NO_2) concentrations, the surface resultant wind directions and wind speeds, and average wind speeds and prevailing directions aloft in the 500- to 1500-m layer, for each of these periods on the case study days. It also notes whether or not helicopter data were available for each day.

Table 20. PEAK O_3 AND NO_2 CONCENTRATIONS, WIND DATA, AND HELICOPTER DATA AVAILABILITY FOR CASE STUDY DAYS FOR THE ENTIRE STUDY AREA.

Date	Peak O_3 (ppm)	Peak NO_2 (ppm)	Wind Direction				Wind Speed (m/s)				Availability of Helicopter Data
			Resultant Surface Time (EST)			Prevailing Aloft	Resultant Surface Time (EST)			Average Aloft	
			04-08	08-12	12-18		04-08	08-12	12-18		
July 12	.147	.110	SW	W	NW	--	1.5	1.5	3.0	--	No
July 13	.183	.170	Var	SE	Var	--	1.0	1.3	2.0	--	No
July 16	.151	.069	E	E	SE	NE-E	1.0	1.8	2.5	2.0	No
July 19	.157	.070	N	NE	SE	NE-E	1.5	2.5	1.5	4.0	No
August 4	.144	.090	NW	N	N	N	1.0	2.0	1.0	4.0	Yes
August 5	.135	.090	NW	N	NW	N-W	1.5	2.0	2.0	4.0	Yes
August 6	.136	.070	NW	NW	NW	NW	1.5	2.0	2.0	3.0	Yes
August 7	.129	.080	N	NE	W	W	1.5	1.5	1.5	2.0	Yes
August 10	.170	.080	SW	SW	W	W	2.5	3.5	3.0	8.0	Yes
August 22	.140	.100	SW	Var	SW	--	1.5	2.0	2.0	--	No

4.1 JULY 12, 1979 (THURSDAY)

Important aspects of the July 12 case include the weak influence of the Bermuda high-pressure cell, indications of significant ozone levels aloft, and high surface ozone concentrations upwind of Philadelphia. The highest ozone concentration observed this day occurred downwind of the industrial areas near Wilmington, DE, although high ozone levels also occurred upwind of the urban complex, indicating long-range transport.

On July 12, 1979, the peak ozone concentration in the study area was 0.147 ppm. Two of the twelve operating stations reported ozone levels higher than 0.12 ppm and eight stations reported ozone levels higher than 0.10 ppm. In addition, two stations reported NO_2 levels higher than 0.10 ppm.

4.1.1 Synoptic Meteorology

The surface synoptic situation at 0700 EST is shown in Figure 15. Pressure gradients were weak over the study area and circulation was weakly dominated by the Bermuda high-pressure cell near the Bahamas. A very moist low pressure cell, the remnants of Hurricane Bob, was approximately 700 km to the southwest and moving toward the northeast. Upper level wind flow was westerly and weak.

The synoptic trajectories of air parcels in the 500- to 1000-m and 1500- to 2000-m MSL layers arriving at Philadelphia at 1300 EST are shown in Figure 16. The paths are generally from the west and are entirely over land. The urban area of Pittsburgh is near the path of the 1500- to 2000-m layer parcel.

4.1.2 Mesoscale Meteorology

The mesoscale flow was weak and from the southwest during the early morning. Figure 17 shows a streamline analysis depicting the flow across the study area at 0700 EST. At 1100 EST the flow was from the west in the southern part of the study area but primarily from the northwest at sites north of Philadelphia. During the afternoon, at 1500 EST, most sites were reporting winds from the northwest, with wind speeds at six sites greater than 5 m/s. Wind speeds were lighter after 1700 EST and primarily from the west or northwest. No winds aloft data were available.

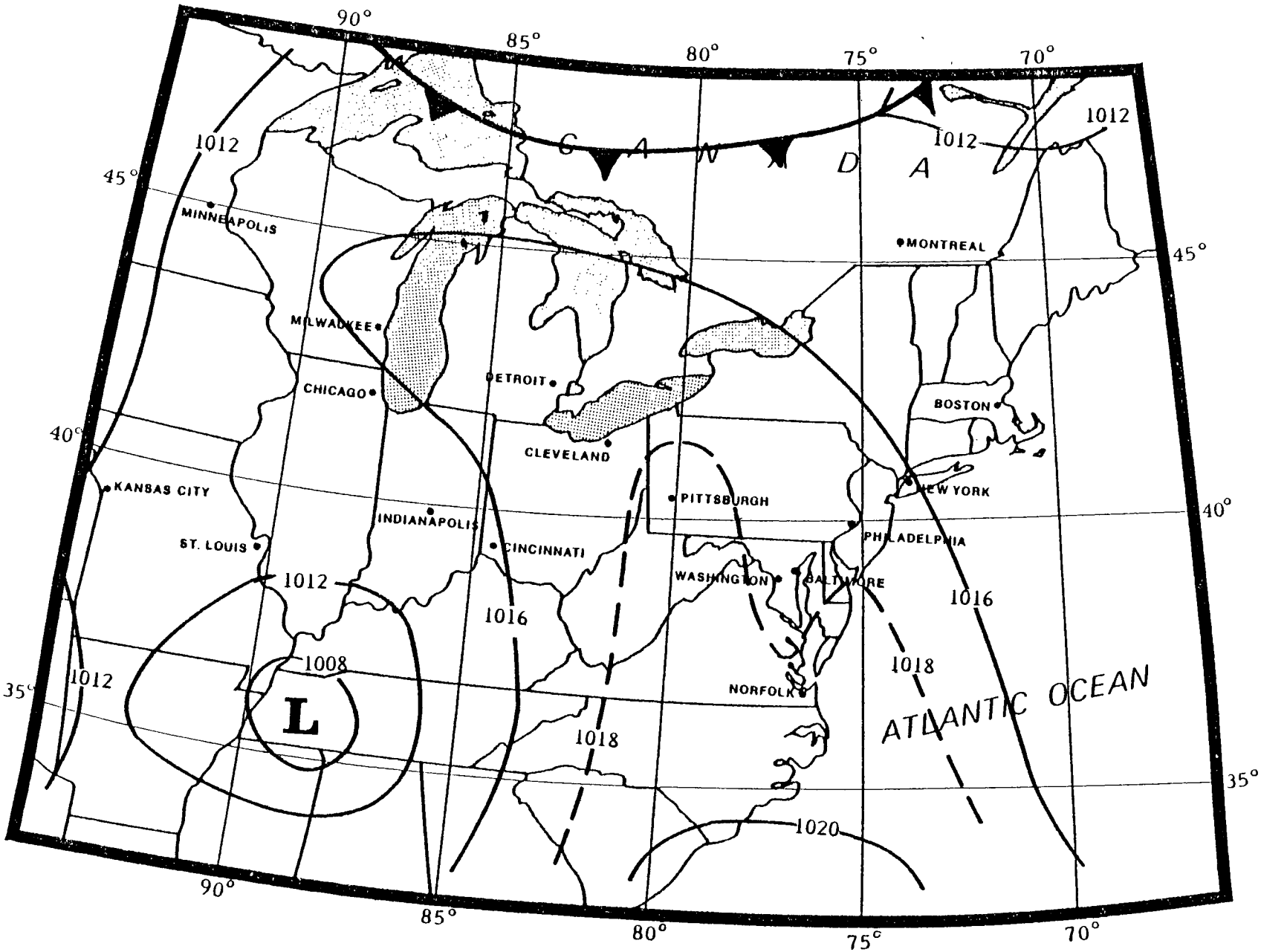


FIGURE 15. Synoptic situation, 0700 EST, July 12, 1979.

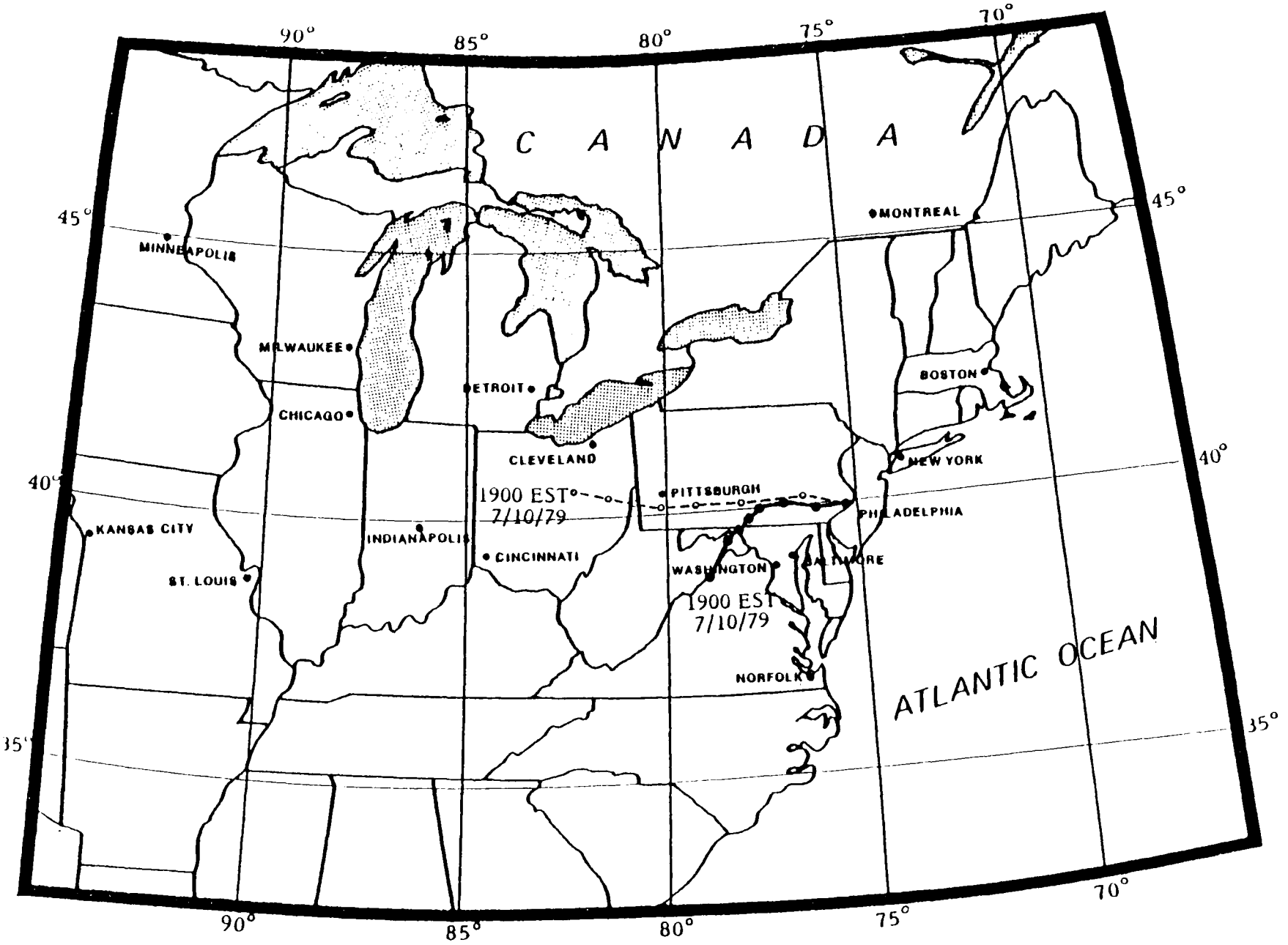


FIGURE 16. Synoptic trajectory of air parcels arriving at Philadelphia at 1300 EST, July 12, 1979. Solid line indicates parcel in the 500 to 1000-meter layer; dashed line is for a parcel in the 1500 to 2000-meter layer. Intervals are six hours.

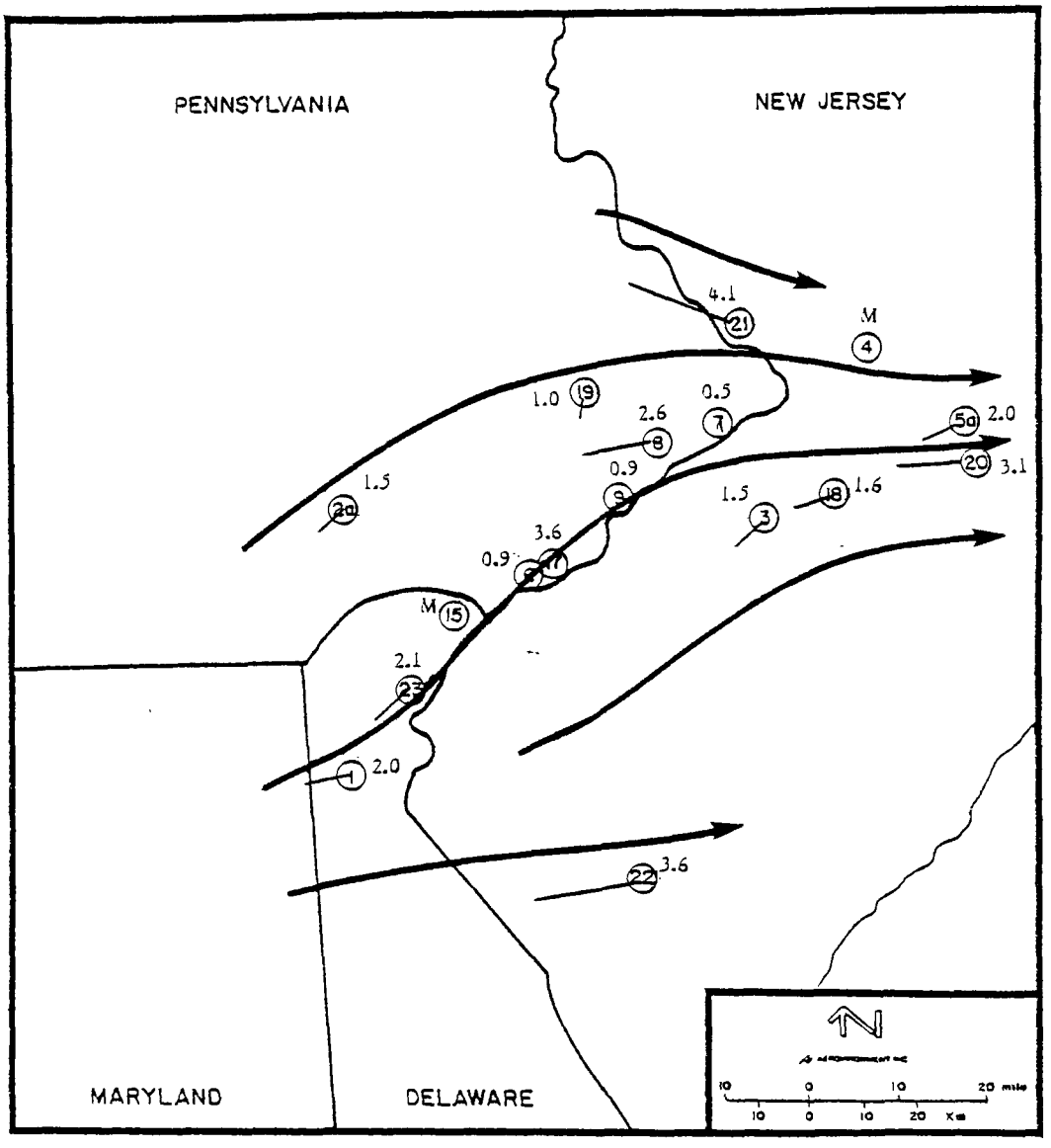


FIGURE 17. Streamline analysis depicting surface flow across the study area at 0700 EST on July 12, 1979. The numbers near the sites indicate wind speeds (meters per second).

4.1.3 Precursor Patterns

The highest levels of morning precursors occurred downtown, a pattern followed on all of the case study days; however, concentrations at Lumberton, NJ (Site 3), and Bristol, PA (Site 7), to the east and northeast, respectively, of the Philadelphia urban area, were abnormally high. The 6:00 to 9:00 a.m. LDT averages of NMHC and NO_x, along with the ratio of NMHC to NO_x are given in Table 21 for rural and urban sites. From this table, the downtown levels on July 12 were about average when compared to other case study days. The morning levels at rural sites indicate an interesting pattern. Low concentrations of both pollutants were measured at Summit Bridge, DE (Site 1), and Downingtown, PA (Site 2), which are to the southwest and west, respectively, of the Philadelphia urban area. However, unusually high levels were measured at Lumberton, NJ (Site 3), which is to the east. The 6:00 to 9:00 a.m. LDT average NMHC concentration of 1.0 ppm measured at Lumberton was the highest recorded at this site during the field program; furthermore, concentrations of NO_x at this site increased to 0.080 ppm (0.068 ppm NO_2) by 0900 EST. This pattern of morning precursors is most likely a result of the airflow which was light and either westerly or southwesterly during the nighttime and early morning hours (Figure 17). This implies transport of these pollutants from Philadelphia.

4.1.4 Ozone Patterns

Considering the afternoon flow directions, the areas of highest ozone levels shown in Figure 18, are as expected. The lowest ozone concentrations occurred near downtown Philadelphia, probably due to NO scavenging. The highest concentrations were measured at locations southeast of Philadelphia, with Ancora, NJ (Site 11), recording the maximum value of 0.147 ppm. Concentrations in excess of 0.10 ppm were recorded by 1100 EST at Downingtown, PA (Site 11), and remained above this level at Lumberton and Ancora through 1700 EST.

To determine possible source and impact areas, mesoscale trajectories were constructed for several air parcels of interest and are shown in Figure 19. A backward trajectory was developed for an air parcel ending at Ancora, NJ (Site 11), at 1300 EST, with the highest recorded ozone level of the day, 0.147 ppm. This air parcel followed a

Table 21. 6:00 to 9:00 a.m. LDT (0500-0800 EST) AVERAGES OF NO_x and NMHC (ppm) AND THE RATIO OF NMHC TO NO_x FOR RURAL AND URBAN SITES ON JULY 12.

Site No.	Rural Sites	6:00 to 9:00 a.m. LDT Averages		
		NO_x	NMHC	NMHC/NO_x Ratio
1	Summit Bridge, DE	0.00	0.0	--
2	Downingtown, PA	0.02	0.0	1.5:1
3	Lumberton, NJ	0.04	1.0	25.8:1
5	Van Hiseville, NJ	0.01	--	--
	Urban Sites			
6	Chester, PA	--	1.1	--
7	Bristol, PA	--	1.4	--
8	North Philadelphia Airport, PA	0.05	--	--
10	Camden, NJ	0.12	--	--
12	So. Broad & Spruce Streets, Philadelphia, PA	0.07	0.6	8.1:1
13	Franklin Institute, Philadelphia, PA	0.07	--	--
14	AMS Lab, Philadelphia, PA	0.10	1.0	10.0:1

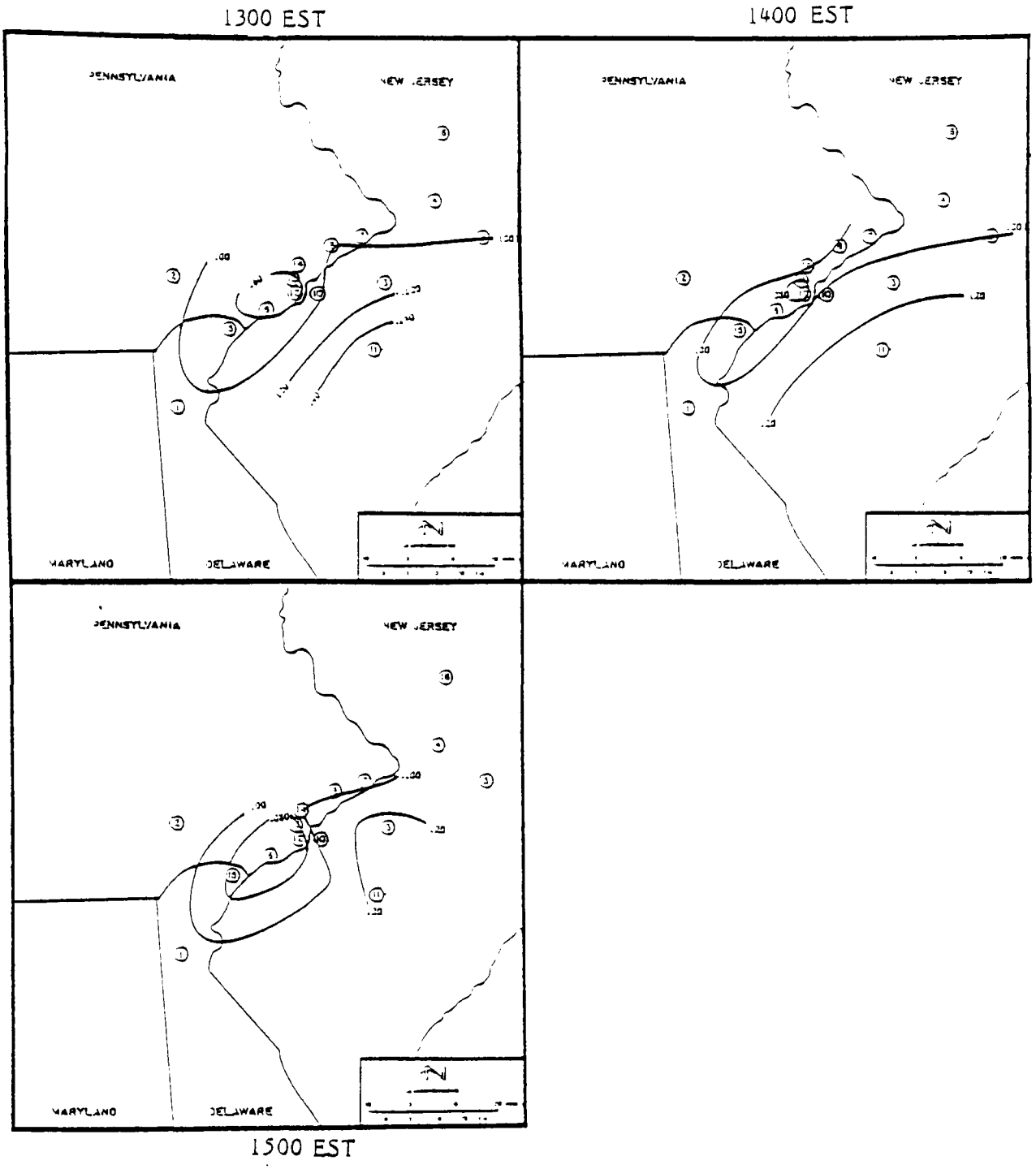


FIGURE 18. Isopleths of ozone at 1300, 1400, and 1500 EST, July 12, 1979.

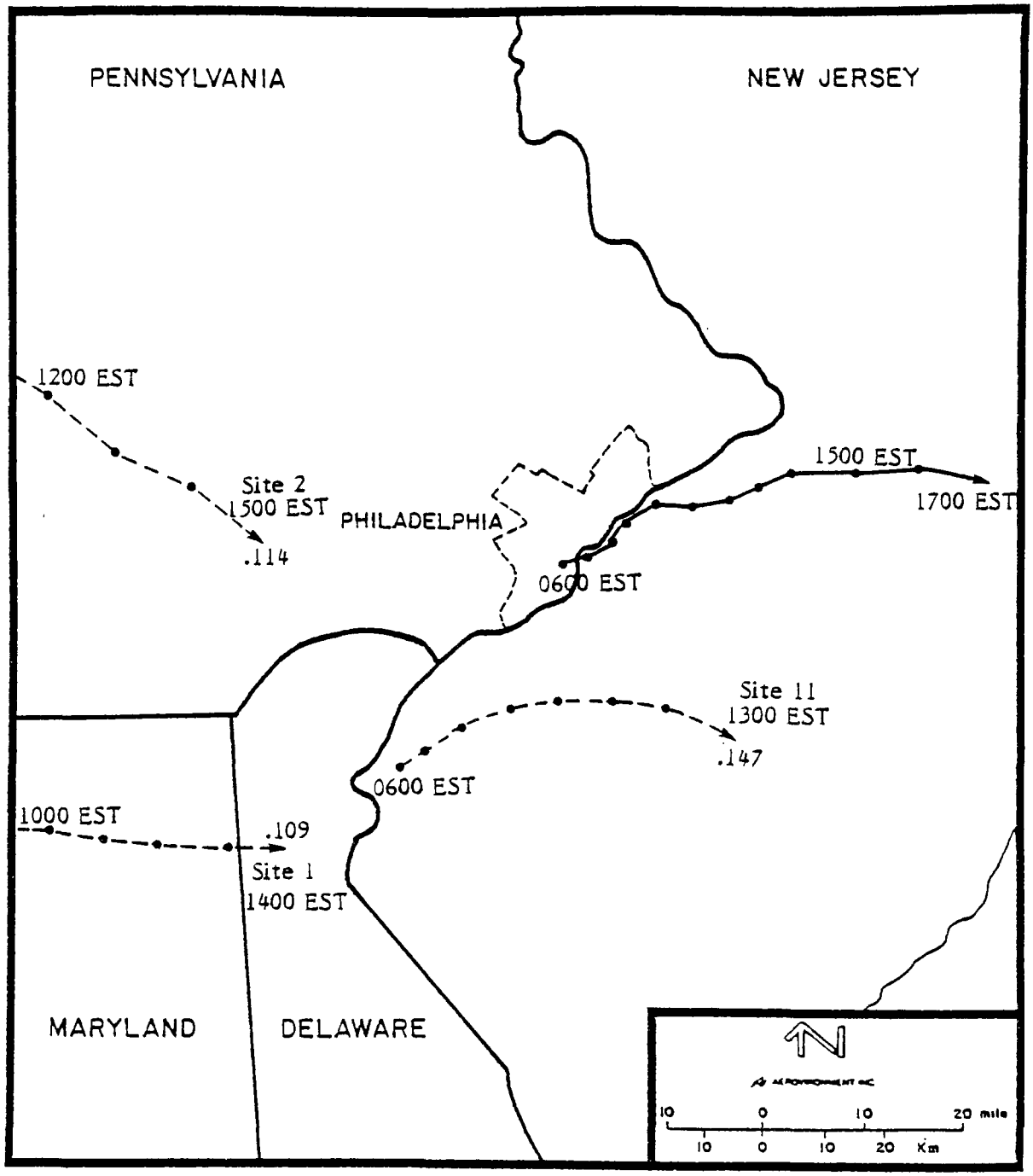


FIGURE 19. Surface trajectory for various air parcels located within the study area on July 12, 1979. Solid line indicates a trajectory beginning at downtown Philadelphia at 0600 EST; dashed lines are for parcels ending at the indicated site and time. Dots show the positions of the parcels at one hour intervals.

trajectory somewhat south of the Philadelphia source area but was close to the highly industrialized area between Philadelphia and Wilmington, Delaware, at 0600 EST.

Mesoscale trajectories are also shown for air parcels with high ozone levels at sites upwind of Philadelphia. Air parcels arriving at Sites 1 and 2 at 1400 EST and 1500 EST, respectively, contained ozone concentrations in excess of 0.10 ppm. These air parcels apparently traversed no major source areas during the five to six hours before reaching the end of the trajectory, indicating the possibility of longer-range transport, particularly in light of the long over-land synoptic trajectory previously shown in Figure 15. The evidence of transport aloft is discussed below.

An air parcel beginning at downtown Philadelphia at 0600 EST was located between Lumberton, NJ (Site 3), and Van Hiseville, NJ (Site 5), at 1500 EST. These stations had high O_3 concentrations of 0.124 and 0.105 ppm, respectively, at this time.

4.1.5 NO_2 Patterns

Peak NO_2 concentrations occurred near the urban area. very late in the evening. Conversion of O_3 into NO_2 by scavenging of NO (relatively plentiful in the urban area) is the probable cause. For example, the Franklin Institute (Site 13) NO_2 peak of 0.090 ppm, which occurred at 2100 EST, followed an ozone concentration trend of 0.070 to 0.020 to 0.000 ppm from 1900 EST to 2100 EST.

4.1.6 Concentrations Aloft

Although no helicopter data were available for July 12, pollutant concentrations at upwind surface stations at the estimated time of morning inversion breakup were reviewed to get some idea of ozone and precursor transport aloft. No acoustic sounder data were available to determine the exact time of inversion breakup, so 1000 EST was assumed, based upon the fact that all but one of the case study days for which acoustic sounder data were available experienced the first hour of uninhibited vertical mixing at 1000 EST.

The diurnal profiles of ozone for the upwind sites at Summit Bridge, DE (Site 1) and Downingtown, PA (Site 2), for July 12 are shown in Figure 20. A rapid morning ozone build-up, characteristic of mixing from aloft, is evident. At 1000 EST, Summit Bridge and Downingtown recorded ozone concentrations of 0.068 ppm and 0.075 ppm, respectively, suggesting significant ozone transport aloft. NO and NMHC concentrations were near zero at this time suggesting no significant precursor transport. Transport of such levels of ozone helps explain the high afternoon ozone concentrations recorded at Sites 1 and 2 (0.109 and 0.114 ppm, respectively) despite their positions predominantly upwind of Philadelphia.

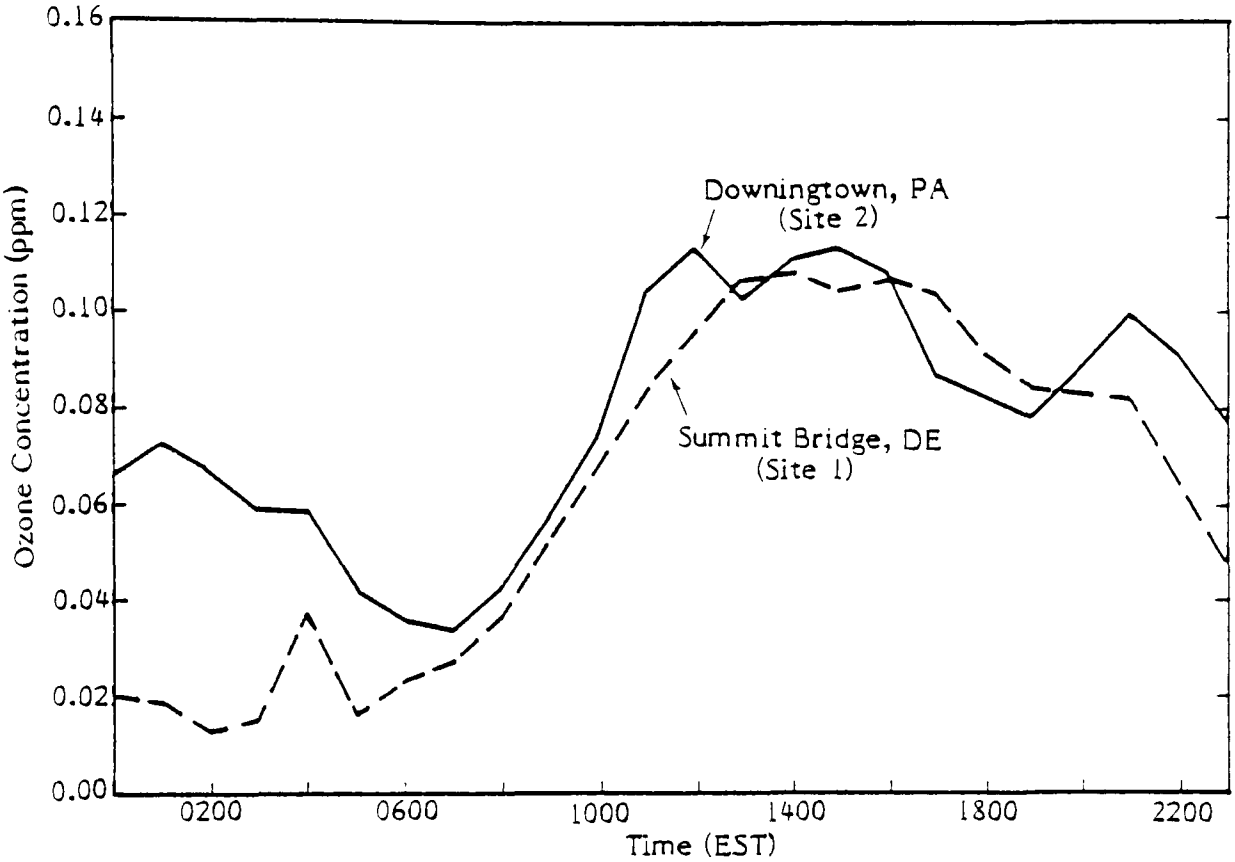


FIGURE 20. Diurnal profiles of ozone at upwind sites on July 12, 1979.

4.2 JULY 13, 1979 (FRIDAY)

Important aspects of the July 13 case include the highest ozone and NO_2 concentrations recorded during the field program, variable flow, and indications of a reservoir of elevated ozone concentrations aloft. Peak concentrations were due to the influence of the urban plume, coupled with near stagnation and ozone mixed down from aloft.

The peak O_3 and NO_2 concentrations recorded during the field program (0.183 and 0.170 ppm, respectively) occurred on July 13. Ten of the thirteen operating stations reported O_3 levels higher than 0.12 ppm and four stations recorded NO_2 concentrations higher than 0.10 ppm. July 13 followed another case study day (July 12) during which high NO_2 and O_3 levels were observed.

4.2.1 Synoptic Meteorology

The surface synoptic pattern is depicted in Figure 21. The Bermuda high-pressure cell, about 500 km east of Florida, exerted a weak influence over the study area. The remnants of Hurricane Bob were 700 km west-southwest of the study area, moving eastward. These two features were reflected in the upper-level flow which was very weak and primarily northwesterly over the study area.

The trajectories of air parcels traveling in the 500- to 1000-m and 1500- to 2000-m layer toward Philadelphia (arrival time 1300 EST) are shown in Figure 22. The paths are very similar to the synoptic trajectories for July 12, which is reasonable, considering the stability of the weather systems. The path brings the 500- to 1000-m parcel near the high emission density area of Washington, D.C.-Baltimore less than 36 hours upstream and provides a continual over-land trajectory with slight anticyclonic curvature.

4.2.2 Mesoscale Meteorology

Early morning wind flow was variable and very weak. Late morning southeasterly wind flows were primarily weak; however, a great deal of variability was evident. In the afternoon, there was a significant spatial variation in the wind speed, with some stations reporting calm winds and some stations reporting winds in excess of 5 m/s; however, most stations reported wind directions with a southerly component.

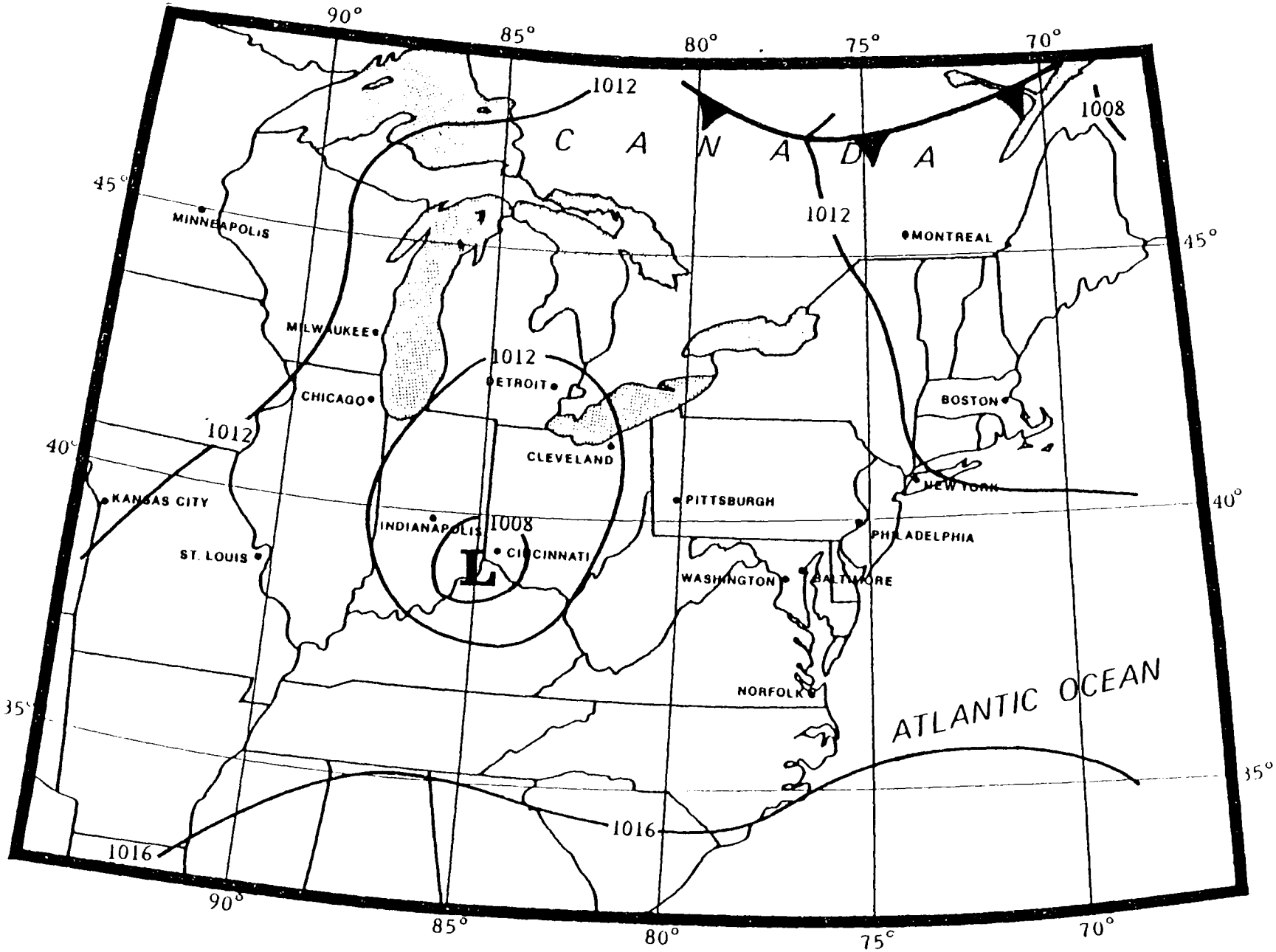


FIGURE 21. Synoptic situation, 0700 EST, July 13, 1979.

FIGURE 22. Synoptic trajectory of air parcels arriving at Philadelphia at 1300 EST, July 13, 1979. Solid line indicates parcel in the 500 to 1000-meter layer; dashed line is for a parcel in the 1500 to 2000-meter layer. Intervals are six hours.

The weak and variable wind flow at the surface, coupled with relatively little movement of air parcels on the synoptic scale (Figure 21) between 0100 and 1300 EST, indicates that July 13 was a case of near stagnation.

4.2.3 Precursor Patterns

Urban precursor levels were elevated while rural areas had characteristically low concentrations. Maximum morning NO and NMHC concentrations at urban stations were in excess of 0.10 ppm and 1.0 ppm, respectively, with 3.5 ppm of NMHC recorded at Chester (Site 6) at 0600 EST. The 6:00 to 9:00 a.m. LDT averages of NMHC and NO_x, along with the ratio of NMHC to NO_x, are given in Table 22 for rural and urban sites. Elevated levels of both pollutants were recorded at the urban sites, whereas levels at outlying rural stations were generally very low. Chester, PA (Site 6), measured the highest average NMHC level (2.6 ppm) and also reported relatively high levels (0.040 to 0.056 ppm) of NO_2 from 6:00 to 9:00 a.m. LDT.

The elevated precursor levels measured at these urban and near-urban sites were above normal and generally above levels observed on other case study days. This, coupled with the near-stagnant weather situation on this day, helps to explain the unusually high ozone concentrations which occurred along the fringe of the urban area.

4.2.4 Ozone Patterns

Isopleths of ozone concentrations at 0900, 1100, 1200, and 1300 EST are shown in Figure 23. By 0900 EST, a concentration of 0.101 ppm was already recorded at Ancora, NJ (Site 11), southeast of Philadelphia, while concentrations were less than 0.04 ppm downtown. After this, highest ozone concentrations were centered near the urban area. At 1100 EST, ozone concentrations in excess of 0.12 ppm were evident at Chester, PA (Site 6), Camden, NJ (Site 10), and Ancora, NJ (Site 11), the first two of which are near urban sites. Thus, high levels were widespread very early, although downtown sites were still low. Downingtown, PA (Site 2) and Lumberton, NJ (Site 3), west and east of Philadelphia, respectively, were recording ozone levels in excess of 0.10 ppm. The following hour (1200 EST), the highest level recorded during the program, 0.183 ppm, occurred at Chester. At 1300 EST,Camden, NJ (Site 10), had the highest ozone

Table 22. 6:00 to 9:00 a.m. LDT (0500-0800 EST) AVERAGES OF NO_x and NMHC (ppm) AND THE RATIO OF NMHC TO NO_x FOR RURAL AND URBAN SITES ON JULY 13.

Site No.	Rural Sites	6:00 to 9:00 a.m. LDT Averages		
		NO_x	NMHC	NMHC/NO_x Ratio
1	Summit Bridge, DE	0.00	0.1	0.0:0
2	Downingtown, PA	0.04	0.2	5.8:1
3	Lumberton, NJ	0.03	0.3	11.0:1
5	Van Hiseville, NJ	0.02	--	--
	Urban Sites			
6	Chester, PA	--	2.6	--
10	Camden, NJ	0.17	--	--
12	So. Broad & Spruce Streets, Philadelphia, PA	0.17	0.9	5.5:1
13	Franklin Institute, Philadelphia, PA	0.15	--	--
14	AMS Lab, Philadelphia, PA	0.12	1.2	10.2:1

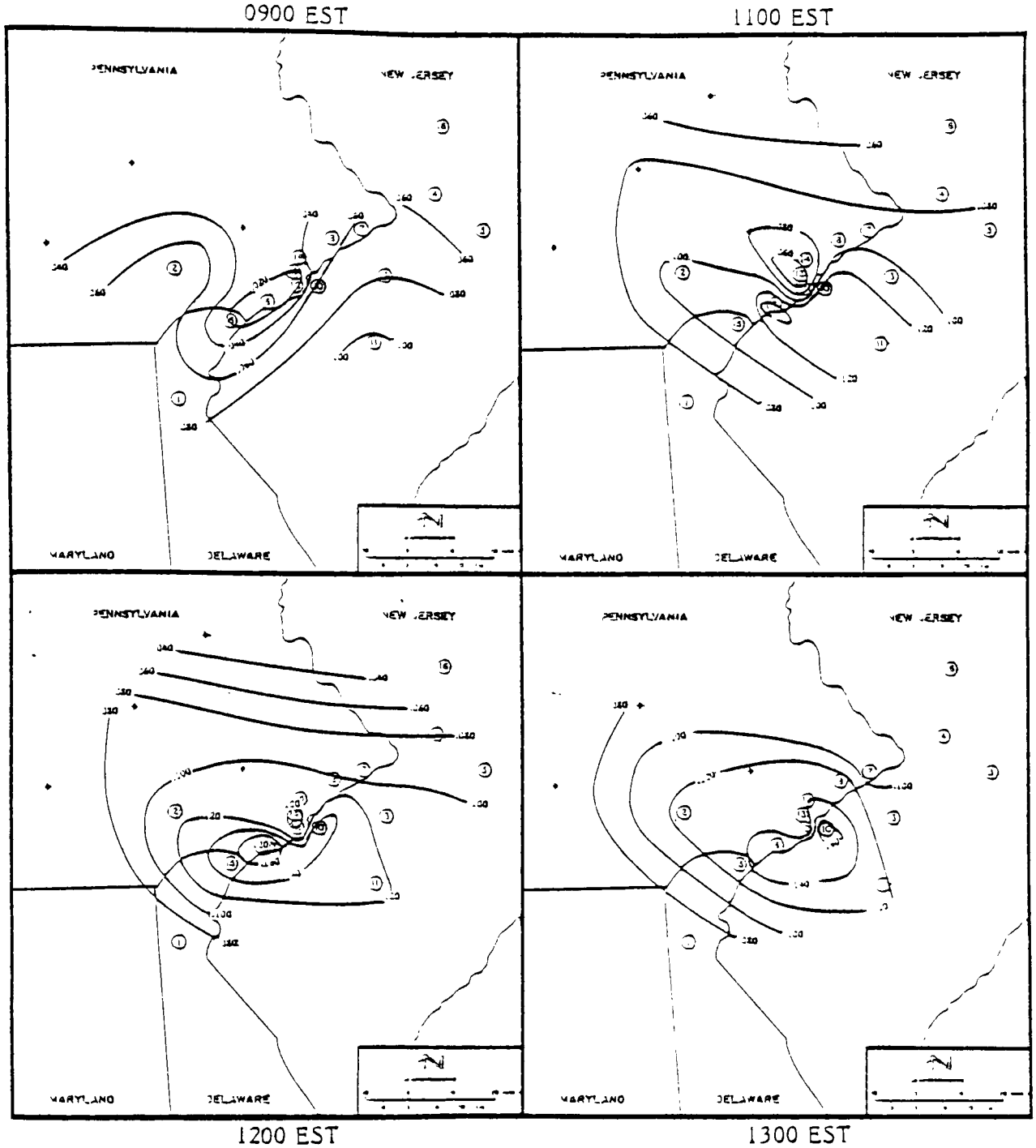


FIGURE 23. Isopleths of ozone at 0900, 1100, 1200, and 1300 EST, July 13, 1979.

concentration (0.161 ppm), but the entire metropolitan area of Philadelphia also had relatively high ozone levels (greater than 0.110 ppm). Moreover, high ozone levels were measured at Sites 2, 3, 8, and 11 as well. Ozone levels persisted in excess of 0.12 ppm until late afternoon at some locations.

Surface mesoscale trajectories were developed to help determine the origin of some of the observed high ozone concentrations. These trajectories are shown in Figure 24. The flow was weak and variable with a tendency towards southerly and southeasterly winds, particularly in the late morning and afternoon.

An air parcel beginning at Philadelphia at 0600 EST was about 20 km east of Downington, PA (Site 2), at 1300 EST. Unfortunately, this is an area for which no data were available; however, this parcel is between Downingtown, PA (Site 2), and the AMS Lab, Philadelphia (Site 14). These two sites reported ozone levels of 0.123 and 0.140 ppm, respectively, at this time, and we might expect even higher levels along the path of the trajectory.

Chester, PA (Site 6), as discussed above, had the highest ozone concentration measured on this day and recorded a value of 0.183 ppm at 1200 EST. A parcel ending at this site and time followed a trajectory from the southeast and started (0600 EST) in an area of expected low precursor concentrations 20 km south-southwest of Philadelphia's central business district.

Air parcels with high ozone levels at 1400 EST at the AMS Lab, Philadelphia (Site 14), and 1500 EST at Lumberton, NJ (Site 3), began in the eastern portion of the study area. In fact, the air parcel ending at the AMS Lab at 1400 EST began very near to Lumberton at 0600 EST. The NMHC and NO_x concentrations at Lumberton at that time were both zero, indicating another high ozone parcel originating in areas of low precursor levels.

A re-examination of the ozone isopleths shown in Figure 23 indicates that the surface mesoscale trajectories do not tell the whole story. The center of high ozone concentrations does not move westward across the study as the mesoscale trajectories imply, but rather shows the spreading out tendency characteristic of a stagnation day. The contribution of ozone transport aloft to this process is discussed below.

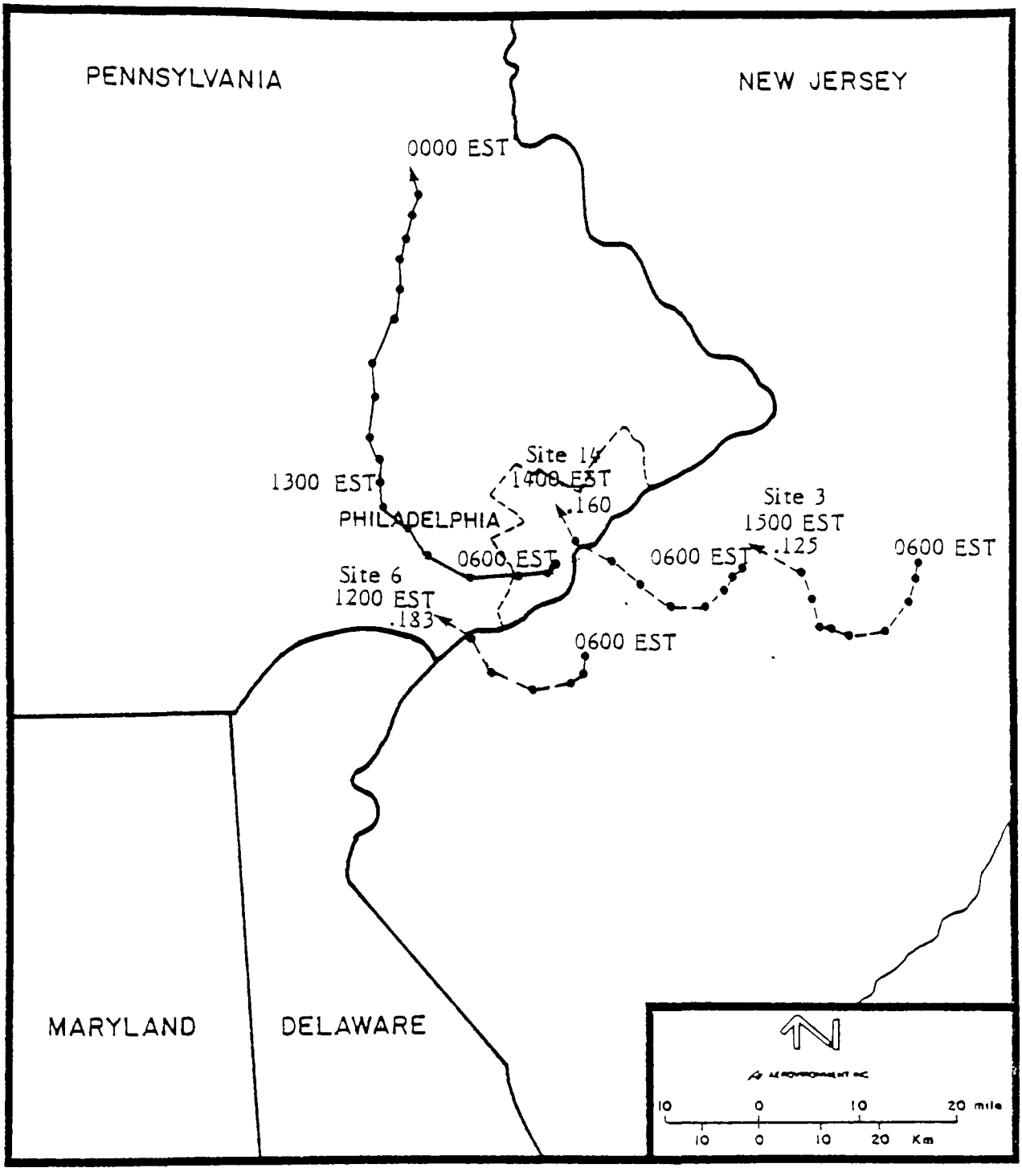


FIGURE 24. Surface trajectory for various air parcels located within the study area on July 13, 1979. Solid line indicates a trajectory beginning at downtown Philadelphia at 0600 EST; dashed lines are for parcels ending at the indicated site and time. Dots show the positions of the parcels at one hour intervals.

A comparison of the mesoscale trajectories with the synoptic trajectories shown in Figure 22 implies some wind shear aloft, since the air parcels approach from different quadrants. However, the variability of the surface winds and the fact that the synoptic trajectories may be based solely upon 0700 EST and 1700 EST winds aloft make this implication speculative.

4.2.5 NO_2 Patterns

NO_2 concentrations were generally higher on this day at all sites than on other case study days. Peak concentrations in excess of 0.10 ppm (including the highest value of the entire program, 0.17 ppm) were recorded at urban and near-urban sites in the late morning. South Broad Street (Site 12) recorded concentrations in excess of 0.10 ppm all day. These concentrations were apparently the result of NO reactions with the very high ozone levels observed even in the urban areas.

4.2.6 Concentrations Aloft

From the above discussion, it is evident that areas both upwind and downwind of Philadelphia experienced high ozone levels. The site which experienced the highest observed levels -- Chester, PA (Site 6) -- was not directly downwind as determined by surface flow. Thus, in light of the high levels observed at the upwind stations at Ancora, NJ (0.141 ppm), and Lumberton, NJ (0.125 ppm), possible explanations are that there was some contribution of long-range transport and/or, since high levels were observed the previous day, there was some carryover or buildup. Unfortunately, no helicopter data are available for that day to assess ozone concentrations aloft prior to inversion breakup. However, a review of concentrations at upwind sites (taken to be to the east, in this case) during the first hour after thorough mixing can provide an indication of ozone levels aloft. Based upon acoustic sounder data obtained for other case study days (no such data are available for July 13), 1000 EST is a good approximation of this first hour of mixing, and the concentrations shown in Figure 25 are consistent with this. Ozone concentrations of 0.097 ppm at Lumberton, NJ (Site 3), 0.064 ppm at Van Hiseville, NJ (Site 5), and 0.123 ppm at Ancora, NJ (Site 11), were observed at 1000 EST. At the time of mixing, these ozone levels were some of the highest observed during the program, implying a substantial ozone reservoir aloft on July 13. The effect of

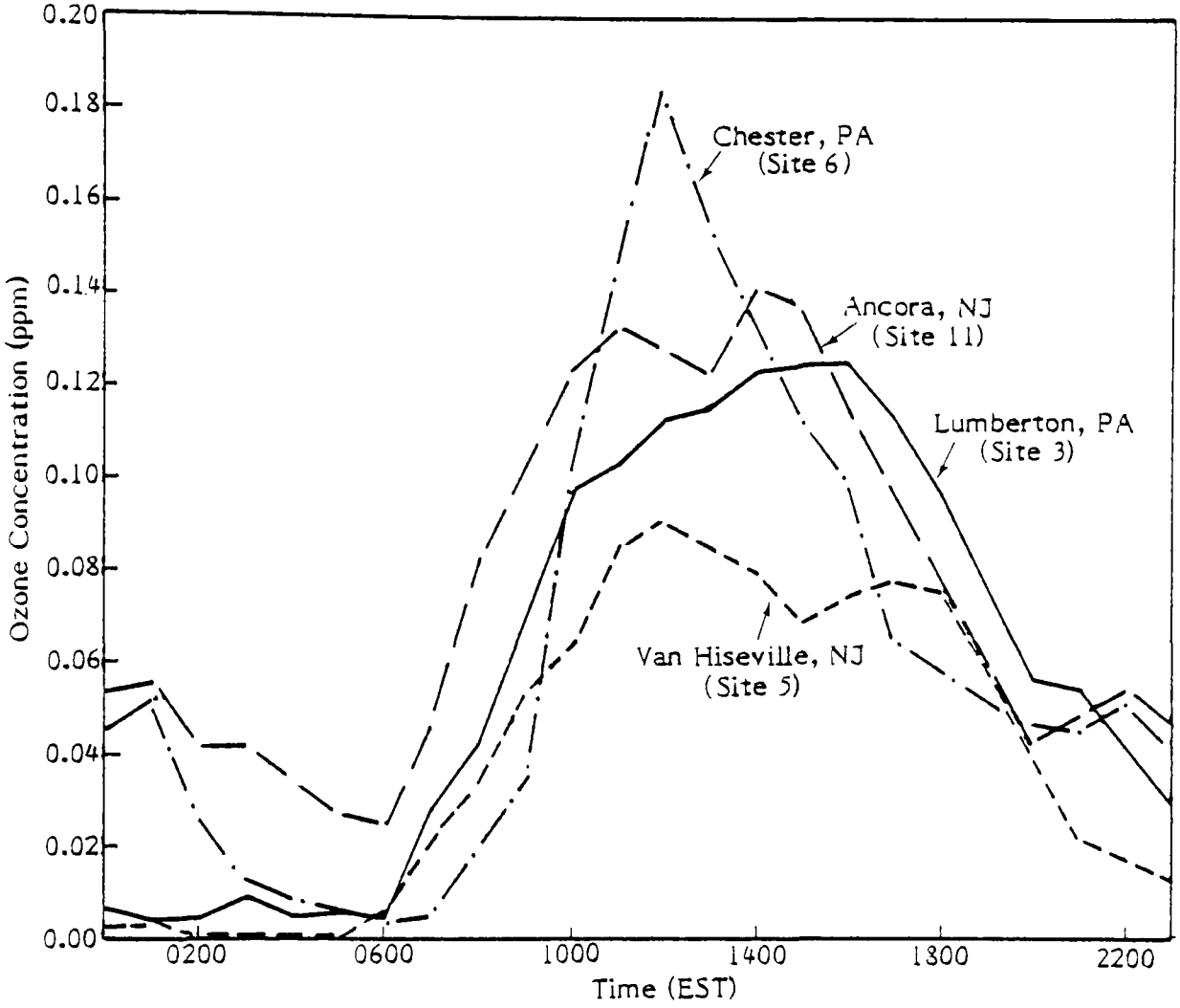


FIGURE 25. Diurnal profiles of ozone at upwind sites and Chester, PA on July 13, 1979.

mixing of ozone aloft down to the surface is further illustrated in Figure 25, showing diurnal profiles of ozone at Chester and several upwind sites. Very rapid increases in ozone levels are evident after mixing begins.

4.3 JULY 16, 1979 (MONDAY)

Important features of the July 16 case include southeasterly flow, confinement of high ozone concentrations to areas downwind of Philadelphia, and an unusual over-the-water synoptic air parcel trajectory. High ozone levels were due primarily to emissions from the greater Philadelphia urban area.

The peak ozone level on July 16 was 0.151 ppm. Three of the twelve operating stations recorded levels higher than 0.12 ppm. All other sites recorded 0.10 ppm or less. NO_2 levels were also fairly low. The peak NO_2 concentration was 0.069 ppm with three stations reporting concentrations in excess of 0.05 ppm.

4.3.1 Synoptic Meteorology

The synoptic situation is shown in Figure 26. A weak, slow-moving cold front was to the northwest, while the wind flow was dominated by a sluggish low pressure center to the southeast, bringing primarily east to southeast flow over the study area. Upper level flow was extremely weak with little pressure gradient evident. Also, thundershowers were present in the study area in the afternoon.

The synoptic trajectory (Figure 27) shows an air parcel in the 500- to 1000-m layer arriving from the southeast, resulting in an over-water trajectory, not normally conducive to high ozone concentrations in the study area. The air parcel in the 1500- to 2000-m layer approached more from the southwest, although it also spent the last hours of its journey over the ocean.

4.3.2 Mesoscale Meteorology

Surface airflow over the study area was characterized by an easterly component throughout the day. During the morning hours, sites near the urban areas, as well as to the west and southwest of Philadelphia, reported winds primarily from the east. However, sites to the northeast showed a wider variation: some sites reported winds from the southeast, while others reported winds from the northeast. Wind speeds remained less than 4 m/s at all sites prior to 1200 EST. During the afternoon, winds were stronger and

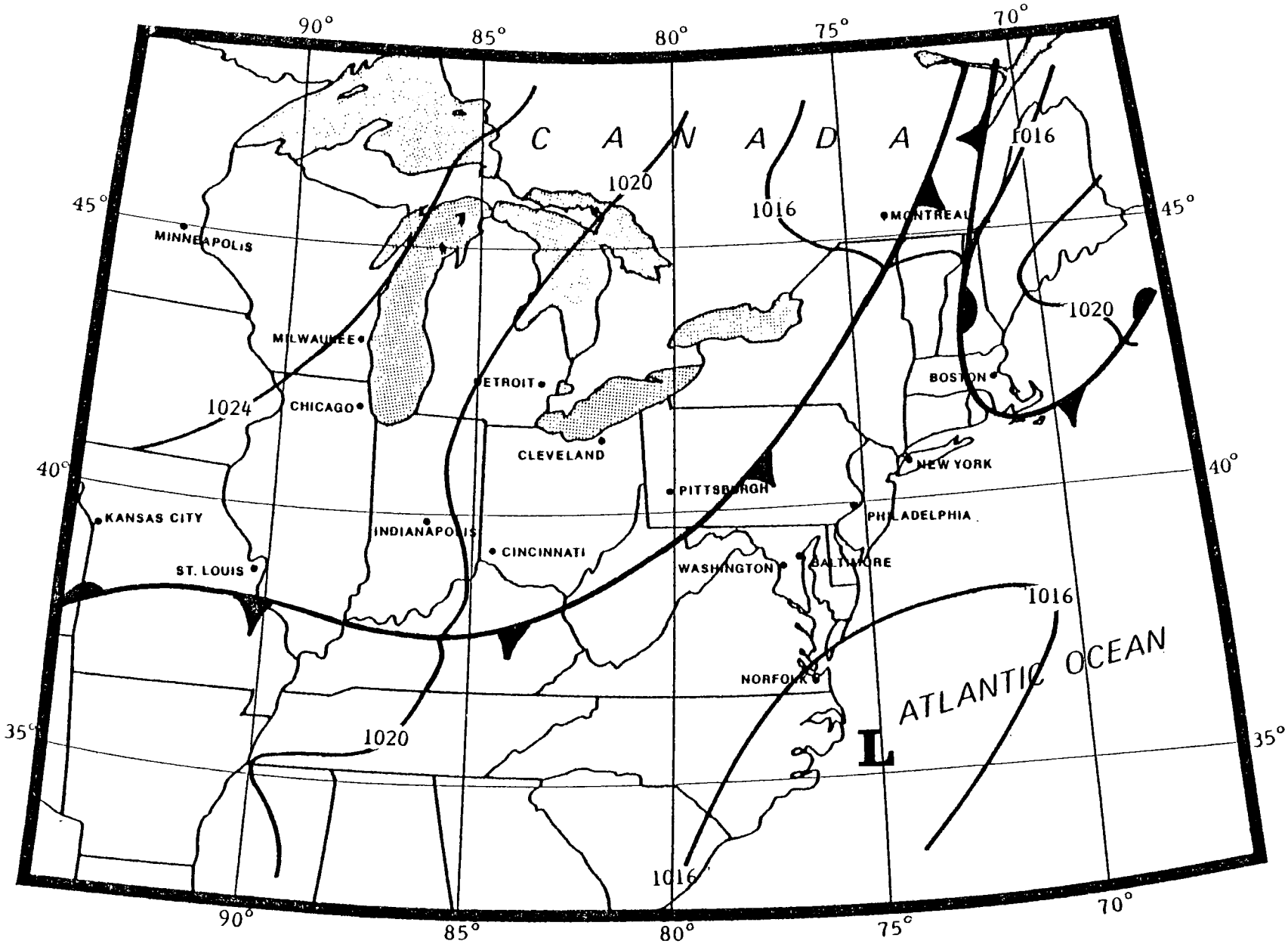


FIGURE 26. Synoptic situation, 0700 EST, July 16, 1979.

FIGURE 27. Synoptic trajectory of air parcels arriving at Philadelphia at 1300 EST, July 16, 1979. Solid line indicates parcel in the 500 to 1000-meter layer; dashed line is for a parcel in the 1500 to 2000-meter layer. Intervals are six hours.

primarily from the southeast over the entire study area. By 1900 EST, some sites were reporting winds from the north or northeast. Winds aloft, as indicated by pibal data at Wilmington, Delaware, and Trenton, New Jersey, were primarily easterly or southeasterly through 2000-m throughout the day.

4.3.3 Precursor Patterns

Morning precursor concentrations were generally lower at all sites than those observed on any other case study day, although no downtown NMHC data were available. The 6:00 to 9:00 a.m. LDT averages of NMHC and NO_x, along with the ratio of NMHC to NO_x, are given in Table 23 for rural and urban sites. The AMS Lab (Site 14) in Philadelphia, within 9 km of the central business district, reported 6:00 to 9:00 a.m. LDT average concentrations of 0.2 ppm for NMHC and 0.03 ppm for NO_x.

4.3.4 Ozone Patterns

Ozone concentrations were low at all sites during the morning hours except for Downington, PA (Site 2), west of Philadelphia. This site reported ozone concentrations exceeding 0.08 ppm by 1100 EST. Through the afternoon, concentrations remained low at all sites upwind of the urban area, as shown in Figure 28, which also shows isopleths of O_3 concentrations at 1200, 1300 and 1400 EST. (Data were obtained for this figure from sites which did not participate in the study but which were downwind under this unusual flow regime.) This figure shows a broad area of elevated O_3 extending from the edge of the urban and industrial areas downwind of Philadelphia. Chester, PA (Site 6), and Claymont, DE (Site 15), although not directly downwind of Philadelphia, reported daily maximum ozone concentrations of 0.131 and 0.130 ppm, respectively, at 1400 EST. Since wind speeds were generally less than 5 m/s throughout the day, and since ozone levels aloft appear to be low on this day (as evidenced by the low daily maximum concentrations at the upwind sites of Lumberton, NJ (Site 3), Ancora, NJ (Site 11), and Van Hiseville, NJ (Site 5) of 0.058, 0.061, and 0.061 ppm, respectively), the high levels at Chester and Claymont are likely due to industrial/automotive emissions within 20 km of the sites. The region of elevated ozone concentrations shown on Figure 28 persisted through 1700 EST.

Table 23. 6:00 to 9:00 a.m. LDT (0500-0800 EST) AVERAGES OF NO_x and NMHC (ppm) AND THE RATIO OF NMHC TO NO_x FOR RURAL AND URBAN SITES ON JULY 16.

Site No.	Rural Sites	6:00 to 9:00 a.m. LDT Averages		
		NO_x	NMHC	NMHC/NO_x Ratio
1	Summit Bridge, DE	0.00	0.0	--
2	Downingtown, PA	0.03	0.1	4.3:1
3	Lumberton, NJ	--	0.1	--
5	Van Hiseville, NJ	0.01	--	--
	Urban Sites			
10	Camden, NJ	0.04	--	--
13	Franklin Institute, Philadelphia, PA	0.04	--	--
14	AMS Lab, Philadelphia, PA	0.03	0.2	6.7:1

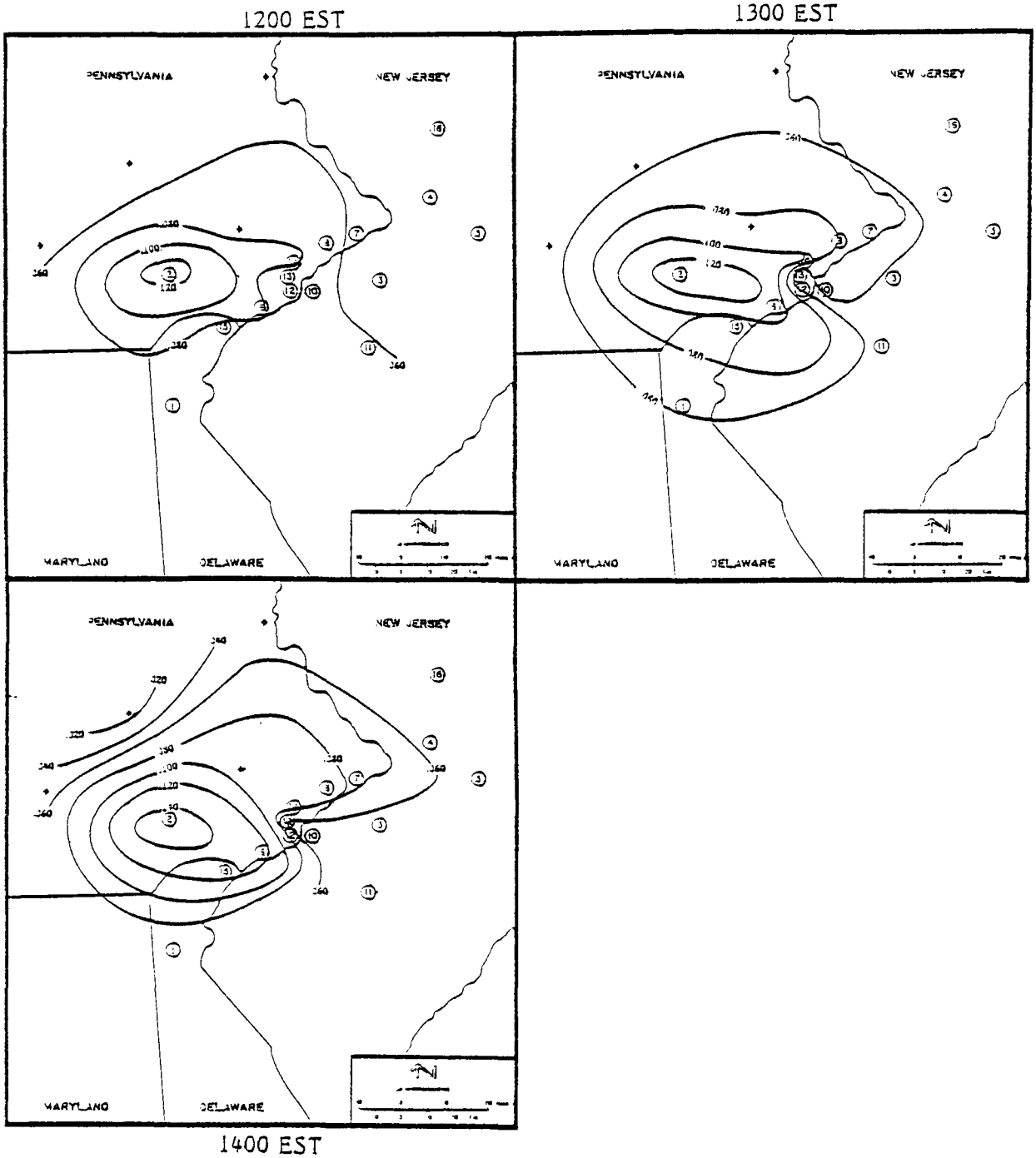


FIGURE 28. Isopleths of ozone at 1200, 1300, and 1400 EST, July 16, 1979.

The surface trajectories for this day shown in Figure 29 indicate that Downingtown, PA (Site 2), was downwind of Philadelphia. An air parcel beginning at 0600 EST in downtown Philadelphia was slightly northwest of Downingtown, PA (Site 2), at 1500 EST. (Site 2 recorded the highest study area ozone concentration at this time.) The parcel followed an eastward path during the morning until winds from the southeast became dominant in the afternoon, then the parcel traveled in a northwest-only direction. An air parcel ending at Chester, PA (Site 6), at 1400 EST with a concentration of 0.131 ppm was 40 km southeast of Philadelphia at 0600 EST, although it passed over highly industrialized areas prior to its arrival at Chester.

4.3.5 NO_2 Patterns

July 16 experienced the lowest NO_2 concentrations of any of the case study days. The peak concentration of 0.069 ppm occurred at Chester, PA (Site 6), at 2300 EST, reflecting the late evening decomposition of ozone. The other two sites recording levels greater than 0.050 ppm (Claymont, DE and Franklin Institute, PA) also reported the 2300 EST peaks.

4.3.6 Concentrations Aloft

Although no pollutant measurements were recorded above the surface level on this day, upwind surface concentrations recorded at 1000 EST indicate that ozone levels aloft were lower than on the first two case study days discussed. (No acoustic sounder data were available for July 16. 1000 EST was selected as the first complete hour of mixing through 1000 m, based upon acoustic sounder data on other case study days.) Observed concentrations were 0.049 ppm for ozone, 0.000 ppm for NO, and 0.000 ppm for NMHC at Lumberton, NJ (Site 3), and 0.061 ppm of ozone and 0.002 ppm of NO at Van Hiseville, NJ (Site 5). Diurnal profiles of ozone at Lumberton, NJ (Site 3), and Van Hiseville, NJ (Site 5), in Figure 30 demonstrate the relatively low ozone levels observed all day upwind of Philadelphia. This indication of lower levels aloft is consistent with the observation that high ozone concentrations were much less widespread and occurred downwind of Philadelphia on July 16.

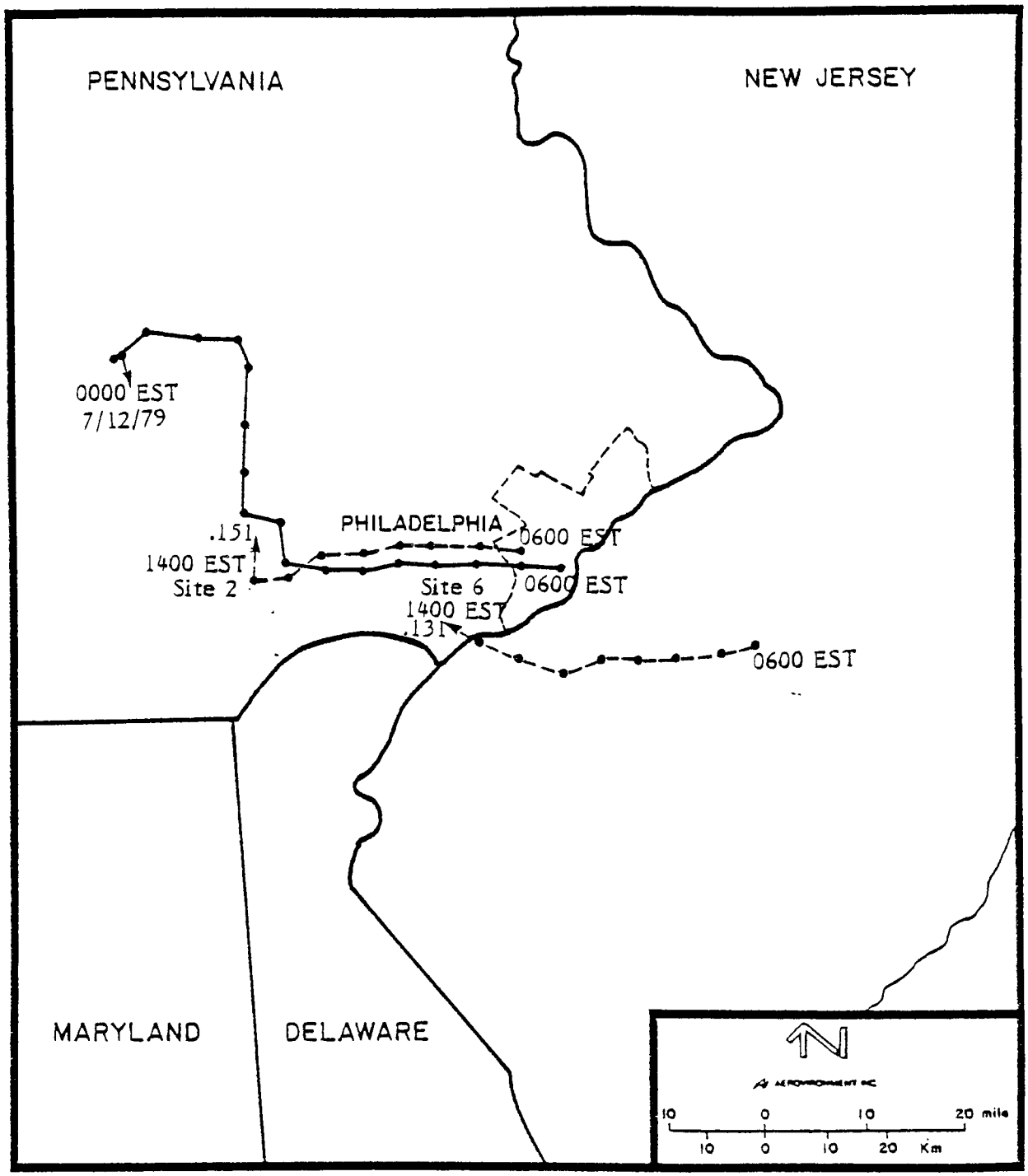


FIGURE 29. Surface trajectory for various air parcels located within the study area on July 16, 1979. Solid line indicates a trajectory beginning at downtown Philadelphia at 0600 EST; dashed lines are for parcels ending at the indicated site and time. Dots show the positions of the parcels at one hour intervals.

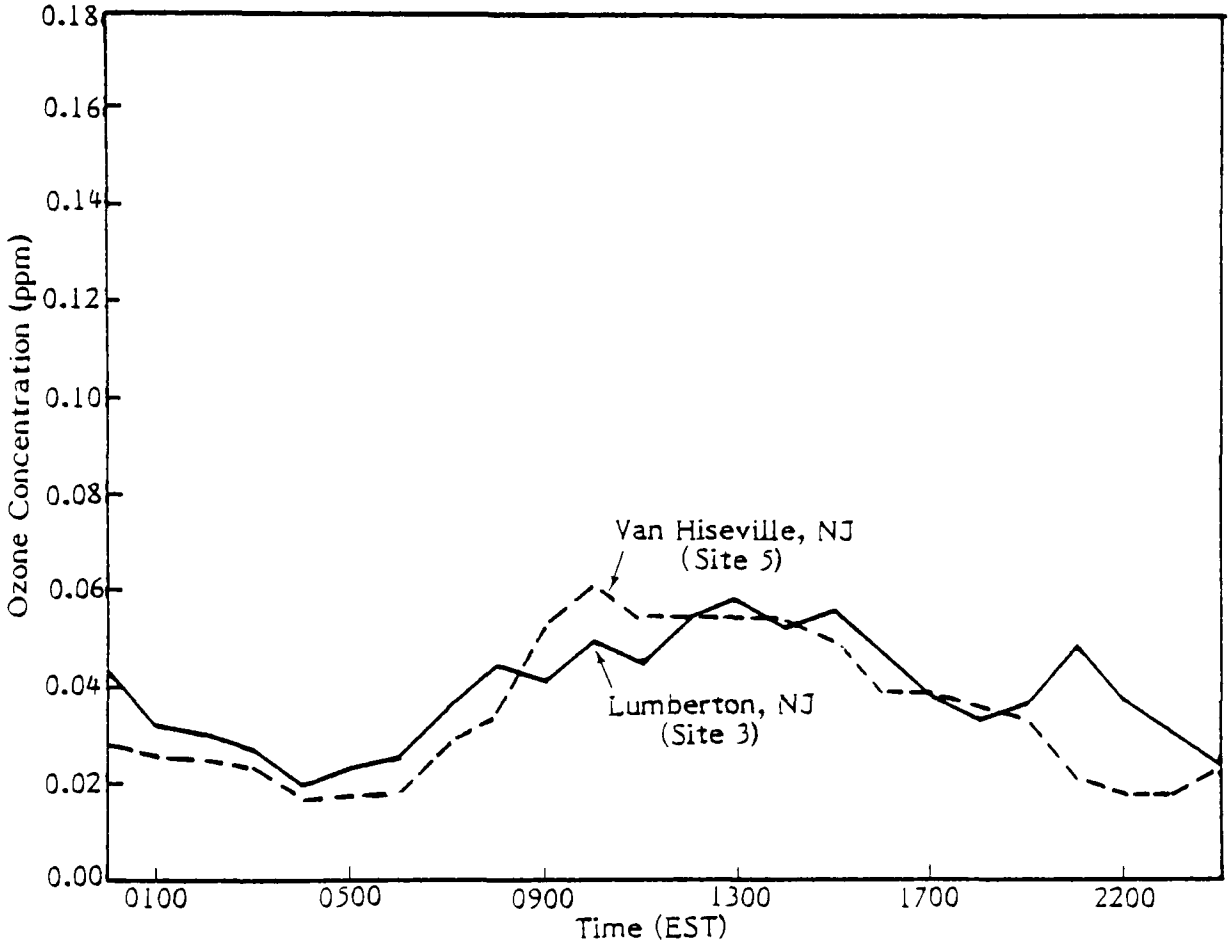


FIGURE 30. Diurnal profiles of ozone at upwind stations on July 16, 1979.

4.4 JULY 19, 1979 (THURSDAY)

The important aspects of the July 19 case were southeasterly flow, the apparently long residence time over the New York City area of a low-level air parcel arriving at Philadelphia at 1300 EST, indications of high concentrations of ozone transported aloft, and some NO transport at the surface. Peak ozone concentrations resulted from both the greater Philadelphia urban plume and transport aloft.

The peak ozone concentration recorded on July 19 was 0.160 ppm. Six of the thirteen operating stations reported ozone concentrations equal to or greater than 0.12 ppm and an additional four stations reported ozone concentrations equal to or greater than 0.10 ppm. The peak NO_2 concentration was 0.070 ppm, with six stations reporting NO_2 concentrations equal to or greater than 0.05 ppm.

4.4.1 Synoptic Meteorology

On July 19, a broad, high-pressure cell dominated the northeastern United States, including Philadelphia, as shown in Figure 31. This high pressure cell was to the west bringing flow with an easterly component to the study area. A stationary front, which had been present for several days, was about 150 km to the southeast. The upper level flow was predominantly west-southwesterly.

The 100- to 500-m and 1500- to 2000-m layer synoptic air parcel trajectories depicting the 96-hour paths of parcels arriving at Philadelphia at 1300 EST are shown in Figure 32. The 100- to 500-m trajectory shows a very erratic path, as might be expected considering the long-term presence of the stationary front mentioned above. The trajectory indicates a prolonged residence time in the vicinity of the New York City metropolitan area.

The 1500- to 2000-m trajectory is quite different. It is a long over-land trajectory traversing the Great Lakes area. Since the maximum mixing height on July 19 in downtown Philadelphia was greater than 2000 m MSL, transport at both levels may be important.

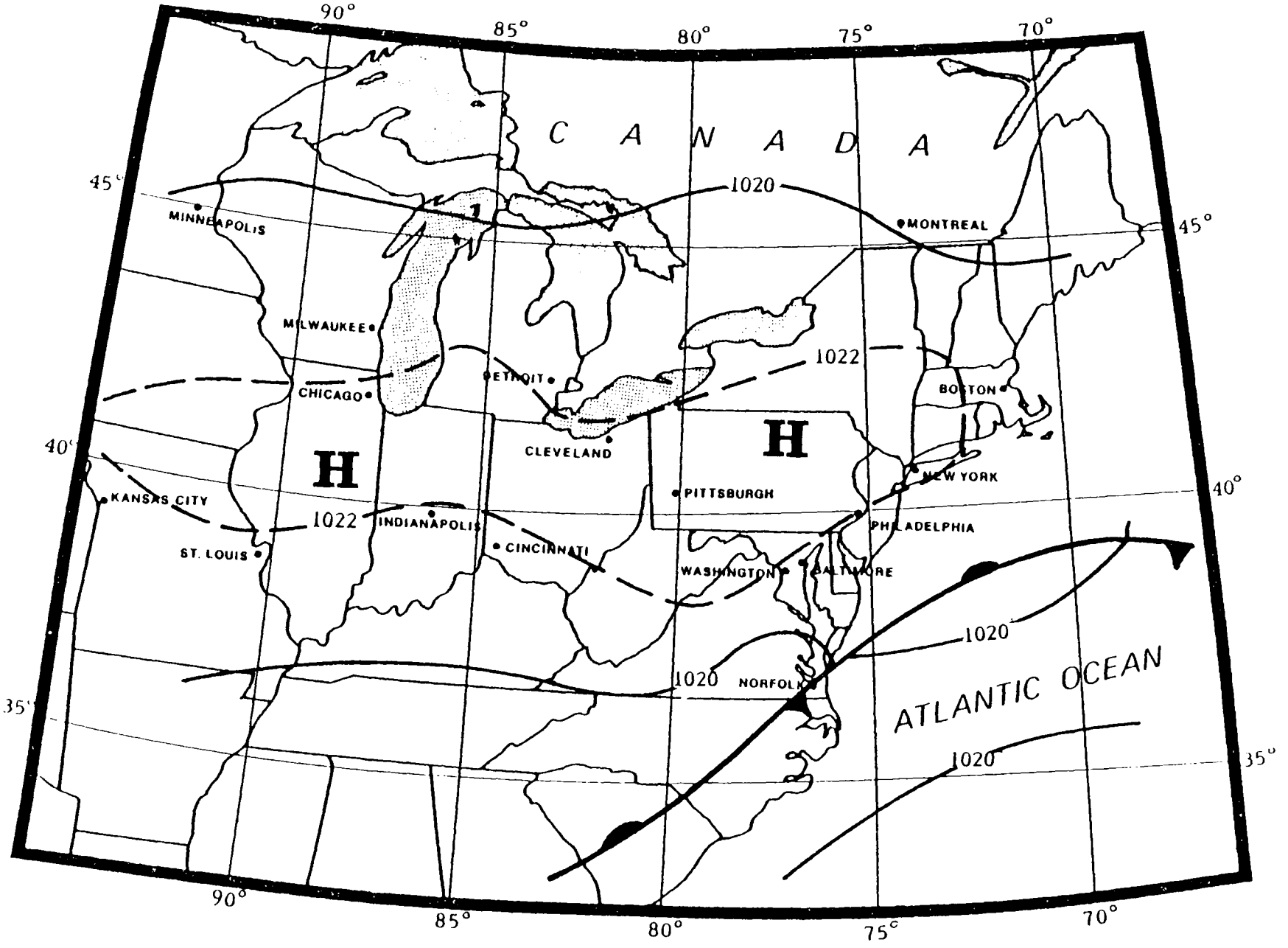


FIGURE 31. Synoptic situation, 0700 EST, July 19, 1979.

FIGURE 32. Synoptic trajectory of air parcels arriving at Philadelphia at 1300 EST, July 19, 1979. Solid line indicates parcel in the 500 to 1000-meter layer; dashed line is for a parcel in the 1500 to 2000-meter layer. Intervals are six hours.

4.4.2 Mesoscale Meteorology

Surface wind flow veered from northerly to northeasterly to southeasterly from early morning to late afternoon. Several sites (North Philadelphia Airport, Philadelphia International Airport, Greater Wilmington Airport, Delaware, Trenton-Mercer County Airport, New Jersey, and Downingtown, Pennsylvania) reported wind speeds greater than 2.0 m/s from 0500 EST through 2100 EST, indicating some significant wind flow was prevalent all day. Winds aloft veered from northeasterly to easterly. The overall wind flow patterns were very similar to those on July 16 discussed previously.

Mixing heights on this day were the highest of all of the seven case study days for which data were available (see Table 18). Rural acoustic sounder data show uninhibited mixing (mixing through 1000 m) at 1000 EST with strong vertical mixing generally confined to lower layers throughout the day. Urban mixing heights, as determined from radiosonde observations, were 741 m at 0900 EST and 2314 m at 1500 EST.

4.4.3 Precursor Patterns

The 6:00 to 9:00 a.m. LDT NMHC and NO_x averages along with the NMHC to NO_x ratios are given in Table 24 for rural and urban sites. Urban morning precursor concentrations were quite low and NO concentrations at outlying stations were even lower (<0.025 ppm), with the exception of Van Hiseville, NJ (Site 5), 75 km east-northeast of Philadelphia, which recorded a 6:00 to 9:00 a.m. LDT NO_x average of 0.08 ppm, the highest morning concentration observed at this site during the program. The high concentration of NO_x observed at Van Hiseville (Site 5) and the synoptic trajectory discussed previously raise the possibility of surface precursor transport. This is supported by peroxyacetyl nitrate (PAN) data at Van Hiseville on this day, presented in Figure 33. Concentrations of this pollutant, a product of the photochemical process, reached 3.70 ppb at 1000 EST, whereas the July average for this hour is 1.4 ppb. Early morning flow at the surface was from the north or northeast in the northern section of the study area, which suggests some transport from the New York City metropolitan area.

Table 24. 6:00 to 9:00 a.m. LDT (0500-0800 EST) AVERAGES OF NO_x and NMHC (ppm) AND THE RATIO OF NMHC TO NO_x FOR RURAL AND URBAN SITES ON JULY 19.

Site No.	Rural Sites	6:00 to 9:00 a.m. LDT Averages		
		NO_x	NMHC	NMHC/NO_x Ratio
1	Summit Bridge, DE	0.02	0.3	16.5:1
2	Downingtown, PA	0.02	0.0	--
3	Lumberton, NJ	0.05	0.4	8.6:1
5	Van Hiseville, NJ	0.08	--	--
	Urban Sites			
6	Chester, PA	--	0.7	--
7	Bristol, PA	--	1.4	--
8	North Philadelphia Airport, PA	0.03	--	--
10	Camden, NJ	0.07	--	--
12	So. Broad & Spruce Streets, Philadelphia, PA	0.05	0.2	3.4:1
13	Franklin Institute, Philadelphia, PA	0.05	--	--
14	AMS Lab, Philadelphia, PA	0.03	0.4	12.3:1

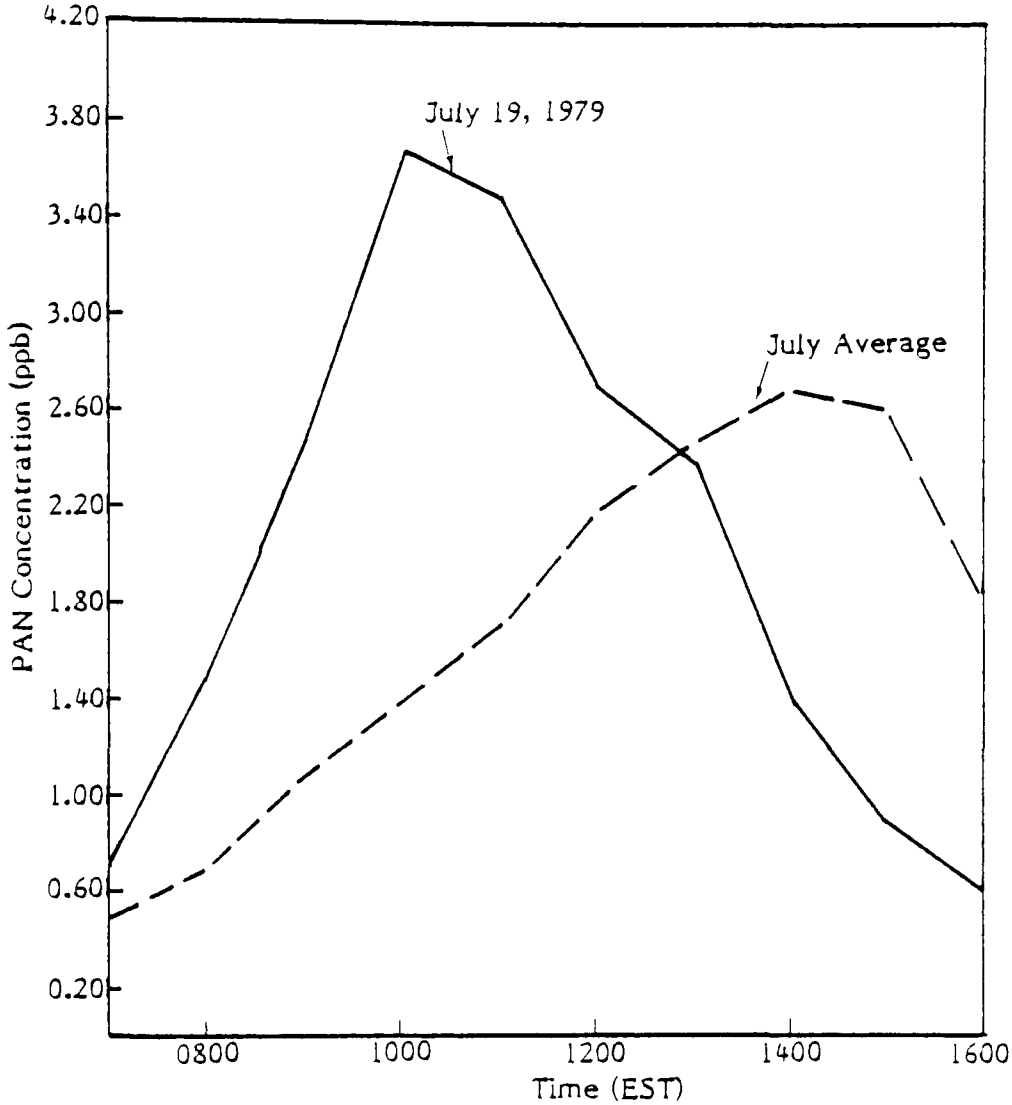


FIGURE 33. Diurnal profiles of PAN at Van Hiseville, NJ (Site 5) on July 19, 1979 and July average.

4.4.4 Ozone Patterns

Ozone isopleths for the study area at 1400, 1500, and 1600 EST are shown in Figure 34. As on July 16, a day in which the surface study area flow was from the southeast, a broad area of elevated ozone was located west and southwest of Philadelphia. Summit Bridge, DE (Site 1), Downingtown, PA (Site 2), Claymont, DE (Site 15), and Chester, PA (Site 6), all reported ozone concentration of 0.120 or higher by 1400 EST. The highest ozone concentration of the day (0.160 ppm) was found at Claymont, DE (Site 15), southwest of Philadelphia, at 1600 EST. During the day, urban and near-urban sites also reported high concentrations. Sites to the east and southeast reported lower peak concentrations.

Surface trajectories for this day are shown on Figure 35. During the early morning hours, winds were from the north or northeast; by 1100 EST, the flow was from the east, and during the afternoon the flow was from the southeast. A parcel starting at 0600 EST in downtown Philadelphia was about eight miles west of Downingtown, PA (Site 2), at 1500 EST when a 0.157 ppm ozone concentration was recorded. As discussed above, the maximum ozone concentration recorded in the study area during this day was 0.160 ppm at Claymont, DE (Site 15), at 1600 EST. Figure 35 shows a parcel ending at this site and time with a trajectory beginning far to the east making an anticyclonically-curved path to arrive at the site from the southeast. The 0600 EST starting point was over an area closest to Lumberton, NJ (Site 3). Peak morning NO and NMHC levels at Lumberton, NJ (Site 3), were 0.024 ppm and 0.5 ppm, respectively, higher than normal for this site and generally higher than other rural sites.

Mesoscale surface trajectories were also developed for two cases in which high ozone levels were reported downtown and to the east. The 0600 EST position of an air parcel arriving at the AMS Lab, Philadelphia (Site 14), at 1300 EST, with an ozone concentration of 0.130 ppm, was near the near-urban station of Bristol, PA (Site 7). An air parcel arriving at Lumberton, NJ (Site 3), at 1100 EST with a 0.104 ppm ozone concentration was 45 km to the northeast at 0600 EST near the rural Robbinsville, NJ (Site 4), station. Such elevated ozone levels at a site upwind of Philadelphia suggest long-range ozone transport, particularly in light of the synoptic trajectory shown in Figure 32.

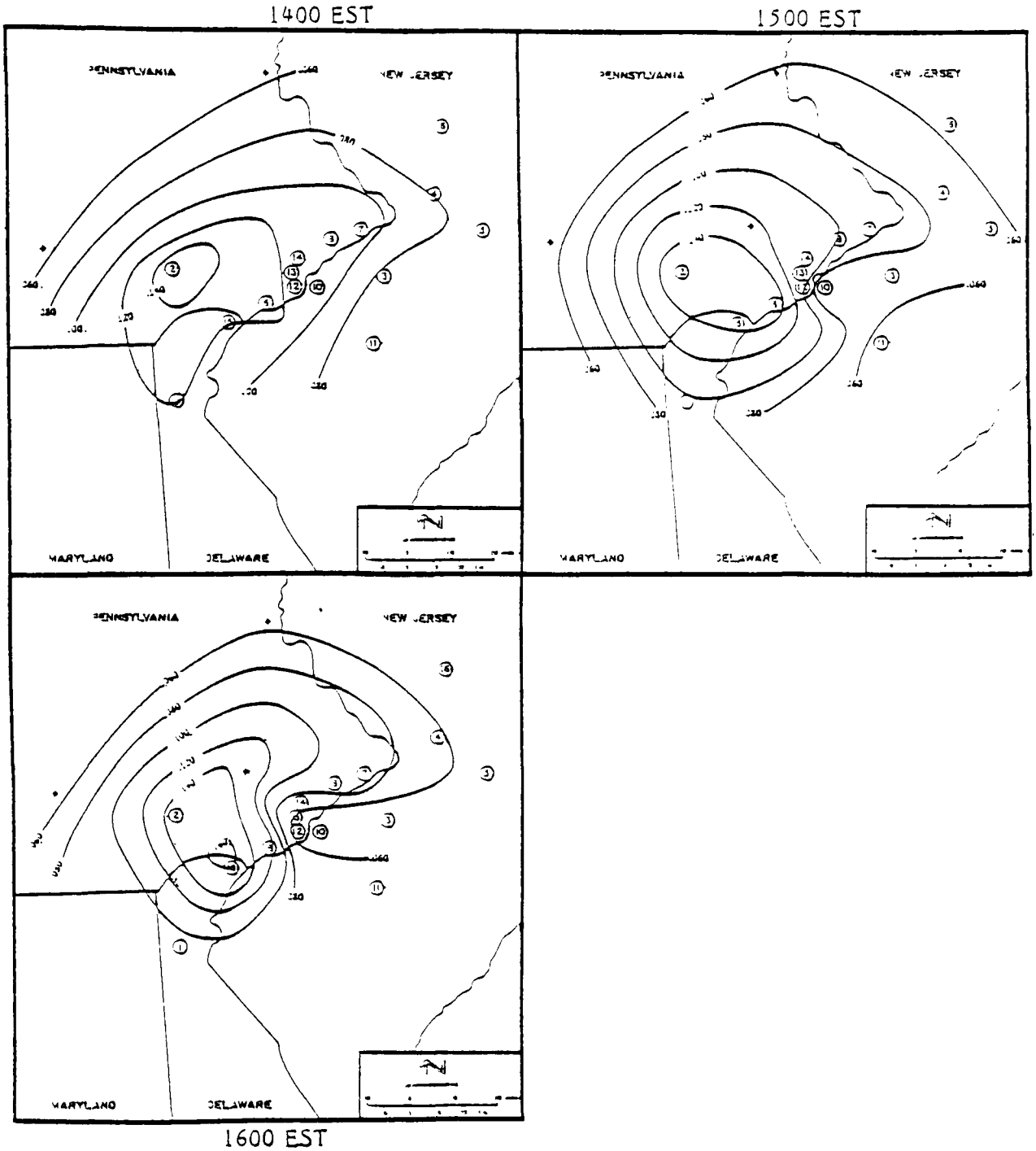


FIGURE 34. Isopleths of ozone at 1400, 1500, and 1600 EST, July 19, 1979.

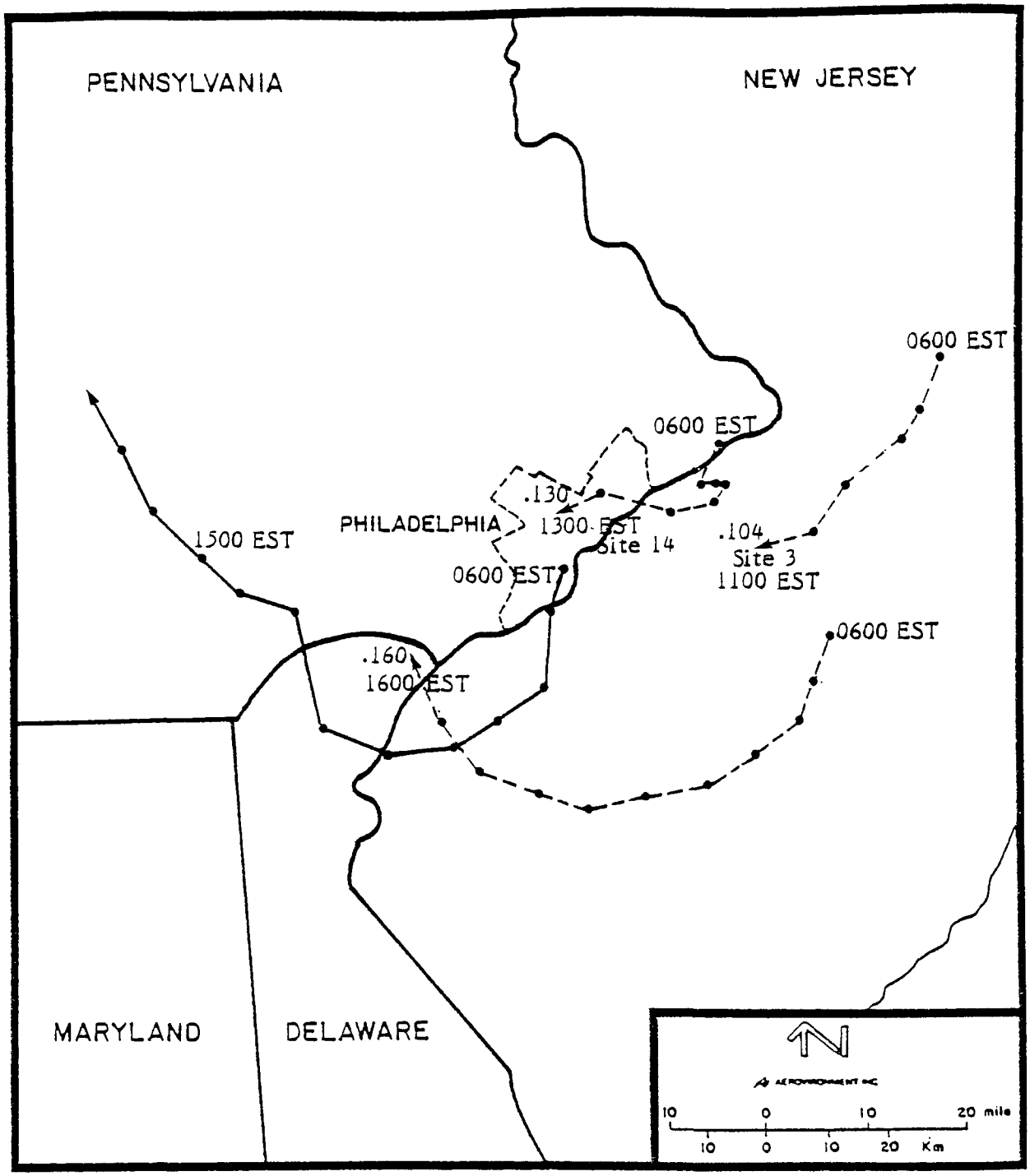


FIGURE 35. Surface trajectory for various air parcels located within the study area on July 19, 1979. Solid line indicates a trajectory beginning at downtown Philadelphia at 0600 EST; dashed lines are for parcels ending at the indicated site and time. Dots show the positions of the parcels at one hour intervals.

4.4.5 NO_2 Patterns

The peak NO_2 concentration (0.070 ppm) occurred at Claymont, DE (Site 15), southwest of Philadelphia. This and other sites recording NO_2 values in excess of 0.05 ppm were primarily downtown and to the southwest (downwind), and nearly all peaked in the late morning. NO_2 peaks downwind of the urban area in the late morning are the characteristic result of the NO/O_3 reaction and preceed the afternoon ozone buildup. Bristol, PA (Site 7), to the northeast, also recorded NO_2 concentration in excess of 0.05 ppm. Van Hiseville (Site 5), east-northeast of Philadelphia, recorded 0.046 ppm at 0800 EST, the highest NO_2 concentrations recorded there during the field program, a reflection of the high NO concentrations observed during the hours preceding 0800 EST.

4.4.6 Concentrations Aloft

The combination of ozone transport aloft and surface precursor transport is a plausible explanation for the high NO_2 levels observed at Van Hiseville, NJ (Site 5), and the high ozone levels observed at Lumberton, NJ (Site 3), both upwind of Philadelphia.

Data from direct measurement of pollutants aloft were not available. Mixing height data collected at Summit Bridge, DE (Site 1), indicated that the first full hour of mixing to 1000 m was at 1000 EST. Ozone and NO pollutant measurements at the upwind sites of Lumberton, NJ, and Van Hiseville, NJ (Sites 3 and 5), at this time were 0.082 and 0.083 ppm, and 0.005 and 0.003 ppm, respectively. The diurnal profiles of ozone and NO at these two upwind locations presented in Figure 36 show these indications of transport. The rapid increase in ozone and concurrent rapid decrease in NO are characteristic of ozone aloft being mixed down. This suggests that high levels of ozone were transported aloft and that there was very little transport of precursors aloft. However, as discussed above, the abnormally high 6:00 to 9:00 a.m. NO_x concentrations observed in the eastern portion of the study area implies surface precursor transport.

4.4.7 Hydrocarbon Species Data

Both samples collected at Franklin Institute and the industrial site had NMHC below the overall average on this day, which is consistent with the fact that mixing heights were

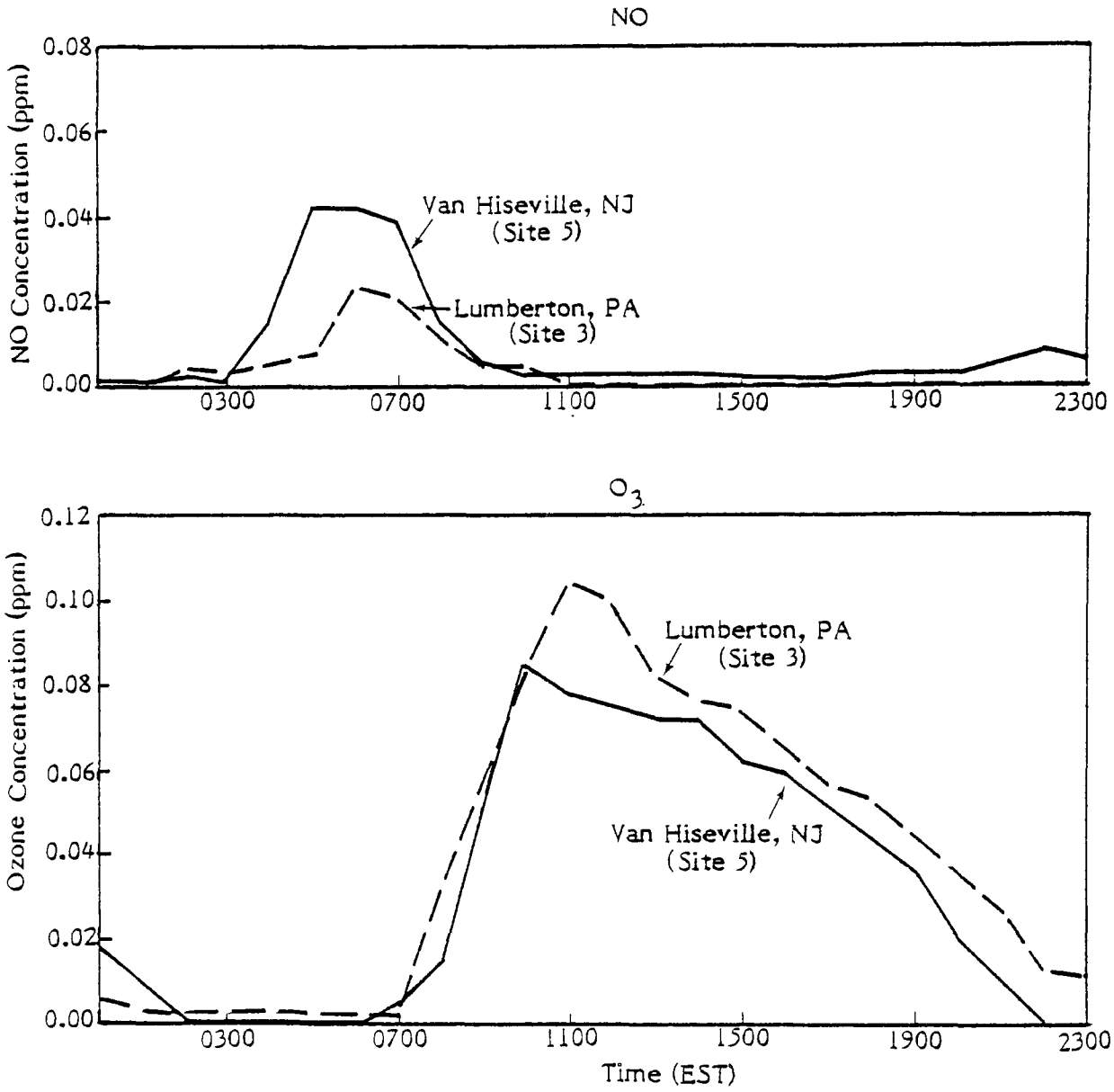


FIGURE 36. Diurnal profiles of ozone and NO at upwind stations on July 19, 1979.

fairly high in the morning hours. The species breakdown showed differing unusual features:

1. The Franklin Institute samples, in addition to the background of automobile exhaust hydrocarbons, showed C_7-C_8 paraffins in unusual amounts. Methyl cyclohexane, which showed large amounts in several samples, was 70 ppbC in the 0500 to 0600 EST sample and somewhat elevated at 0700 to 0800 EST.

2. The industrial site samples did not have unusual amounts of this hydrocarbon but showed unusually high concentrations of iso-propylbenzene (cumene). This is an industrially important hydrocarbon, so this might reflect a chance spill of this hydrocarbon.

4.5 AUGUST 4, 5, 6, 7, 1979 (SATURDAY, SUNDAY, MONDAY, TUESDAY)

These days represent the only extended ozone episode observed during the monitoring period. August 4 was interesting because it was a weekend day with high observed ozone. The highest concentrations appeared to be transported into the study area from the north, and a low-level surface trajectory brought the parcel up along the Atlantic seaboard. August 5, another weekend day (Sunday), had the following interesting characteristics: (1) peak ozone concentrations directly downwind of Philadelphia; (2) indications of significant early morning ozone concentrations aloft; and (3) a long, over-land synoptic trajectory. August 6 was remarkably similar to August 5 with similar ozone patterns, indications of transport, and air parcel trajectories. August 7 demonstrated significant wind shear, very little early morning ozone aloft, and surface flow reversal during the day.

This four-day series represented an extended episode period in which ozone concentrations in excess of 0.120 ppm on each day were recorded within the study area. Table 25 gives the maximum ozone and NO_2 concentrations and the number of sites exceeding certain levels on the four days. This table shows that, although peak ozone concentrations were fairly high on each of the four days, the number of stations experiencing high ozone concentrations did not increase from day to day during the episode; furthermore, high ozone concentrations were less widespread than on most of the other case study days. Peak NO_2 concentrations were less than 0.10 ppm, as was the case for all but two of ten case study days examined.

4.5.1 Synoptic Meteorology

Figures 37a through 37d show the surface synoptic progression for the four days. A high-pressure cell was centered just to the southwest of the study area on August 4 and became stronger so that most of the eastern half of the United States was dominated by a high-pressure cell during the days following. A surface front situated off the coast of the northeastern states on August 4 underwent frontolysis on August 5. A weak cold front just north of the Great Lakes on August 5 moved through the study area on August 6.

Table 25. MAXIMUM OZONE AND NO_2 CONCENTRATIONS OBSERVED IN THE STUDY AREA DURING THE PERIOD AUGUST 4 THROUGH AUGUST 7, 1979.

Date	Ozone			NO_2	
	Concentration (ppm)	Number of Sites ≥		Concentration (ppm)	Number of Sites ≥0.05 ppm
		0.12 ppm	0.10 ppm		
August 4	.144	3	6	.090	5
August 5	.135	2	5	.090	6
August 6	.136	3	5	.074	5
August 7	.129	3	5	.080	5

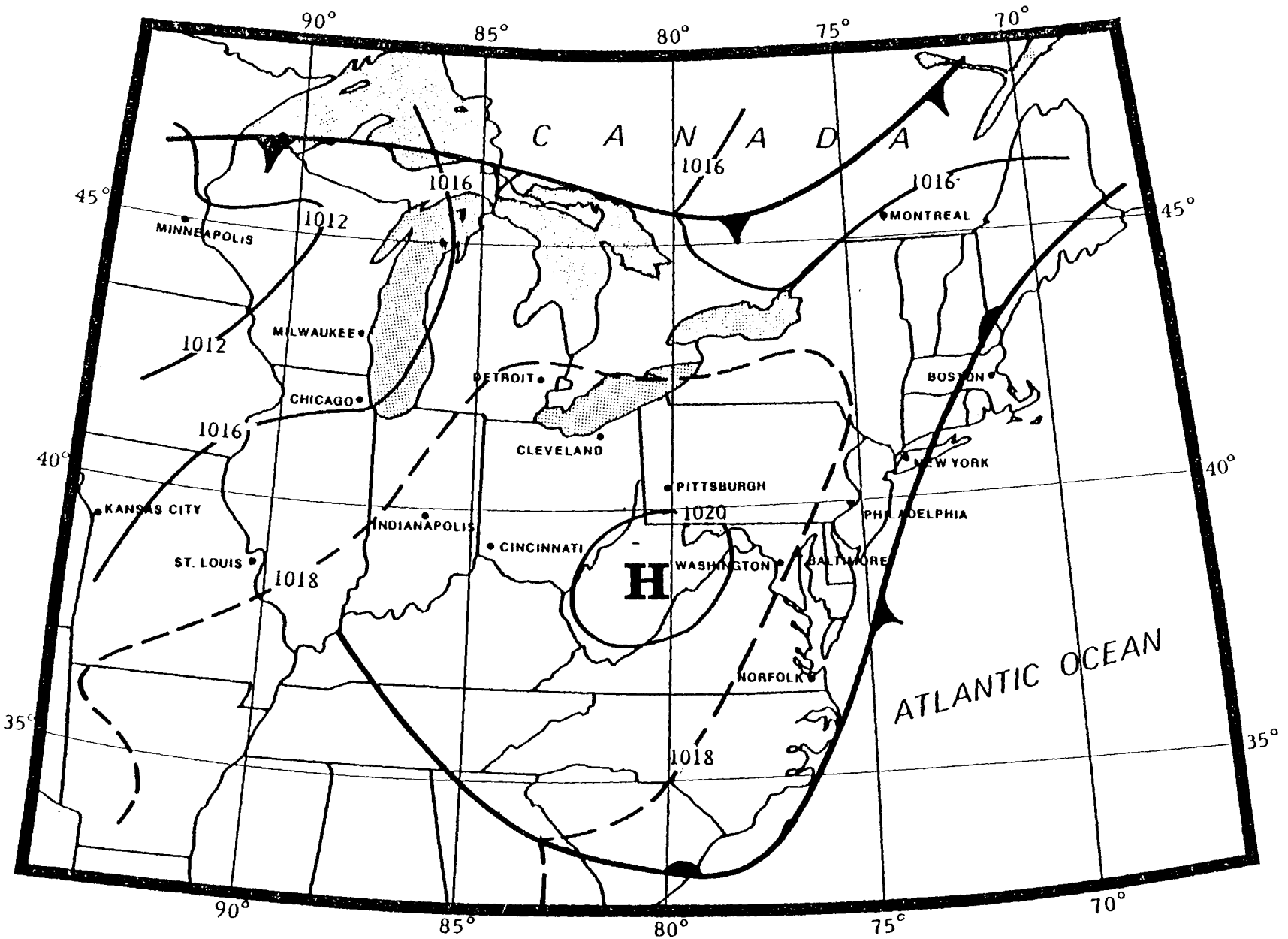


FIGURE 37a. Synoptic situation, 0700 EST, August 4, 1979.

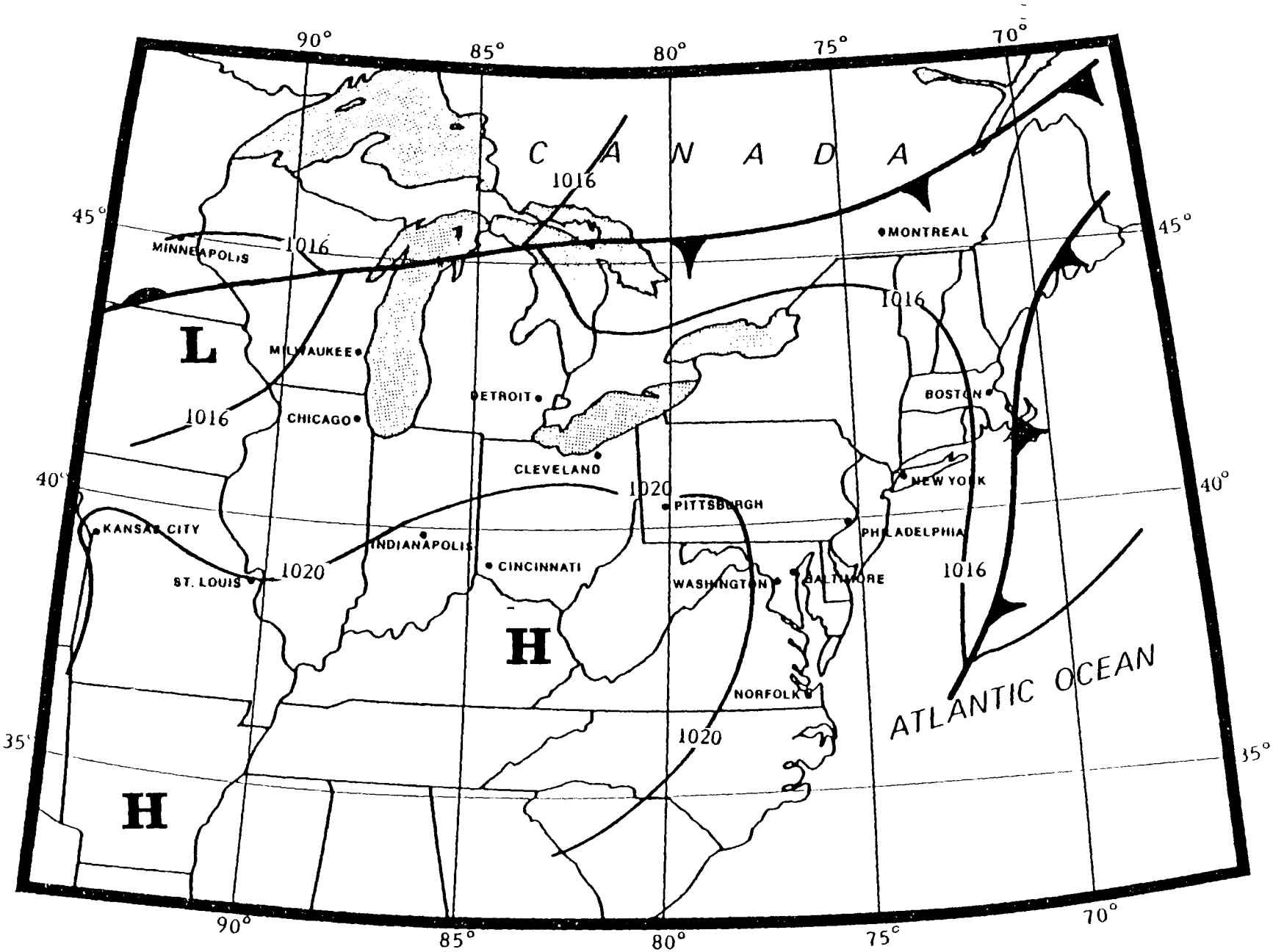


FIGURE 37b. Synoptic situation, 0700 EST, August 5, 1979.

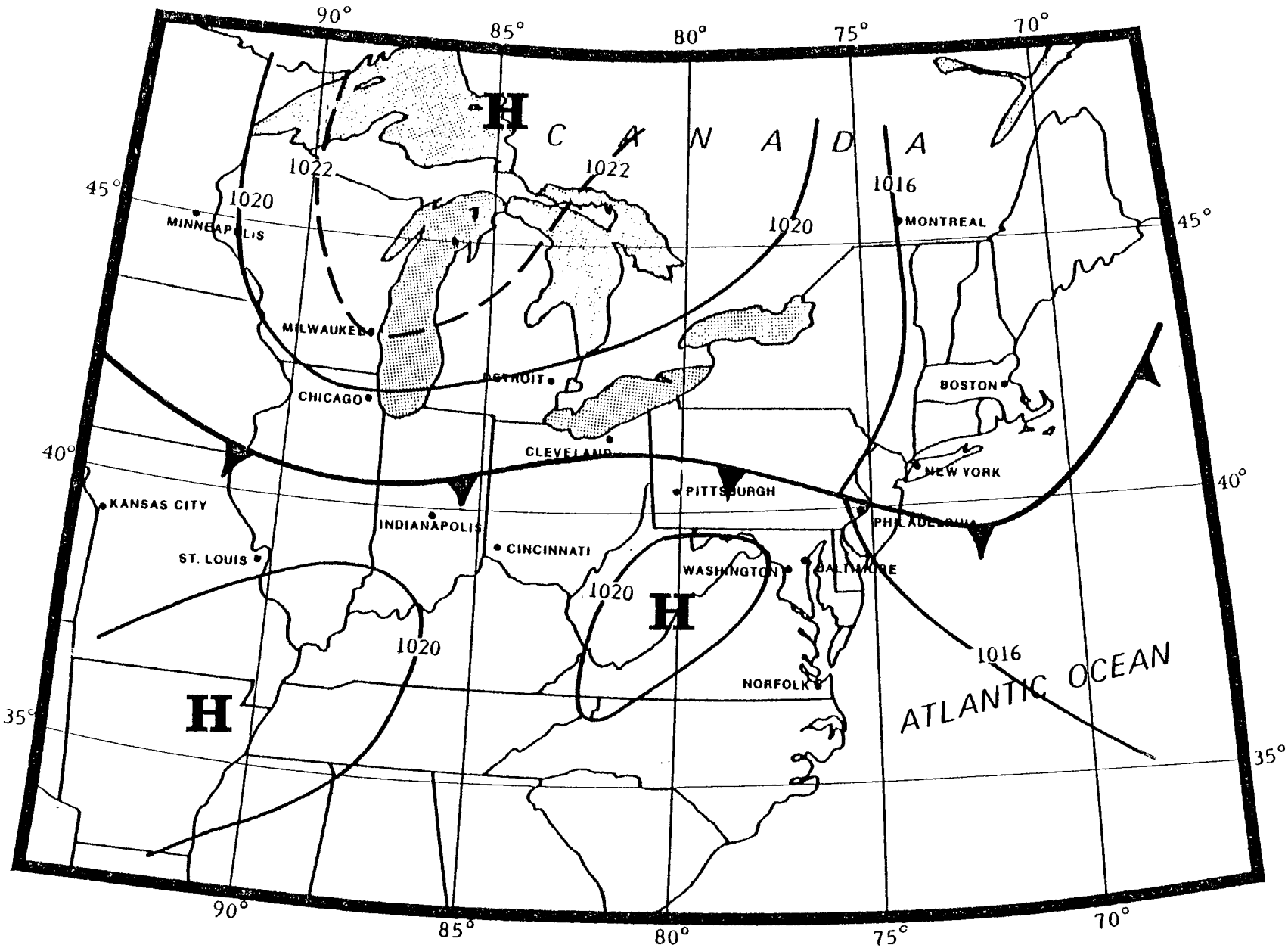


FIGURE 37c. Synoptic situation, 0700 EST, August 6, 1979.

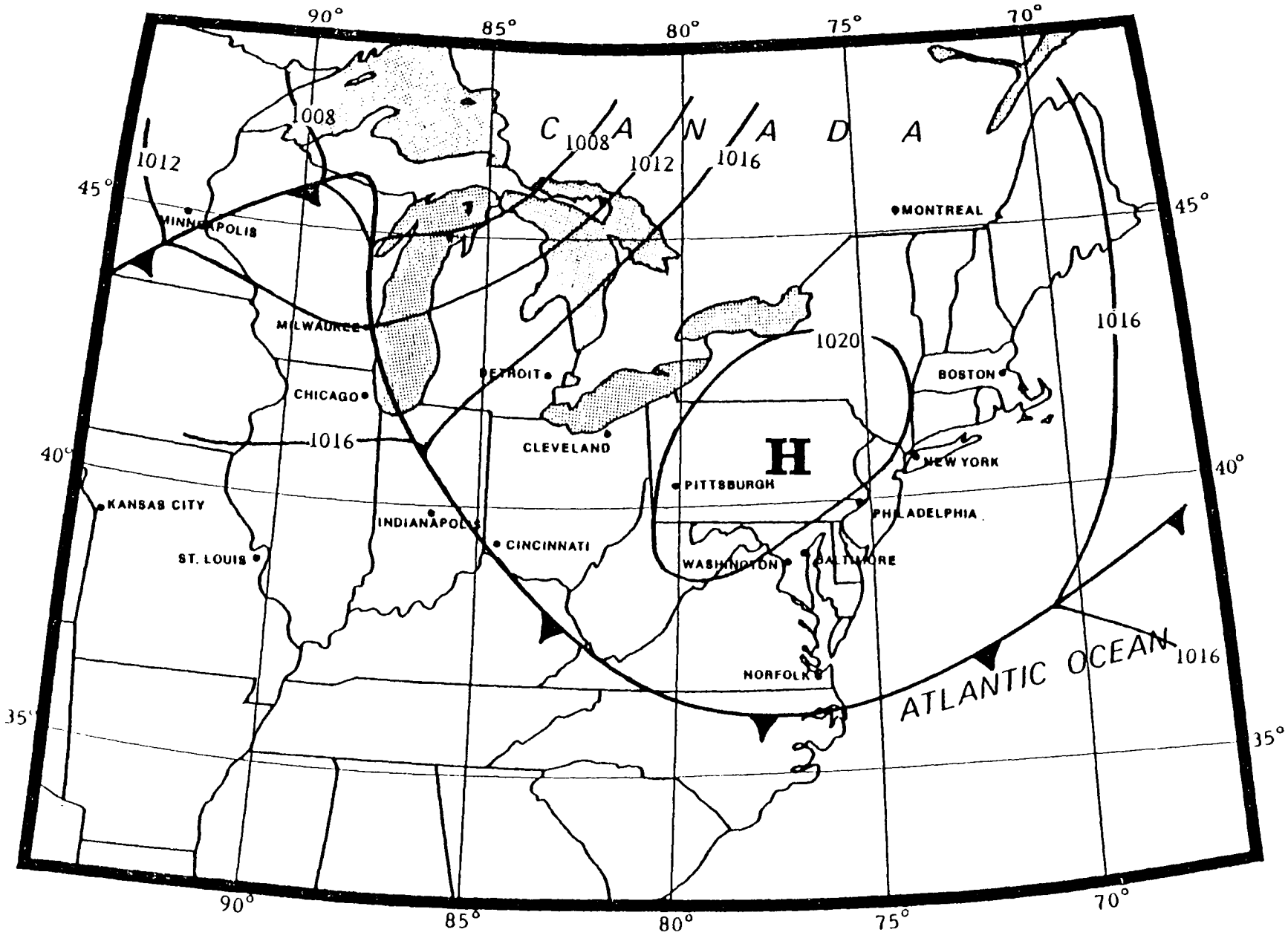


FIGURE 37d. Synoptic situation, 0700 EST, August 7, 1979.

It is interesting to note that a similar synoptic pattern and sequence of weather events was also associated with the only extended episode situation observed during a similar 1978 study in Philadelphia (Chan et al., 1979).

The approach of air parcels to the study area became more northerly as the episode progressed. Figures 38a through 38d show the synoptic trajectories of air parcels arriving at Philadelphia at 1300 EST on August 4 through 7, respectively. On August 4, the 100- to 500-m and 1500- to 2000-m layer trajectories were quite different. The path followed by the 100- to 500-m parcel was erratic and included a long, over-land trajectory along the Atlantic seaboard. The path followed by the 1500- to 2000-m layer parcel was overland and from the west. On the last three days of the episode, the 100- to 500-m layer parcels followed anticyclonically-curved paths approaching from the west, northwest, and then north of Philadelphia. The lower-level air parcel arriving on August 4 appeared to have traversed the high emission density areas of Baltimore and Washington, D.C., while parcels arriving on August 5 and 6 did not directly traverse any major source area but traversed areas near the major urban centers of Cincinnati, Cleveland, and the lower Great Lakes. The lower-level trajectory ending on August 7 approached through the New York City area.

4.5.2 Mesoscale Meteorology

The general surface study area flow was north to northwest on August 4 and was predominantly from the northwest on August 5 and 6. On August 7 the flow was from the northeast in the morning but from the southwest during the afternoon.

Upper air wind flow over the study area was generally northerly on August 4 through the morning of August 5, backing to westerly in the afternoon of August 5. Northwesterly flow aloft prevailed on August 6 and westerly on August 7.

Urban mixing heights on August 4 through 6 were the lowest of any of the seven case study days for which data were available (see Table 18). Mixing heights on August 4 were particularly low. The 0900 EST mixing height was 157 m and urban mixing heights remained under 1000 m most of the day. The maximum urban mixing heights on August 4, 5, 6, and 7 were 1270 m, 1287 m, 1044 m and 1439 m, respectively. Rural mixing height

FIGURE 38a. Synoptic trajectory of air parcels arriving at Philadelphia at 1300 EST, August 4, 1979. Solid line indicates parcel in the 500 to 1000-meter layer; dashed line is for a parcel in the 1500 to 2000-meter layer. Intervals are six hours.

FIGURE 38b. Synoptic trajectory of air parcels arriving at Philadelphia at 1300 EST, August 5, 1979. Solid line indicates parcel in the 500 to 1000-meter layer; dashed line is for a parcel in the 1500 to 2000-meter layer. Intervals are six hours.

FIGURE 38c. Synoptic trajectory of air parcels arriving at Philadelphia at 1300 EST, August 6, 1979. Solid line indicates parcel in the 500 to 1000-meter layer; dashed line is for a parcel in the 1500 to 2000-meter layer. Intervals are six hours.

FIGURE 38d. Synoptic trajectory of air parcels arriving at Philadelphia at 1300 EST, August 7, 1979. Solid line indicates parcel in the 500 to 1000-meter layer; dashed line is for a parcel in the 1500 to 2000-meter layer. Intervals are six hours.

data, as determined from the Summit Bridge, DE (Site 1), acoustic sounder records indicate that rural mixing heights exceeded 1000 m on all days during the episode and reached this level between 0900 and 1000 EST. However, analysis of the acoustic sounder traces reveals that the intensity of mixing ranged from weak to very weak on August 4, 5, and 6. The intensity of mixing within the mixed layer is related to "thermal roots" appearing on acoustic sounder traces. Thermal roots appear on acoustic sounder traces as vertical spikes that taper with height. They are typical of free convection conditions (after the breakup of the ground-based inversion) with light winds and strong radiational heating (Baxter et al., 1978). The degree of mixing is a function of both the darkness and vertical extent of the thermal roots. The vertical extent of the thermal roots for August 4, 5, 6, and 7 after the surface-based inversion was lifted is given in Table 26. The table shows that, while mixing occurred through the 1000 m level, it was not vigorous and thermal roots displayed little vertical extent, seldom exceeding 300 m. Vertical mixing on August 7 was somewhat more vigorous in comparison to the other case study days.

4.5.3 Precursor Patterns

The 6:00 to 9:00 a.m. LDT averages of NMHC and NO_x, along with the ratio of NHMC to NO_x for rural and urban sites, are given in Tables 27 through 30 for August 4, 5, 6, and 7, respectively. Precursor concentrations were generally lower on these days than on other case study days. With the exception of Camden, NJ (Site 10), urban and near-urban sites recorded 6:00 to 9:00 a.m. LDT average NO_x concentrations lower than 0.10 ppm on each of these days. Camden reached an NO_x concentration of 0.10 ppm on August 6, but measured lower concentrations on the other days. Franklin Institute (Site 13) recorded hourly-averaged NO_x levels in excess of 0.10 ppm later in the morning on August 6 and 7. Much of the NMHC data at the urban and near-urban sites is missing for these days. The Air Management Service Laboratory (Site 14) was the only urban site that recorded NMHC on each of these days and the 6:00 to 9:00 a.m. LDT average concentrations at this site were less than 0.50 on each day. Whereas most sites recorded low precursor concentrations, it should be noted that Chester, PA, recorded a 6:00 to 9:00 a.m. LDT average NMHC concentration of 2.5 ppm on August 4. Precursor concentrations at rural sites were, as usual, low, although on August 4 Lumberton, NJ (Site 3), experienced 6:00 to 9:00 a.m. LDT NO and NMHC concentrations of 0.03 and 0.3 ppm,

Table 26. VERTICAL EXTENT OF THERMAL ROOTS (meters) AS DETERMINED FROM ACOUSTIC SOUNDER DATA AT SUMMIT BRIDGE, DE (Site 1).

Date	Time (EST)							
	0900	1000	1100	1200	1300	1400	1500	1600
August 4	0	180	180	200	250	240	180	100
August 5	180	250	270	270	240	210	200	140
August 6	220	300	300	320	340	290	240	160
August 7	280	400	400	360	280	300	340	300

Table 27. 6:00 to 9:00 a.m. LDT (0500-0800 EST) AVERAGES OF NO_x and NMHC (ppm) AND THE RATIO OF NMHC TO NO_x FOR RURAL AND URBAN SITES ON AUGUST 4.

Site No.	Rural Sites	6:00 to 9:00 a.m. LDT Averages		
		NO_x	NMHC	NMHC/NO_x Ratio
1	Summit Bridge, DE	0.01	0.1	7.0:1
2	Downingtown, PA	0.02	0.1	4.3:1
3	Lumberton, NJ	0.03	0.3	10.0:1
4	Robbinsville, NJ	0.02	--	--
5	Van Hiseville, NJ	0.01	--	--
	Urban Sites			
6	Chester, PA	--	2.5	--
8	Northeast Airport, PA	0.01	--	--
10	Camden, NJ	0.05	--	--
12	So. Broad & Spruce Streets, Philadelphia, PA	0.07	--	--
13	Franklin Institute, Philadelphia, PA	0.06	--	--
14	AMS Lab, Philadelphia, PA	0.04	0.5	11.8:1

Table 28. 6:00 to 9:00 a.m. LDT (0500-0800 EST) AVERAGES OF NO_x and NMHC (ppm) AND THE RATIO OF NMHC TO NO_x FOR RURAL AND URBAN SITES ON AUGUST 5.

Site No.	Rural Sites	6:00 to 9:00 a.m. LDT Averages		
		NO_x	NMHC	NMHC/NO_x Ratio
1	Summit Bridge, DE	0.00	0.0	--
2	Downingtown, PA	0.01	0.1	10.0:1
3	Lumberton, NJ	0.03	0.2	5.7:1
4	Robbinsville, NJ	0.00	--	--
5	Van Hiseville, NJ	0.00	--	--
	Urban Sites			
10	Camden, NJ	0.04	--	--
12	So. Broad & Spruce Streets, Philadelphia, PA	0.03	--	--
13	Franklin Institute, Philadelphia, PA	0.03	--	--
14	AMS Lab, Philadelphia, PA	0.03	0.3	10.0:1

Table 29. 6:00 to 9:00 a.m. LDT (0500-0800 EST) AVERAGES OF NO_x and NMHC (ppm) AND THE RATIO OF NMHC TO NO_x FOR RURAL AND URBAN SITES ON AUGUST 6.

Site No.	Rural Sites	6:00 to 9:00 a.m. LDT Averages		
		NO_x	NMHC	NMHC/NO_x Ratio
1	Summit Bridge, DE	0.01	0.0	3.0:1
2	Downingtown, PA	0.01	0.1	7.0:1
3	Lumberton, NJ	0.03	0.3	5.5:1
4	Robbinsville, NJ	0.03	--	--
5	Van Hiseville, NJ	0.01	--	--
	Urban Sites			
10	Camden, NJ	0.10	--	--
12	So. Broad & Spruce Streets, Philadelphia, PA	0.05	--	--
13	Franklin Institute, Philadelphia, PA	0.06	--	--
14	AMS Lab, Philadelphia, PA	0.04	0.4	10.0:1

Table 30. 6:00 to 9:00 a.m. LDT (0500-0800 EST) AVERAGES OF NO_x and NMHC (ppm) AND THE RATIO OF NMHC TO NO_x FOR RURAL AND URBAN SITES ON AUGUST 7.

Site No.	Rural Sites	6:00 to 9:00 a.m. LDT Averages		
		NO_x	NMHC	NMHC/NO_x Ratio
1	Summit Bridge, DE	0.02	--	--
2	Downingtown, PA	0.03	0.0	1.0:1
3	Lumberton, NJ	0.04	0.2	4.2:1
4	Robbinsville, NJ	0.02	--	--
5	Van Hiseville, NJ	0.01	--	--
	Urban Sites			
6	Chester, PA	--	0.2	--
10	Camden, NJ	0.07	--	--
12	So. Broad & Spruce Streets, Philadelphia, PA	0.04	0.4	10.0:1
13	Franklin Institute, Philadelphia, PA	0.06	--	--
14	AMS Lab, Philadelphia, PA	0.05	0.3	6.6:1

respectively. These were almost as high as the concentrations measured at the near-urban Air Management Service Laboratory (Site 14) on this day.

4.5.4 Ozone Patterns

The areas of peak afternoon ozone on each of the four study days are shown in Figures 39 through 42. On August 4, high ozone levels (greater than 0.10 ppm) were recorded at stations to the southeast and northeast of Philadelphia. On August 5, high levels were measured at Summit Bridge, DE (Site 1), and Ancora, NJ (Site 11), southwest and southeast of Philadelphia, respectively. On August 6 the high levels were measured at Lumberton, NJ (Site 3), east of Philadelphia, and Ancora, NJ. On August 7, the highest concentrations occurred to the east and southwest.

A comparison of the areas of peak concentrations, as shown in Figures 39 through 42, and the resultant wind directions listed earlier in Table 20, show a general pattern of peak ozone concentrations occurring downwind of Philadelphia, with some interesting exceptions.

August 4 is a case of peak ozone concentrations not occurring downwind of Philadelphia. Robbinsville, NJ (Site 4), recorded the highest ozone level in the study area (0.144 ppm) on August 4 despite its location northeast of Philadelphia. At this site, weak northerly or northwesterly flow occurred in the morning hours, whereas stronger northeasterly flow was prevalent by 1500 EST. Other sites in the northeast section of the study area also reported winds from the northeast in the afternoon, whereas winds at Downingtown, PA (Site 2), Chester, PA (Site 6), New Brunswick, NJ (Site 16), and Philadelphia International Airport (Site 17) reported winds from the northwest. An example of the afternoon surface wind flow on this day is presented on Figure 43, which shows a streamline analysis at 1500 EST. This flow pattern set up an area of convergence just east of Philadelphia. This is supported by National Weather Service observations of towering cumulus clouds to the southeast of Philadelphia during the afternoon, and by pibal data which indicate that the winds were northerly or northwesterly over Wilmington, DE and northerly to northeasterly over Trenton, NJ throughout the afternoon. The convergent wind flow possibly resulted in a merging of the New York and Philadelphia plumes just southeast of Philadelphia, which helps explain the ozone pattern indicated in

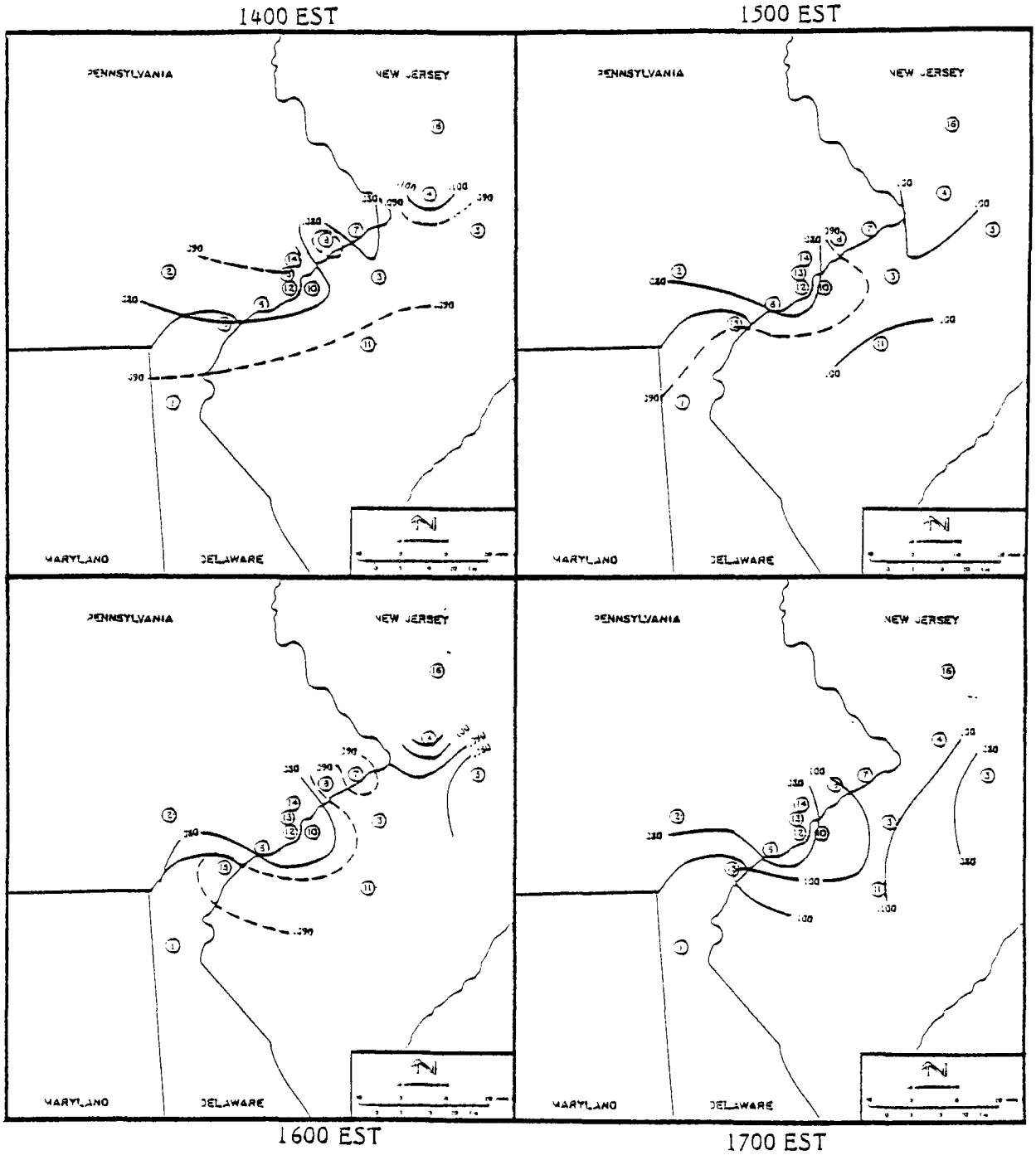


FIGURE 39. Isopleths of ozone at 1400, 1500, 1600, and 1700 EST, August 4, 1979.

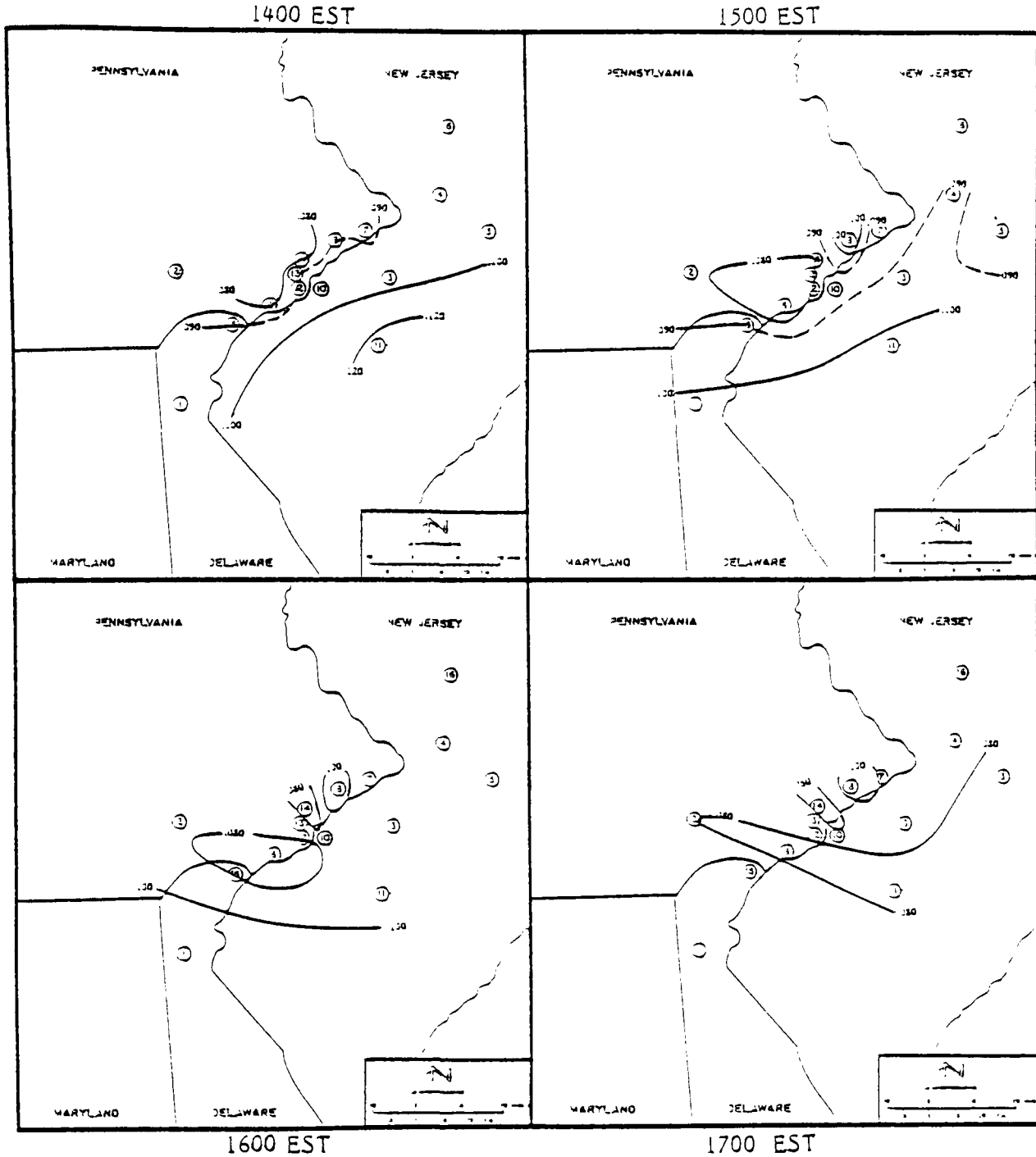


FIGURE 40. Isopleths of ozone at 1400, 1500, 1600, and 1700 EST, August 5, 1979.

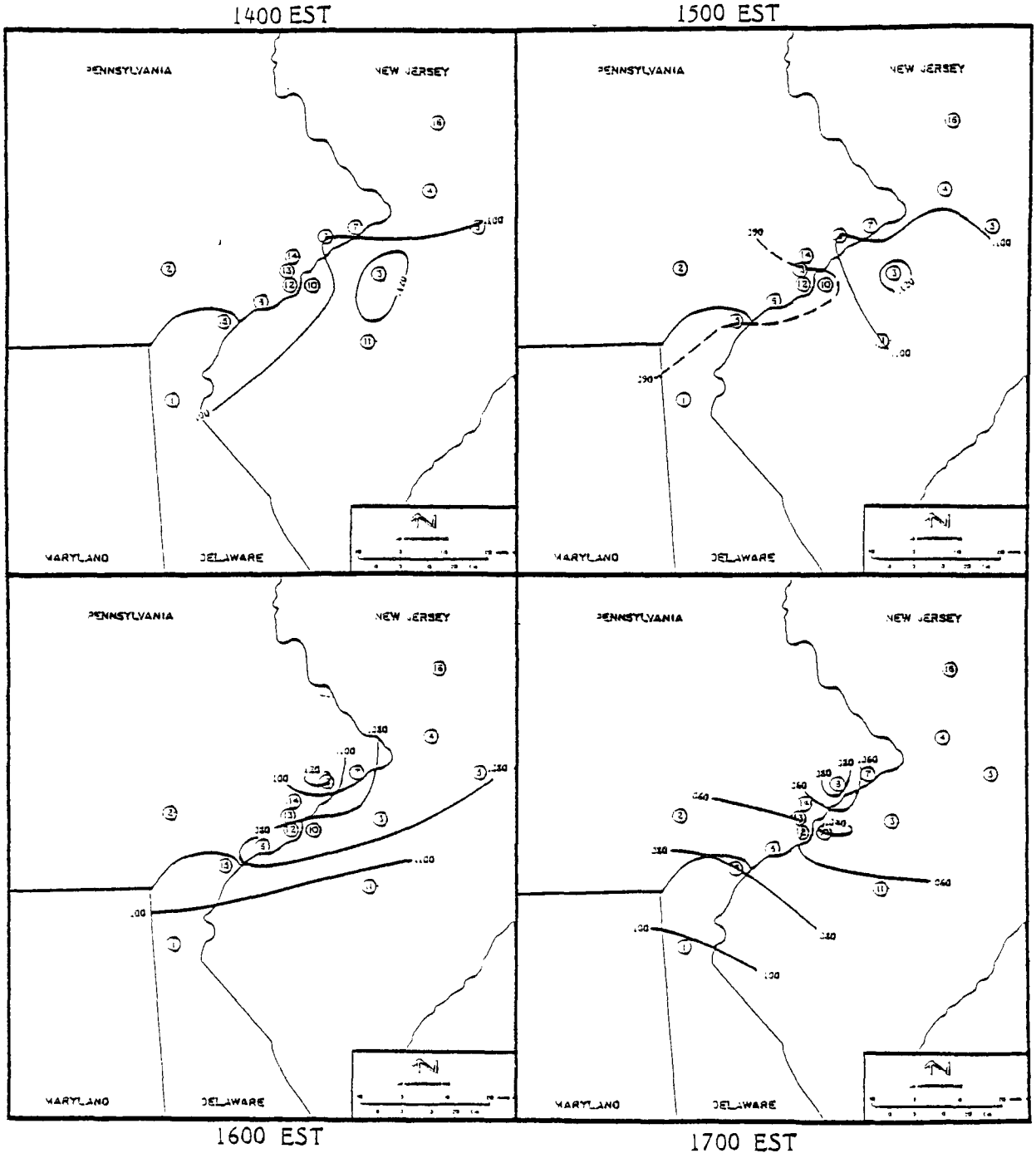


FIGURE 41. Isopleths of ozone at 1400, 1500, 1600, and 1700 EST, August 6, 1979.

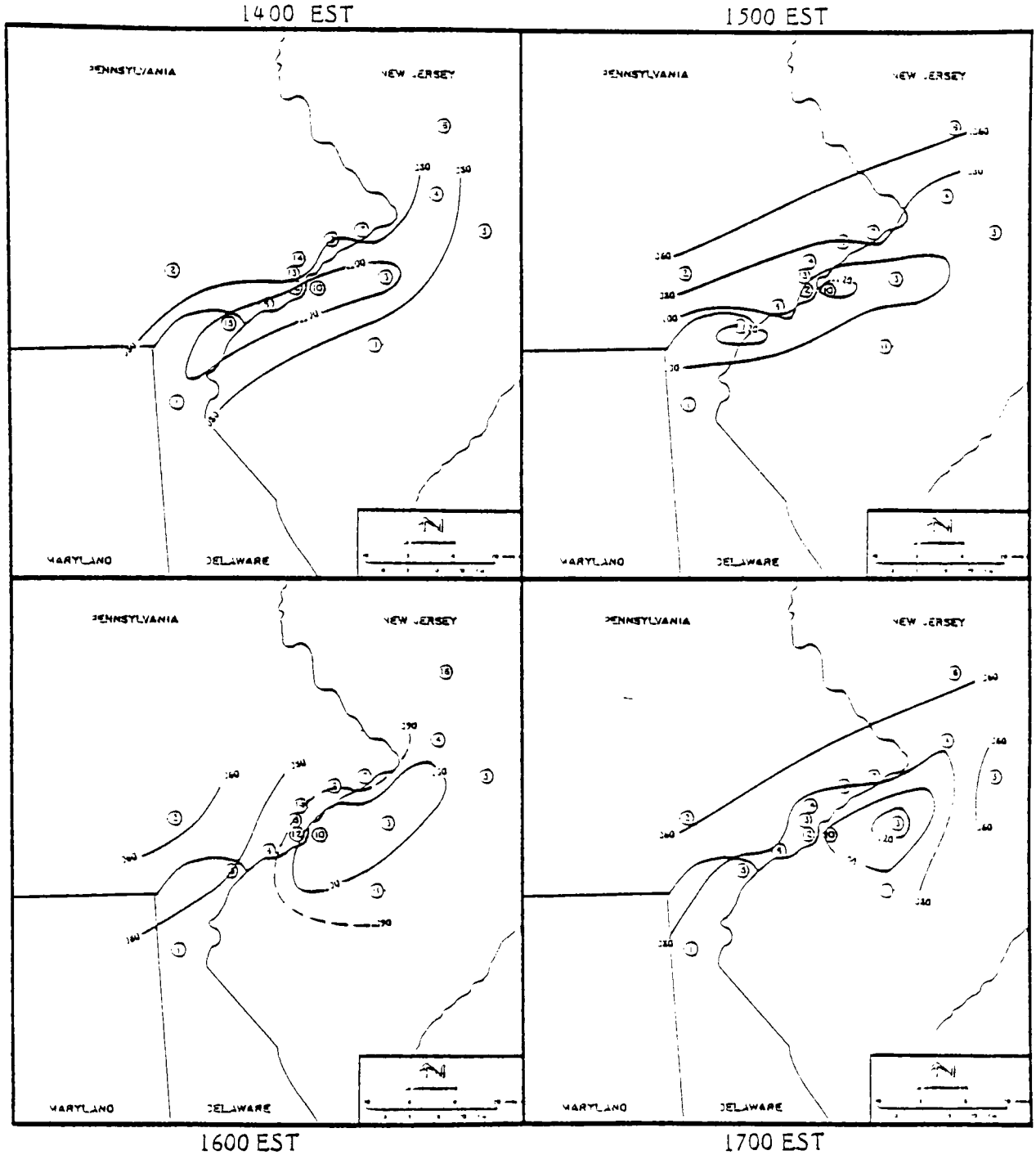


FIGURE 42. Isopleths of ozone at 1400, 1500, 1600, and 1700 EST, August 7, 1979.

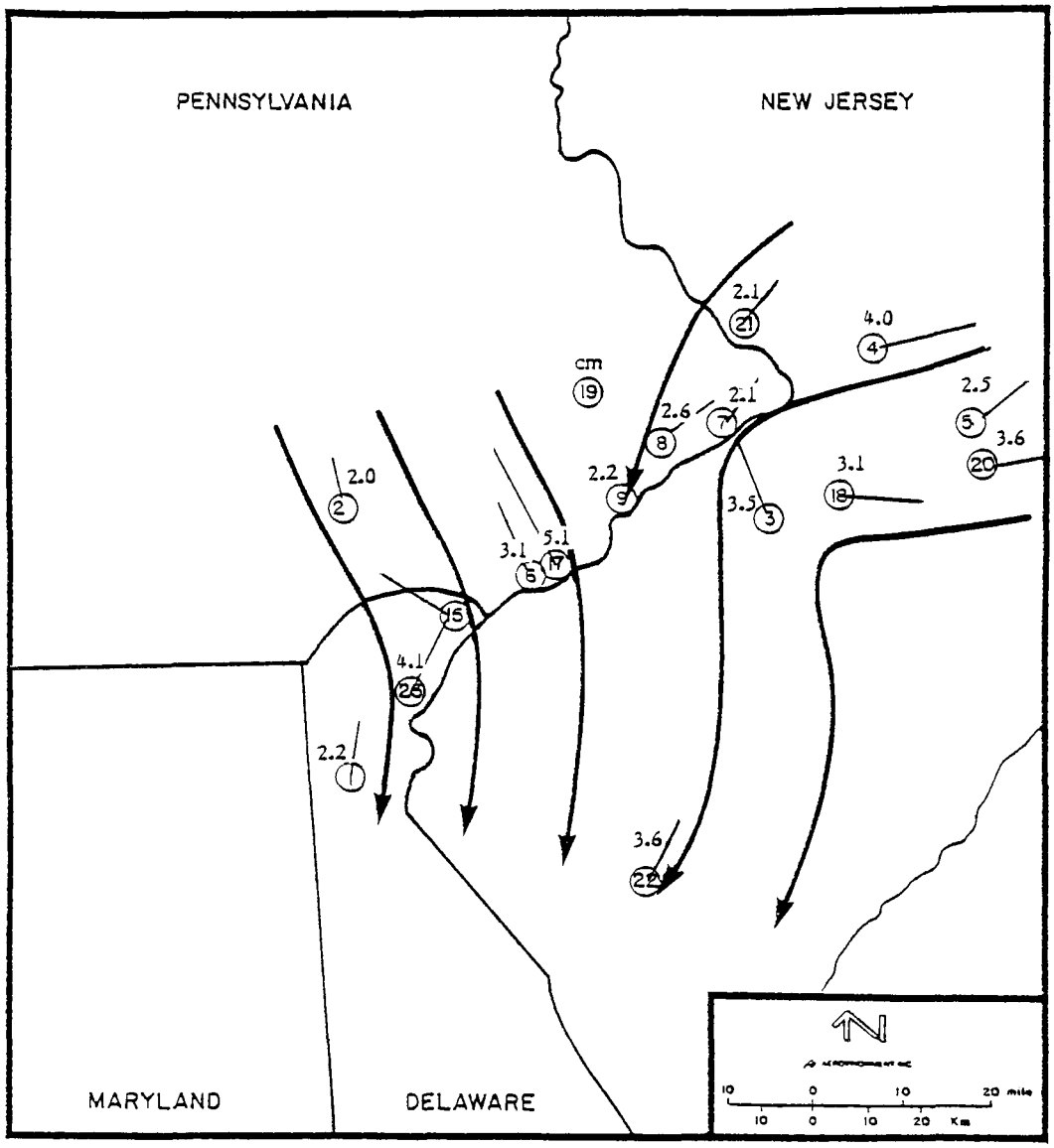


FIGURE 43. Streamline analysis depicting the surface flow across the study area at 1500 EST on August 4, 1979. The numbers by the site indicate wind speeds (meters per second).

Figure 39. In particular, in light of the observed low morning concentrations in Philadelphia on this day, it appears that high ozone formed from emission sources in northern New Jersey was transported across central New Jersey and impacted Robbinsville, NJ (Site 4), Bristol, PA (Site 7), North Philadelphia Airport (Site 8), and Lumberton, NJ (Site 3), in the late afternoon. Evidence of ozone transported aloft is presented later.

Mesoscale surface trajectories constructed for selected air parcels on August 4 confirm the above theory. Air parcels traveled generally north to south and Philadelphia emissions were advected far to the south. Figure 44 shows trajectories ending at Robbinsville, NJ (Site 4), and North Philadelphia Airport (Site 8) at times of peak ozone concentrations (1600 and 1900 EST, respectively). Also shown is a trajectory beginning in downtown Philadelphia at 0600 EST. The air parcels arriving at Robbinsville, NJ (Site 4), and North Philadelphia Airport (Site 8) carried ozone concentrations of 0.144 ppm and 0.130 ppm, respectively. They originated near the precursor-rich areas of northern New Jersey. The air parcel originating in downtown Philadelphia is advected southward into an area for which no ozone data are available, although Ancora, NJ (Site 11), southeast of Philadelphia, reported a peak concentration of 0.102 ppm at 1700 EST. Flow reversal at the end point of this trajectory at about 1700 EST indicates that the Philadelphia plume did not continue to the south but remained in the study area for possible contribution to pollutant concentrations on August 5.

The highest ozone concentration recorded on August 5 (0.135 ppm) occurred to the southeast of Philadelphia at Ancora, NJ (Site 11), at 1300 EST. The surface mesoscale trajectories shown in Figure 45 show that this site was almost directly downwind of Philadelphia. However, as was noted earlier, there was no indication of high precursor concentration in Philadelphia on this day. The 6:00 to 9:00 a.m. LDT average NO_x concentrations were less than 0.05 at all the urban and near-urban sites that reported this pollutant on this day (Table 28). Therefore, the high ozone level measured at Ancora may have resulted from long-range transport or carry-over from the previous day. This idea is supported by the fact that high ozone concentrations were measured throughout the study area during the day. Specifically, some high values recorded on this day were 0.119 ppm at Summit Bridge, DE (Site 1), at 1600 EST; 0.105 ppm at Van Hiseville, NJ (Site 5), at 1100 EST; 0.120 ppm at North Philadelphia Airport (Site 8), at 1600 EST; and 0.100 at

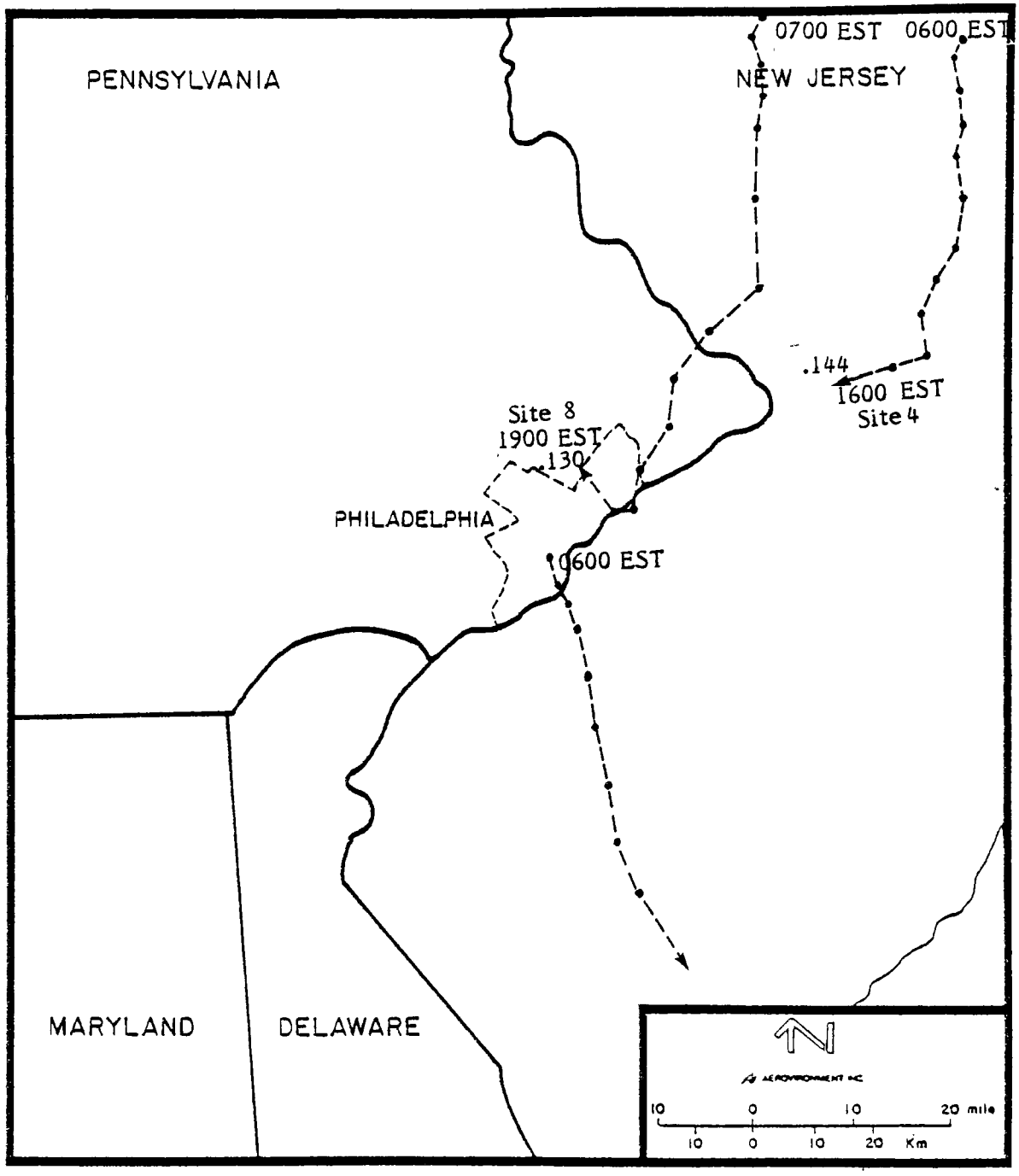


FIGURE 44. Surface trajectory for various air parcels located within the study area on August 4, 1979. Solid line indicates a trajectory beginning at downtown Philadelphia at 0600 EST; dashed lines are parcels ending at the indicated site and time. Dots show positions of the parcels at one-hour intervals.

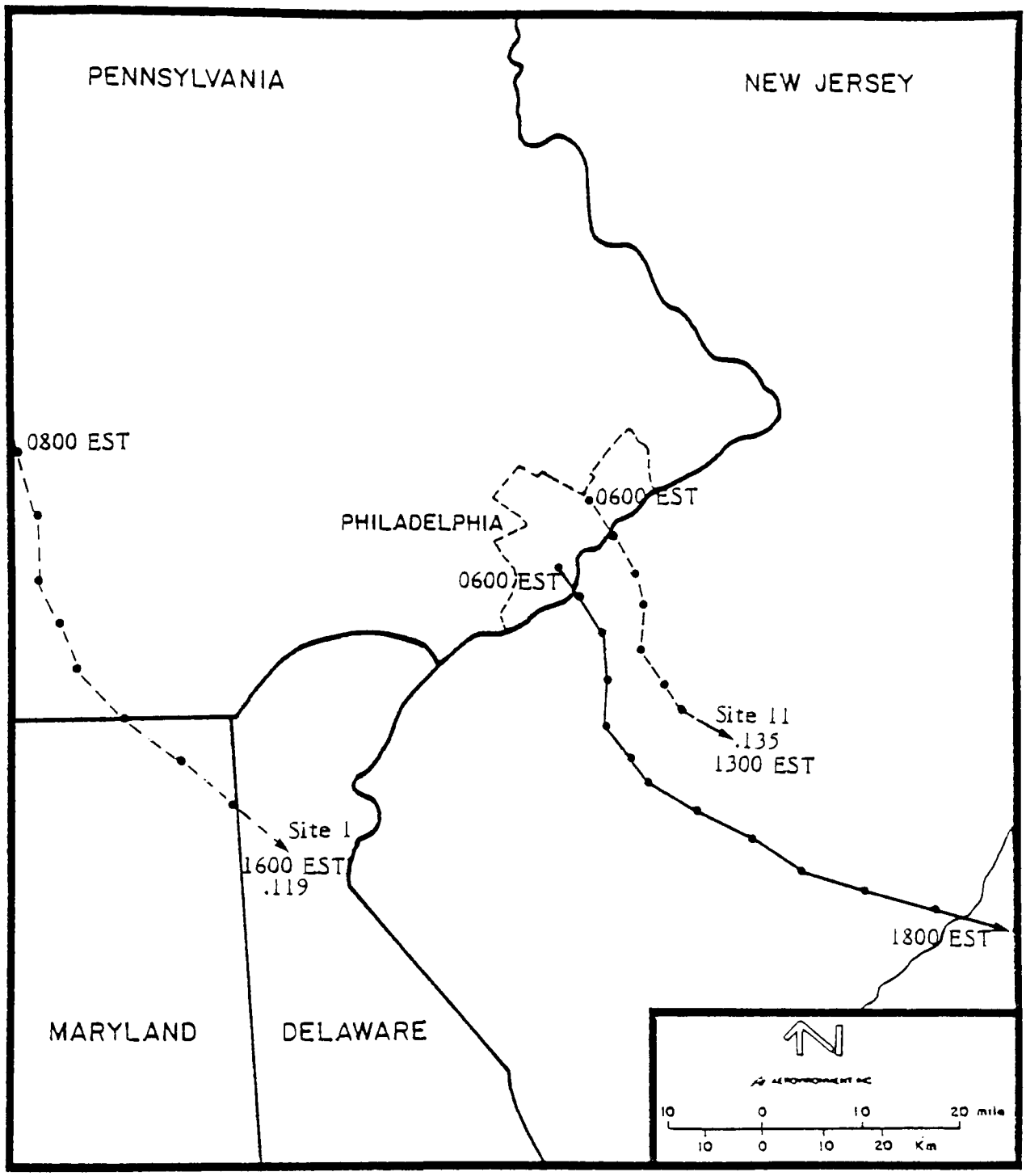


FIGURE 45. Surface trajectory for various air parcels located within the study area on August 5, 1979. Solid line indicates a trajectory beginning at downtown Philadelphia at 0600 EST; dashed lines are for parcels ending at the indicated site and time. Dots show the positions of the parcels at one hour intervals.

Franklin Institute (Site 13) at 1200, 1400, and 1800 EST. These sites are located in urban and non-urban areas which do not appear to be downwind of major source areas. The surface trajectory for Summit Bridge, DE (Figure 45), indicates source areas for these air parcels to be primarily rural. Pibal data at Trenton, New Jersey, and Wilmington, Delaware, indicate that the winds aloft were also primarly westerly or northwesterly through 2000 m most of the day; however, northerly or northeasterly winds were reported below 800 m at Trenton prior to 1100 EST. Therefore, ozone transported aloft probably originated northwest of the study area. The magnitude of ozone levels transported aloft is discussed below.

On August 6, the ozone patterns and airflow patterns were very similar to those observed on August 5. The peak ozone concentration of 0.136 ppm was again recorded at Ancora, NJ (Site 11), again at 1300 EST. The mesoscale trajectories shown in Figure 46 indicate that (as on August 5) Ancora, NJ (Site 11), was directly downwind of Philadelphia. Ozone concentrations in excess of 0.10 ppm were again recorded at locations not downwind of Philadelphia (e.g., Sites 1, 3, and 5). The interesting point about the remarkable similarity between concentration patterns on August 5 and 6 is that August 5 was a Sunday and August 6 a Monday, and the central business district was the apparent upwind source area on both days. However, there was no indication of high morning precursors on August 5, whereas on August 6, Camden, New Jersey, measured a 6:00 to 9:00 a.m. LDT average NO_x concentration of 0.10 ppm.

Ozone patterns on the last day of the four-day episode revealed high ozone concentrations from the east to southwest of Philadelphia. The southwestern-most station on August 7, Summit Bridge, DE (Site 1), peaked much earlier than Lumberton, NJ (Site 3), to the east -- 1300 EST, as compared to 1700 EST. The mesoscale trajectories shown in Figure 47 help explain this phenomenon. A dramatic flow reversal is indicated at about 1100 EST. At this time, air parcels carried to the southwest were advected back toward the northeast. An air parcel originating downtown at 0600 EST was advected to near Wilmington, and then back up to Claymont, DE (Site 15), by 1500 EST, where a 0.120 ppm ozone was recorded.

The area of origin of the parcel carrying the maximum study area ozone concentration (0.129 ppm) on August 7, as indicated in Figure 47, is very near to the area of peak

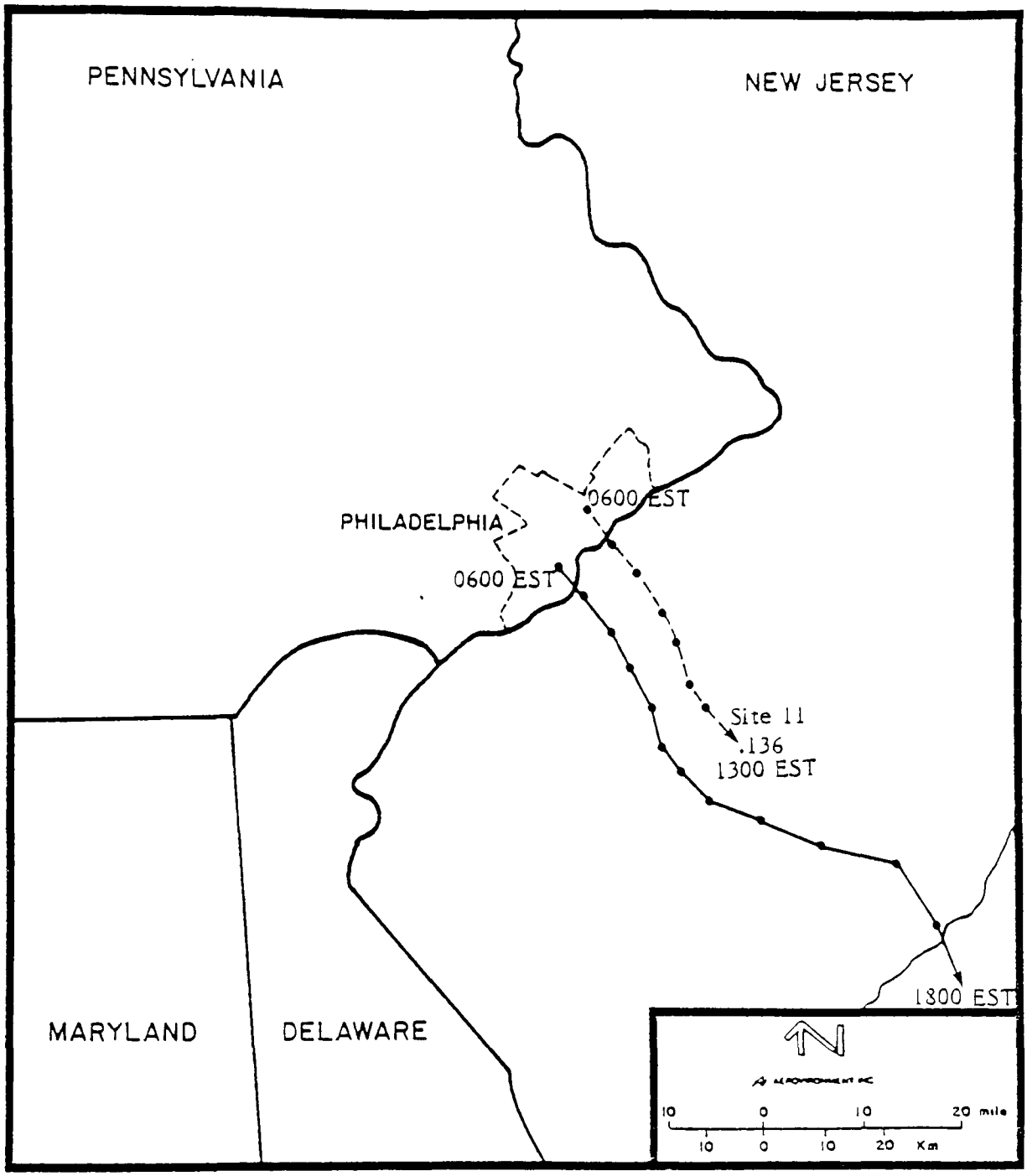


FIGURE 46. Surface trajectory for various air parcels located within the study area on August 6, 1979. Solid line indicates a trajectory beginning at downtown Philadelphia at 0600 EST; dashed lines are for parcels ending at the indicated site and time. Dots show the positions of the parcels at one hour intervals.

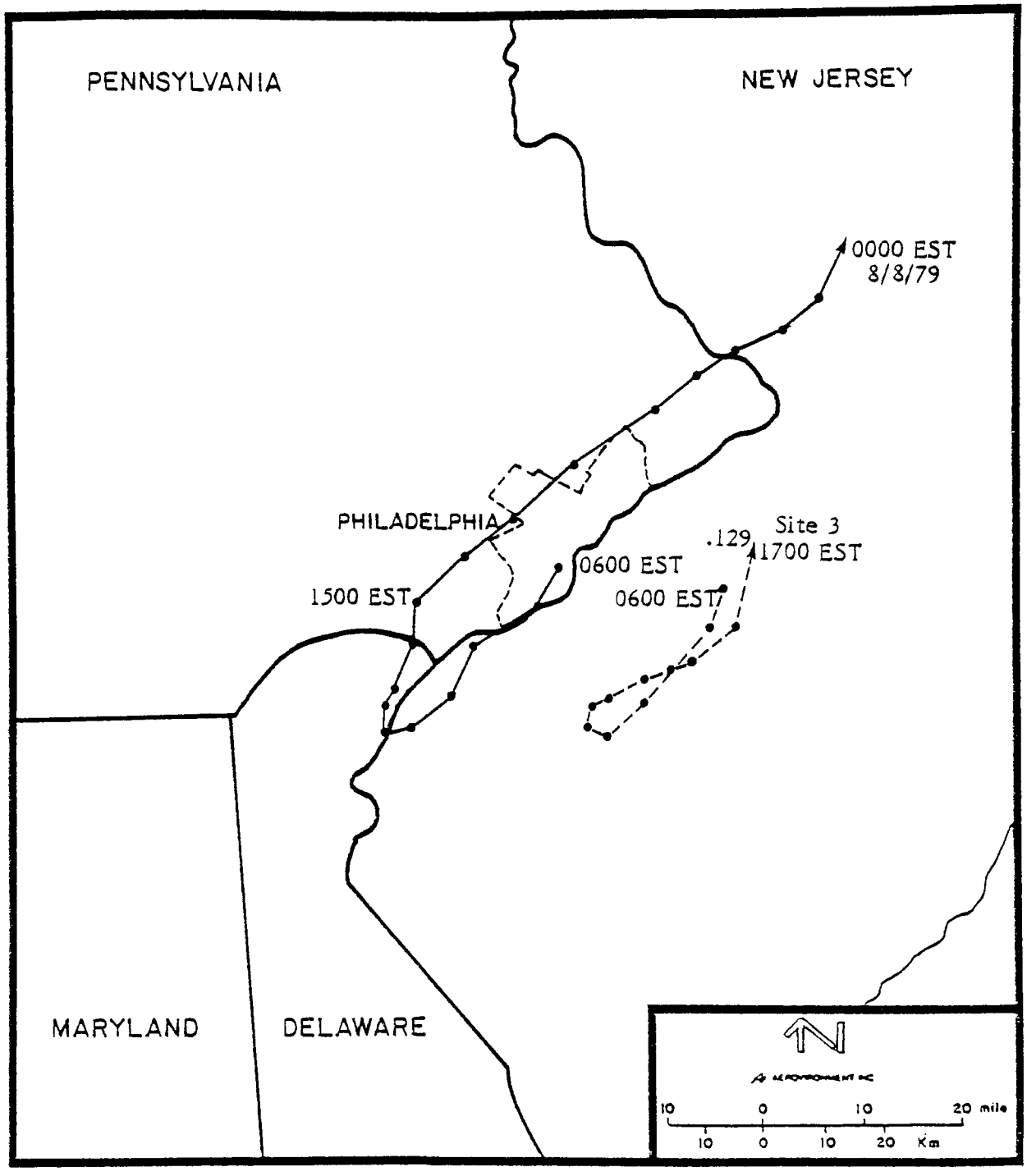


FIGURE 47. Surface trajectory for various air parcels located within the study area on August 7, 1979. Solid line indicates a trajectory beginning at downtown Philadelphia at 0600 EST; dashed lines are for parcels ending at the indicated site and time. Dots show the positions of the parcels at one hour intervals.

ozone -- Lumberton, NJ (Site 3). Morning NO and NMHC precursor concentrations at Lumberton, NJ (Site 3), were 0.04 and 0.2 ppm, respectively (6:00 to 9:00 a.m. EDT average), levels not usually associated with high ozone concentrations.

4.5.5 NO_2 Patterns

Peak NO_2 concentrations for the four days (August 4 through 7) ranged from 0.070 to 0.090 ppm. These peak concentrations occurred in Philadelphia, with the exception of August 6, when the peak NO_2 concentration occurred east of Philadelphia at Lumberton, NJ (Site 3). The NO_2 peak of 0.074 ppm at Site 3 occurred at the unusual time of 0200 EST. Sites to the west (Philadelphia) and to the northeast (Robbinsville, NJ, Site 4) of Site 3 also reported elevated levels at this time. All the peak concentrations occurring in Philadelphia on August 4, 5, and 7 were reported in the late evening or early morning hours, reflecting the decomposition of ozone into NO_2 and oxygen. Daytime NO_2 levels were generally much lower, with rural stations reporting less than 0.01 ppm.

4.5.6 Concentrations Aloft

Direct measurement of concentrations aloft by the helicopter was made on all four study days. Average ozone concentrations aloft were determined from helicopter soundings at upwind sites and are summarized in Table 31. No early morning soundings were made on August 4 or 5.

Transport aloft on August 4 appears to be about average when compared to other case study days. Average ozone concentrations of 0.05 to 0.06 ppm were observed in late morning soundings made over West Chester, PA, to the west of Philadelphia, over Philadelphia, and over Medford, NJ, to the east of Philadelphia. Moreover, concentrations aloft recorded during transects between West Chester, PA, downtown Philadelphia, and Medford, NJ, on this flight were between 0.03 and 0.06 ppm. Surface stations reported similar levels at 1000 EST, the first hour of uninhibited vertical mixing. Concentrations aloft obtained during the mid-afternoon helicopter flight present some interesting data. Evidence was presented earlier in discussing ozone patterns, which indicated that the high ozone levels recorded at the surface to the northeast, east, and southeast of Philadelphia in part resulted from ozone transported from northern New Jersey and New York City.

Table 31. AVERAGE MIXED LAYER OZONE CONCENTRATIONS ALOFT ON AUGUST 4, 5, 6, AND 7, 1979 (morning concentrations reflect levels from the top of that afternoon's mixing layer to the top of the layer of ozone depletion).

Date	Time (EST)	Approximate Location	Position with Respect to Philadelphia Under Prevailing Flow	Ozone (ppm)
August 4	0936	West Chester, PA	Crosswind	0.060
	1012	Downtown	--	0.050
	1052	Medford, NJ	Crosswind	0.060
	1328	Downtown		0.060
	1410	Robbinsville, NJ	Crosswind	0.070
	1452	15 km SE of Medford, NJ	Crosswind	0.110
August 5	0758	West Chester, PA	Crosswind	0.050
	0833	Downtown	--	0.055
	0907	Medford, NJ	Downwind	0.060
August 6	0555	Pipersville, PA	Upwind	0.030
	0631	Pottstown, PA	Upwind	0.030
	0702	Downtown	--	0.025
	0919	Willow Grove, PA	Upwind	0.035
	0948	Downtown	--	0.040
	1028	Seabrook, NJ	Downwind	0.060
	1418	Hammonton, NJ	Downwind	0.090
August 7	0557	Pipersville, PA	Crosswind	0.015
	0628	Pottstown, PA	Crosswind	0.020
	0656	Downtown	--	0.015
	0855	Willow Grove, PA	Upwind	0.020
	0925	Downtown	--	0.025
	1020	Seabrook, NJ	Crosswind	0.020
	1328	Downtown	--	0.050
	1407	Hammonton, NJ	Crosswind	0.050
	1437	Seabrook, NJ	Crosswind	0.060

Figure 48 shows ozone concentrations recorded by the helicopter during mid-afternoon transects from (a) downtown Philadelphia to Robbinsville, NJ; (b) from Robbinsville, NJ, to the site 15 km southeast of Medford, NJ (Site G in Figure 6); and (c) from Site G to Wilmington, DE, where the helicopter landed. Moderate ozone levels, between 0.05 and 0.08 ppm were recorded between Philadelphia and Robbinsville and similar levels were recorded during a sounding made over Robbinsville. As the helicopter transected to the southeast portion of the study area, from Robbinsville to Site G, at an approximate altitude of 350 m MSL, higher ozone levels, between 0.08 and 0.12 ppm, were seen; the sounding made over Site G revealed ozone levels above 0.13 ppm at bout 700 m MSL. As the helicopter flew from Site G to Wilmington, DE, ozone levels were more variable than during the two previous transects, fluctuating between 0.08 and 0.15 ppm. As noted earlier, a zone of convergence characterized by towering cumulus existed earlier, southeast of Philadelphia at this time, which helps explain the variation.

Indications of transport aloft on August 5 are ambiguous. A mid-morning vertical sounding over West Chester, PA, is shown in Figure 49. It shows an average concentration in the mixed layer of 0.05 ppm, which is not particularly high. An inversion based just below 500 m is also apparent with generally light northerly winds at all levels. The ground- level concentration at nearby Downingtown, PA (Site 2), during the first hour of uninhibited vertical mixing (as determined from the Site 1 acoustic sounder) was 0.058 ppm, corresponding fairly well to the ozone levels aloft shown in Figure 49. However, ground-level ozone concentrations at Summit Bridge, DE (Site 1), and Van Hiseville, NJ (Site 5), during the first hour of uninhibited vertical mixing (as determined from the Site 1 acoustic sounder) were 0.084 and 0.104 ppm, respectively. Both these levels were among the highest 1000 EST concentrations observed at these sites and imply high levels of ozone transported aloft. While no helicopter data are available for near these sites in the morning on this day, the helicopter did record occasional values in excess of 0.150 ppm while transecting from Philadelphia to Medford, NJ, at about 1000 EST, as shown in Figure 50. Thus, morning ozone levels aloft were not homogeneous across the study area and pockets of elevated ozone aloft were apparent. This inhomogeneity may have been the result of the previous day's convergent wind flow as discussed earlier.

Measurements aloft in the afternoon indicate ozone levels of about 0.08 ppm over central New Jersey, increasing sharply to the southeast and south of Philadelphia. Very

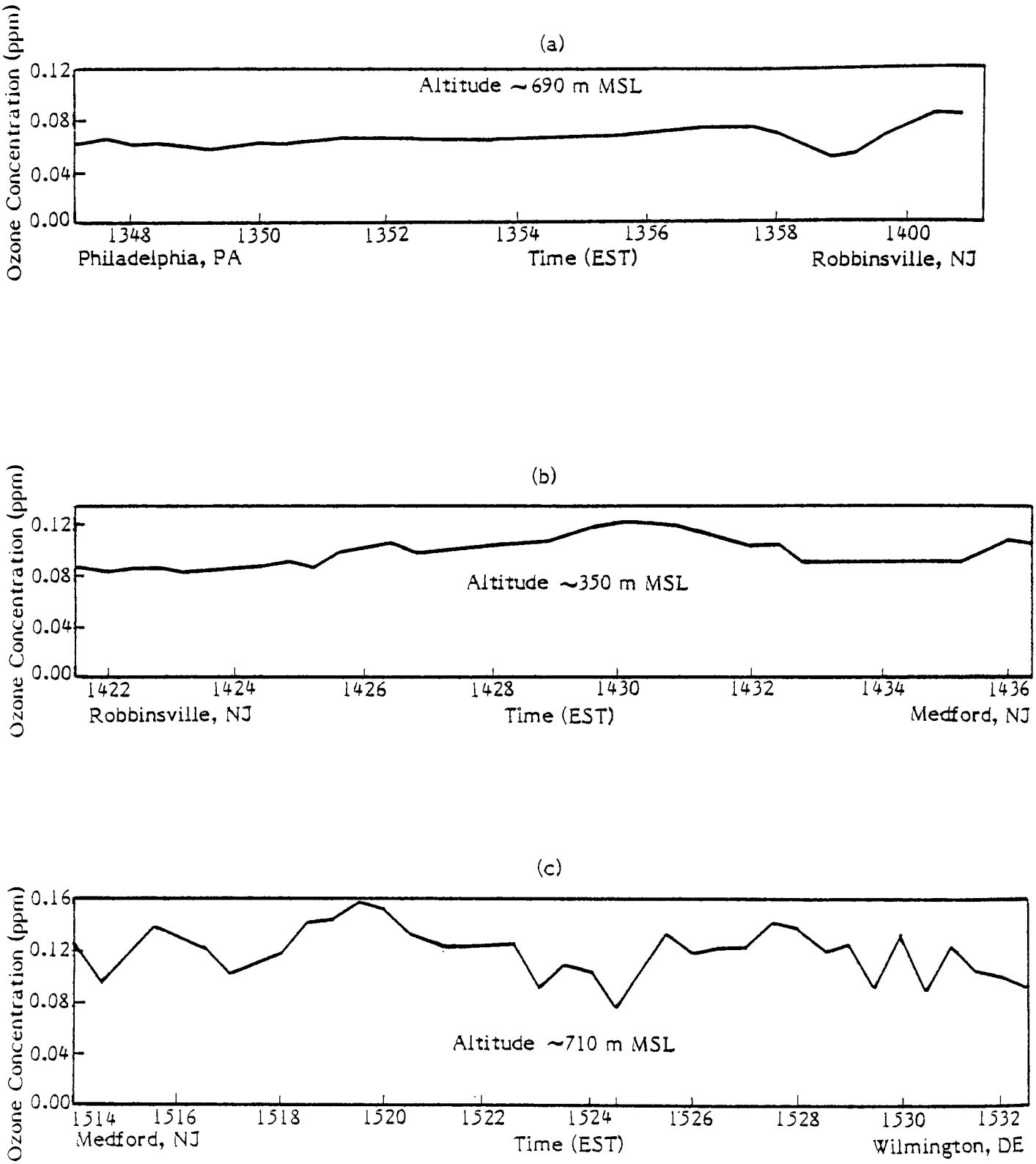


FIGURE 48. Ozone concentrations reported during helicopter transects during mid-afternoon flight on August 4, 1979. (a) Philadelphia, PA to Robbinsville, NJ; (b) Robbinsville, NJ to about 15 km southeast of Medford, NJ; (c) from 15 km southeast of Medford, NJ to Wilmington, DE.

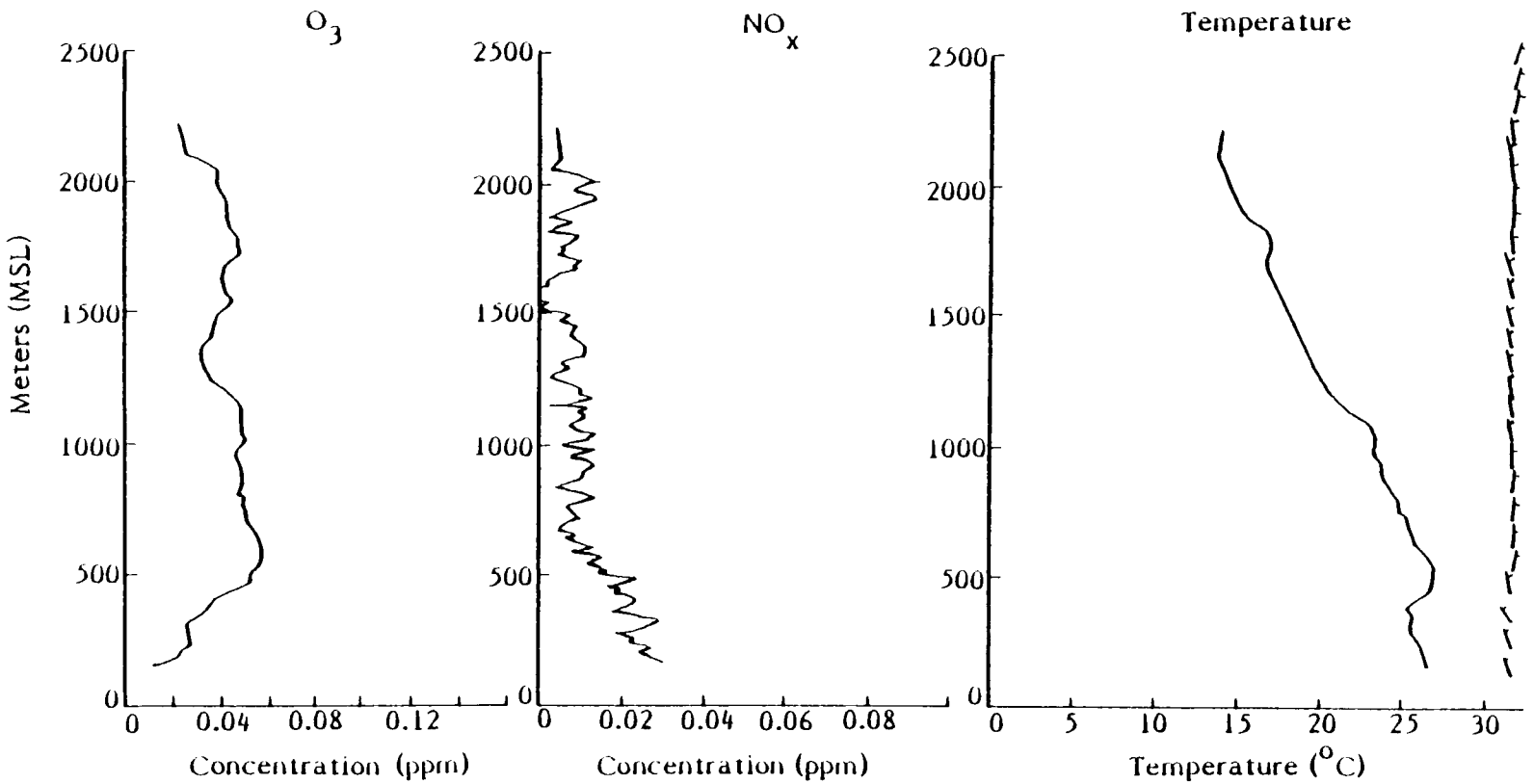


FIGURE 49. Vertical profiles of O_3, NO_x, and Temperature obtained by the instrumented helicopter over West Chester, PA (Site B) at 0758 on August 5, 1979. Also shown is the corresponding vertical wind profile. (Key: ↾ = North at 5 m/s)

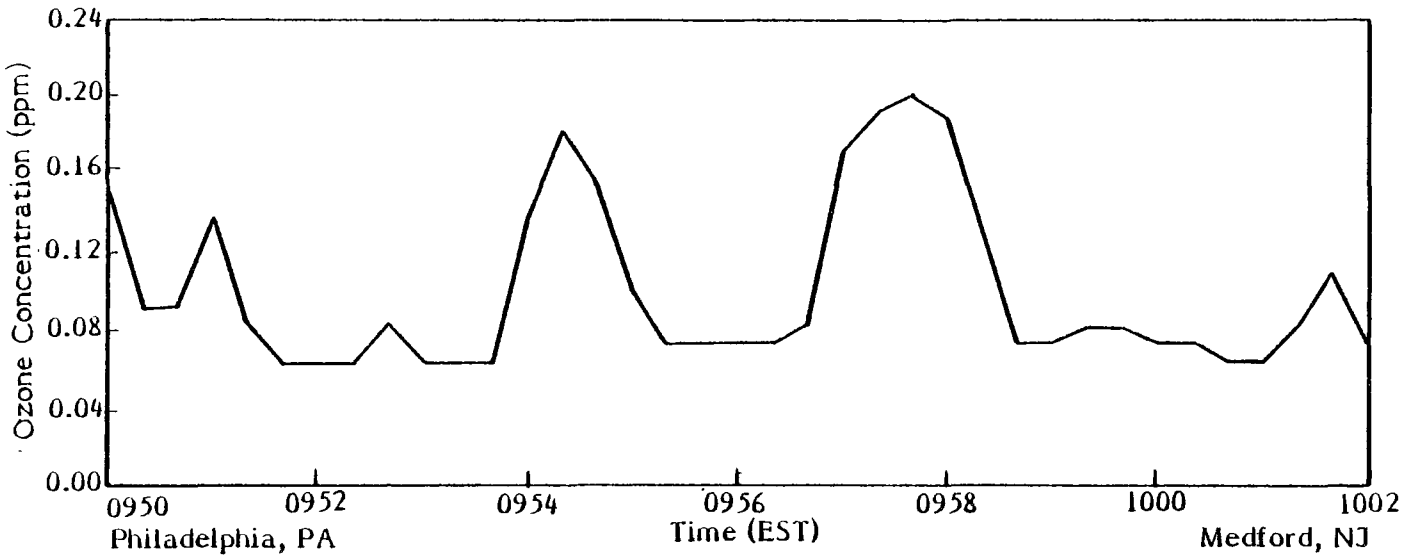


FIGURE 50. Ozone concentrations reported during helicopter transect from downtown Philadelphia to Medford, NJ on August 5, 1979 at an altitude of approximately 550 m MSL.

high concentrations (in excess of 0.200 ppm) were measured aloft during a transect from a location 15 km southeast of Medford, NJ, to Wilmington, DE, at about 1500 EST.

On August 6, indications of transport aloft from surface measurements are quite different from helicopter soundings. Many sites recorded elevated ozone levels during the first full hour of uninhibited vertical mixing, as determined by the acoustic sounder. At 1000 EST, the ozone levels were 0.080 ppm at Summit Bridge, DE (Site 1), 0.065 ppm at Lumberton, NJ (Site 3), 0.076 ppm at Robbinsville, NJ (Site 4), and 0.074 ppm at Van Hiseville, NJ (Site 5). These were all well-above average 1000 EST ozone concentrations and indicate significant ozone levels aloft. Considering that the flow direction on August 5 was from the northwest (see Figure 45), it is posible that a reservoir of elevated ozone was left aloft to the east and southeast of Philadelphia from the previous day. However, early morning helicopter soundings indicate much lower average ozone concentrations (about 0.03 ppm) aloft in the northwestern portion of the study area (see Table 31). Transects made during the morning flights also indicate low ozone concentrations aloft -- less than 0.05 ppm. Similar levels were measured at sites to the northwest of Philadelphia at 1000 EST; 0.035 ppm at Allentown, PA; 0.038 ppm at Lancaster, PA; 0.026 ppm at Reading, PA; 0.046 ppm at Morristown, PA; and 0.021 ppm at Bethlehem, PA (these sites record ozone concentrations but did not participate in the study). An afternoon transect made at approximately 430 m MSL between Hammonton, NJ, and Seabrook, NJ, southeast of Philadelphia (see Figure 6), at about 1430 EST indicated ozone concentrations in excess of 0.10 ppm and a sounding over Hammonton, NJ, showed an average ozone level in the mixed layer of 0.09 ppm. Ancora, NJ (Site 11), reported a surface concentration of 0.119 at this time.

Transport of ozone aloft on August 7 was apparently minimal. As on August 6, the early morning helicopter soundings show very low ozone levels aloft (Figure 51). This figure shows vertical profiles of ozone, NO_x, and temperature over Pottstown, PA, along with the vertical wind profile obtained at Robbinsville, NJ (Site 4). The wind profile is interesting, considering the dramatic flow reversal from northeast to southwest experienced at the surface later in the day. Average ozone levels observed aloft during all morning soundings were less than 0.025 ppm. Furthermore, ozone concentrations measured by the helicopter while transecting between sites were less than 0.06 ppm during the morning and mid-morning flights, and less than 0.08 ppm during afternoon

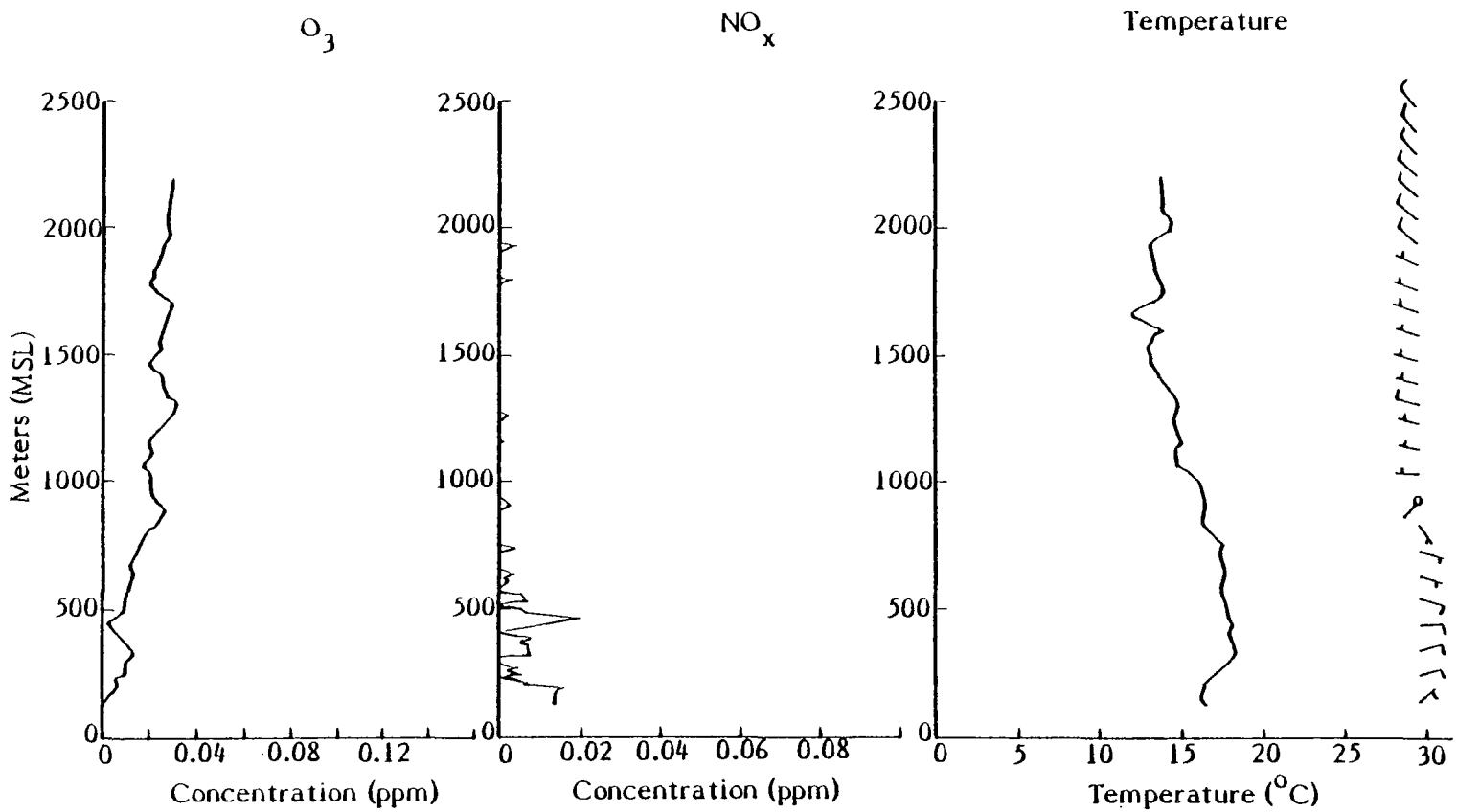


FIGURE 51. Vertical profiles of O_3, NO_x, and Temperature obtained by the instrumented helicopter over Pottstown, PA (Site J) at 0628 EST on August 7, 1979. Also shown is the corresponding wind profile. (Key: ↑ = North at 5 m/s)

flights after uninhibited mixing had occurred. Thus, little ozone was available aloft to supplement local production. Ozone levels observed at the surface on this day confirm the helicopter observations. The first hour of uninhibited vertical mixing was 1000 EST. Surface ozone levels observed at this time were 0.047 ppm at Summit Bridge, DE (Site 1), 0.031 ppm at Downingtown, PA (Site 2), and 0.042 ppm at Lumberton, NJ (Site 3), all much lower than the levels observed on the previous two days.

4.5.7 Hydrocarbon Species Data

Although August 4 was a Saturday, the early morning hydrocarbon levels at the Franklin Institute site were higher (but only slightly) than average and also higher than the industrial site samples. Again, some departures from average speciation were seen. Both samples at Franklin Institute were quite high in aromatics, especially C_8-C_{10}. In the 0700 to 0800 EST sample, this was balanced by high levels of C_4-C_5 paraffins, probably from a local source of gasoline vapor. In the early Franklin Institute sample, the iso-butane exceeded n-butane, which is unusual. In most samples, n-butane exceeds iso-butane, but n-butane is smaller than iso-pentane. But gasoline brands do differ in the distribution among those four species. The two industrial site samples were nearly average with only a slight increase in C_4 olefins, especially in the 0700 to 0800 EST sample.

Also on August 4, a sample taken at Flat Rock Park at the outskirts of Philadelphia at noon showed 222 ppbC of NMHC. This sample was quite near the overall sample average. The propene/acetylene ratio was 0.33; very near the automobile exhaust value and that for unreacted air. Most samples in this program were appreciably higher in propene than this.

Helicopter samples were also taken in the late morning of August 4 over the river near downtown. The two samples taken were similar in composition and quite normal, except for the 450-m altitude sample which showed 17.5 ppbC of iso-propylbenzene (cumene). As mentioned earlier, this is an important industrial hydrocarbon, and sporadic high concentrations may reflect chance sampling of a point source. The propene/acetylene ratios were again near those of gasoline engine exhaust.

A sample taken at 1255 EST in northwest Philadelphia on August 4 had an NMHC concentration of only 119 ppbC. Only 15 hydrocarbons were measurable, but these were compounds normally present in the largest concentrations.

Although peak ozone values of 0.135 ppm occurred on August 5, both Franklin Institute and industrial site samples had quite low NMHC in all four early morning samples. The type distributions were very close to the average. The species distribution was also very close to average. Since it was a Sunday, perhaps the composition of the air mass was not significantly affected by the emissions associated with low traffic density.

Two helicopter samples were taken on this Sunday over the Delaware River near downtown at about 0845 EST. The sample at 457 m had only 10 measurable hydrocarbons, totaling 59 ppbC. The type distribution appears abnormal because only one aromatic and no olefins (except ethylene, which is not credible) were measurable. The very low NMHC suggests that this sample was taken above the inversion. The mixing height was just over 147 m at this time. At 24 m altitude, the total NMHC was 447 ppbC, with a normal distribution. The iso-propylbenzene was only 1 ppbC compared to 17.5 ppbC on the previous day (August 4). A sample taken in Downingtown, PA at 0600 EST on August 5 yielded 149 ppbC with no abnormalities. This total is substantially lower than at the other sites probably because of its distance from heavy traffic areas.

The airflow on August 6 when the ozone reached 0.136 ppm was from the northwest. The mixing heights in late morning were about 600 meters. At Franklin Institute and industrial sites, NMHC was near or below average and the type distributions were within the normal range. All but the 0600 to 0700 EST Franklin Institute samples showed slightly elevated C_3-C_4 olefins.

Helicopter samples taken at 1000 EST near downtown at 488 m and at 18 m MSL were quite similar. In this case, the upper sample was taken just below the mixing height, which was 591 m. The species and type distributions showed no recognizable abnormalities. Iso-propylbenzene was not measurable (or at least not reported).

At 0600 EST samples were taken above Pipersville, PA (a rural area 52 km north of Philadelphia) at 457 m MSL. Only seven hydrocarbons were measured totaling 23 ppbC.

Near the surface about 127 ppbC were found. The unusual feature of this analysis is that methyl styrene was the only olefin reported except for 34 ppbC of ethylene. This is surely an artifact, since the higher elevation sample showed the same concentration. Acetylene was also not reported, otherwise this could be light automobile exhaust.

A sample taken at an unspecified time in northwest Philadelphia had only 102 ppbC of NMHC in a normal species distribution.

Winds on August 7 were light but the mixing heights were fairly high. The NMHC at 0500 to 0600 EST at the industrial site was, therefore, only 272 ppbC and only 369 at 0700 to 0800 EST. The early sample at Franklin Institute is missing but the 0700 to 0800 EST sample was fairly high (949 ppbC). A somewhat elevated level of higher aromatics ($C \geq 8$) may indicate an intrusion of a solvent. Otherwise, these three samples are quite normal. An early afternoon sample taken at Flat Rock Park in northwest Philadelphia was quite low (NMHC = 108 ppbC). The paraffin percentage is high probably because many aromatics were too small to measure, but the butanes and pentanes were readily measurable. Four helicopter samples were taken on this day. The two taken over Pipersville, PA far north of Philadelphia showed only 37 ppbC (at 0606 EST and 457 m MSL, and 26 ppbC at 0608 EST and 46 m MSL). The compounds detected are just those usually present in largest concentration. The other two helicopter samples were taken near downtown during mid-morning and had concentrations comparable to the Franklin Institute and industrial site samples (305 ppbC at 457 m MSL at 0936 EST, and 230 ppbC at 46 m MSL at 0939 EST). The distributions were normal, but it may be noteworthy that the higher altitude gave the higher concentrations.

4.6 AUGUST 10, 1979 (FRIDAY)

The interesting features of the August 10 case were (1) the implication of source areas to the southwest, (2) the advection of the central business district's emissions out of the study area under the influence of strong winds, and (3) the prefrontal nature of the high ozone levels.

The peak ozone concentration recorded on August 10 was 0.170 ppm. Seven of the fifteen operating stations recorded ozone concentrations in excess of 0.12 ppm and an additional five reported levels equal to or greater than 0.10 ppm. The peak NO_2 concentration was 0.080 ppm with five stations reporting NO_2 concentrations $\geq$ 0.05 ppm.

4.6.1 Synoptic Meteorology

The synoptic situation is shown in Figure 52. The study area was positioned in the warm sector of a frontal system after a warm frontal passage on the previous day. The Bermuda high-pressure cell, centered just off the Georgia coast, exerted some influence and, together with a low pressure center moving north of the Great Lakes, brought southwesterly flow to the study area. Afternoon and evening thundershowers occurred over the area, and the cold front associated with this cyclone passed through Philadelphia the following morning (August 11) cleansing out the study area. Thus, the high ozone levels of August 10 were associated with prefrontal conditions.

Synoptic trajectories terminating at Philadelphia on August 10 are shown in Figure 53. A long, over-land trajectory is evident. Due to high wind speeds, the air parcel in the 100- to 500-m layer passed over the Washington, D.C.-Baltimore area less than 12 hours prior to its arrival in Philadelphia.

4.6.2 Mesoscale Meteorology

Winds at all levels exhibited the highest speeds of any case study day. Resultant wind speeds were generally > 2.5 m/s at the surface all day, while winds aloft were generally about 8.0 m/s, as compared to 2 to 4 m/s on other case study days. Surface flows were southwesterly in the morning hours with significant horizontal shear in the

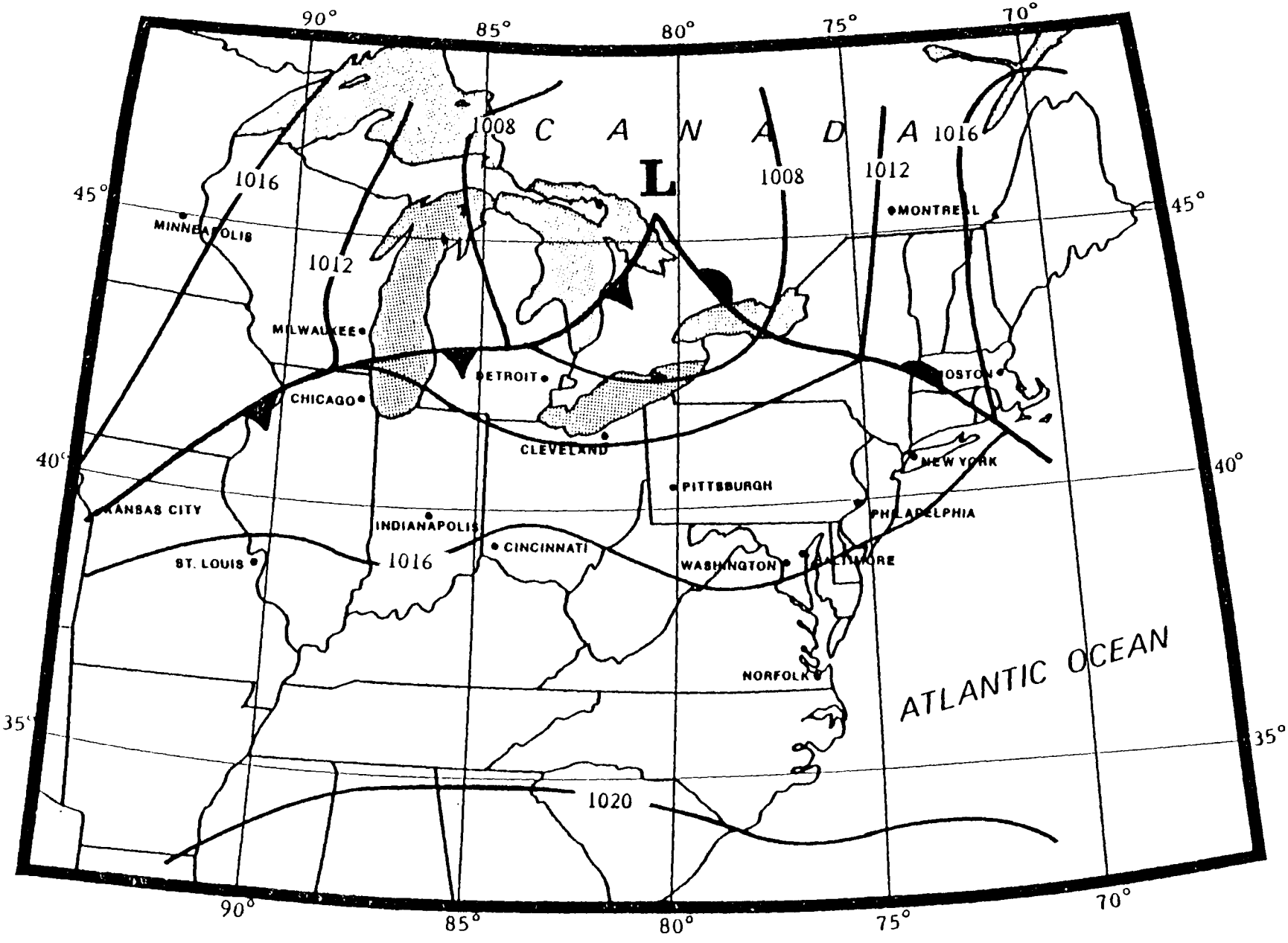


FIGURE 52. Synoptic situation, 0700 EST, August 10, 1979.

FIGURE 53. Synoptic trajectory of air parcels arriving at Philadelphia at 1300 EST, August 10, 1979. Solid line indicates parcel in the 500 to 1000-meter layer; dashed line is for a parcel in the 1500 to 2000-meter layer. Intervals

afternoon. Winds were southwesterly in the southwestern portion of the study area with stations elsewhere reporting northwesterly, all with high speeds. Winds aloft were more consistent from the west across the study area.

Late morning urban mixing heights were lower compared with other case study days, although afternoon mixing heights were relatively high. The 0900 EST mixing height (as determined by radiosonde observations) was 339 m, as compared to 1516 m at 1500 EST. Based upon surface temperatures between 0900 and 1500 EST and the 0900 sounding, mixing heights did not rise above 503 m MSL until 1300 EST and reached a maximum value of 1516 m MSL at 1400 EST. Rural mixing height, as derived from acoustic sounder data, did not break the 1000-m level until 1100 EST, the latest of any case study day. Vertical mixing was fair when compared to other case study days, while horizontal mixing was very vigorous due to high wind speeds.

4.6.3 Precursor Patterns

The 6:00 to 9:00 a.m. LDT averages of NO_x and NMHC, along with the ratio of NMHC to NO_x, are given in Table 32 for rural and urban sites. Morning downtown NMHC levels were substantial, as reflected in the 1.0 ppm 6:00 to 9:00 a.m. LDT average at South Broad Street (Site 12). The corresponding NO_x average was 0.050 ppm. Other urban sites were above average when compared to other case study days, despite the fact that ventilation was excellent due to the high wind speeds.

4.6.4 Ozone Patterns

Isopleths of ozone concentrations at 1300, 1400, 1500, and 1600 EST are shown in Figure 54. High concentrations (greater than 0.10 ppm) were recorded at sites east to the northeast, southeast, and southwest of Philadelphia during the afternoon. At 1500 EST, Claymont, DE (Site 15), reported the highest ozone concentration in the study area that day. It is interesting to note that, with strong flow from the southwest, the peak concentrations occurred southwest of Philadelphia, suggesting that emissions from Philadelphia were not contributing to those peaks.

Further evidence implicating a source area other than Philadelphia is seen in Figure 55. Air parcels tracked backward from Claymont, DE (Site 15), at 1500 EST (time

Table 32. 6:00 to 9:00 a.m. LDT (0500-0800 EST) AVERAGES OF NO_x and NMHC (ppm) AND THE RATIO OF NMHC TO NO_x FOR RURAL AND URBAN SITES ON AUGUST 10.

Site No.	Rural Sites	6:00 to 9:00 a.m. LDT Averages		
		NO_x	NMHC	NMHC/NO_x Ratio
1	Summit Bridge, DE	0.00	0.2	0.0:1
2	Downingtown, PA	0.01	0.0	--
3	Lumberton, NJ	0.01	0.0	--
4	Robbinsville, NJ	0.02	--	--
5	Van Hiseville, NJ	0.00	--	--
	Urban Sites			
6	Chester, PA	--	0.3	--
10	Camden, NJ	0.04	--	--
12	So. Broad & Spruce Streets, Philadelphia, PA	0.05	0.1	19.4:1
13	Franklin Institute, Philadelphia, PA	0.07	--	--
14	AMS Lab, Philadelphia, PA	0.08	0.6	7.5:1

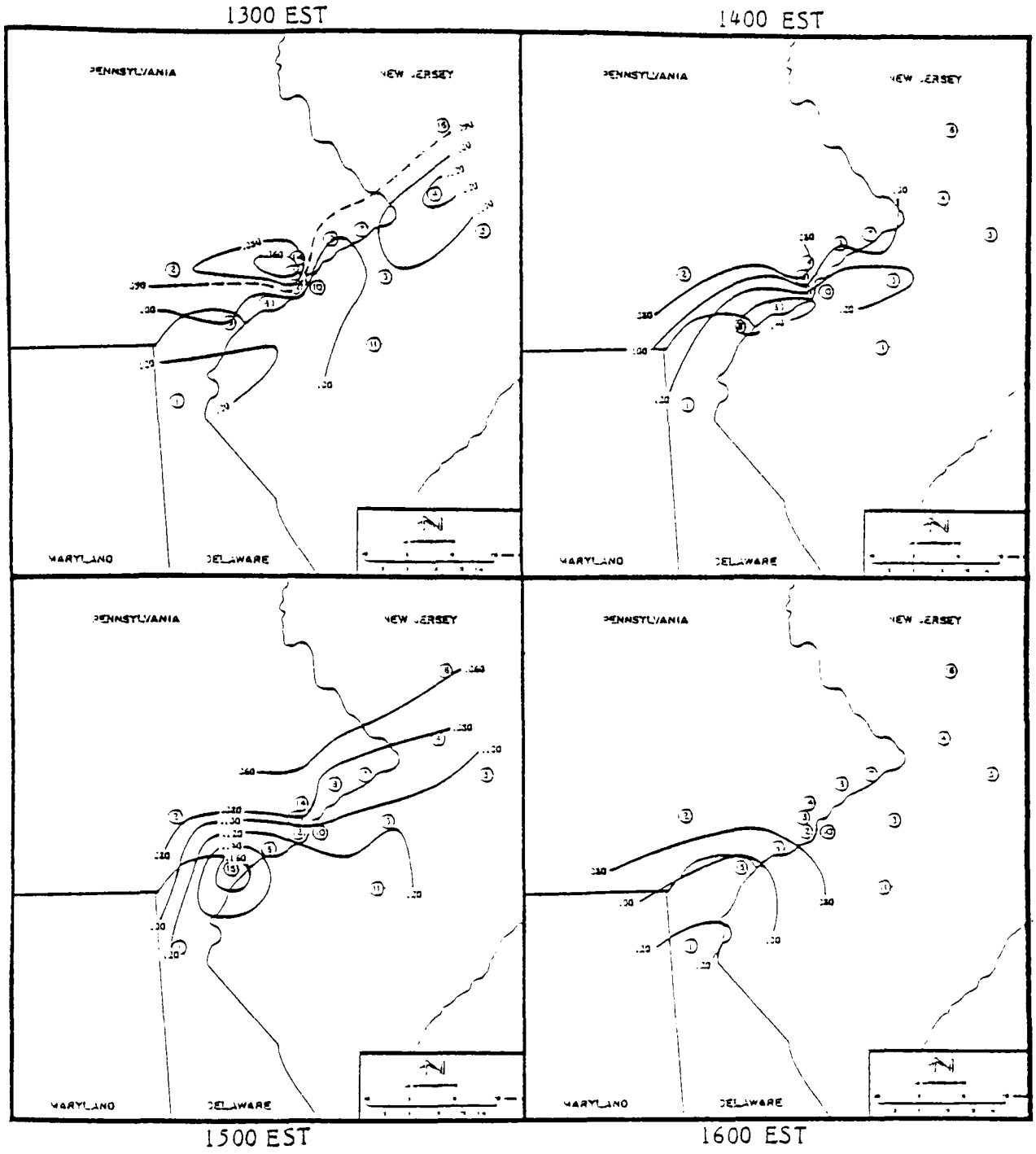


FIGURE 54. Isopleths of ozone at 1300, 1400, 1500, and 1600 EST, August 10, 1979.

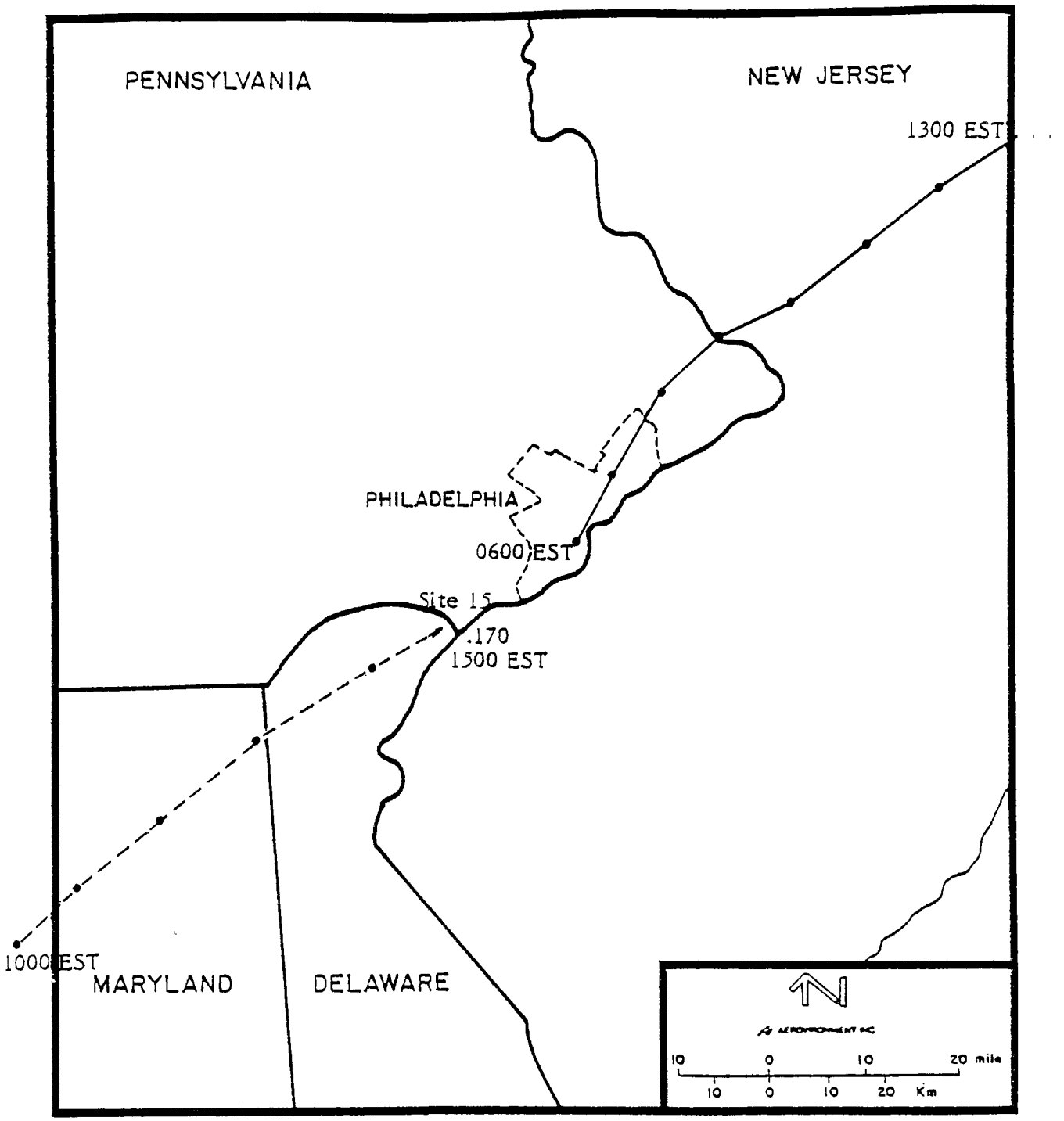


FIGURE 55. Surface trajectory for various air parcels located within the study area on August 10, 1979. Solid line indicates a trajectory beginning at downtown Philadelphia at 0600 EST; dashed lines are for parcels ending at the indicated site and time. Dots show the positions of the parcels at one hour intervals.

of peak ozone) and forward from the central business district at 0600 EST indicate a source region far to the southwest and that emissions from the central business district are advected out of the study by 1400 EST. The urban centers of Baltimore and Washington, D.C., are upwind of the study area on this day. The high wind speeds provided the necessary mechanism for the rapid transport of the emissions from these urban centers into the study area in less than ten hours.

4.6.5 NO_2 Patterns

The peak NO_2 concentration (0.080 ppm) was observed at the AMS Lab (Site 14), during the late morning hours. South Broad Street, PA (Site 12), another urban site, also peaked during late morning. Such late morning peaks are probably the result of the reaction of high levels of early morning NO with ozone and occur before NO_2 destruction by sunlight and reactions with hydrocarbons. NO_2 levels were quite low at outlying sites with the exception of Robbinsville, NJ (Site 4), which reported elevated concentrations (0.067 ppm) in the evening (2000 EST) reflecting the scavenging of the day's ozone.

4.6.6 Concentrations Aloft

Early morning helicopter soundings show evidence of ozone transport aloft of 0.06 ppm in the 500- to 2000-m layer. The sounding made near the area's southwestern-most site, Summit Bridge, DE (Site 1), is shown in Figure 56. Peak ozone levels were found at approximately 900 m MSL where the wind was from the west-southwest at 9.1 m/s. Virtually no NO_x was detected aloft, while an inversion based near the surface is evident. Ozone concentrations measured by the helicopter while transecting from West Chester, PA, to Philadelphia at about 0630 EST varied between 0.06 and 0.09 ppm. The mid-morning helicopter flight showed higher ozone levels. Concentrations between 0.09 and 0.12 ppm were measured by the helicopter during a transect between Brandywine, PA (about 8 km southeast of West Chester, PA), and Philadelphia at about 0916 EST, as shown in Figure 57.

Another indication of transport aloft is that Summit Bridge, DE (Site 1) and Downingtown, PA (Site 2) reported 0.079 and 0.087 ppm, respectively, during the first hour of uninhibited vertical mixing (1100 EST). Diurnal profiles of ozone concentrations

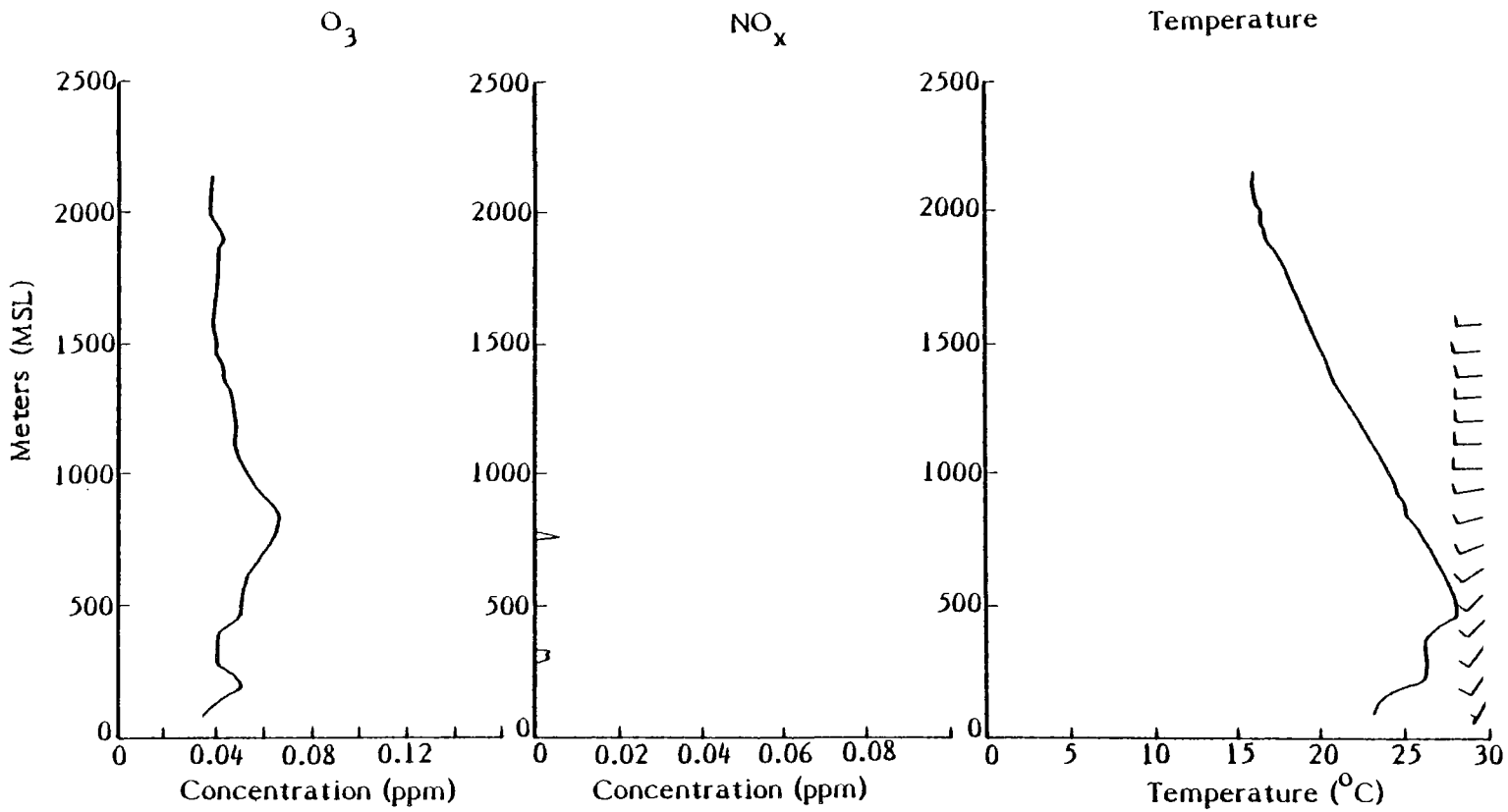


FIGURE 56. Vertical profiles of O_3, NO_x, and Temperature obtained by the instrumented helicopter over Summit Bridge, DE (Site A) at 0535 EST on August 10, 1979. Also shown is the corresponding wind profile. (Key: ⟩ = North at 5 m/s)

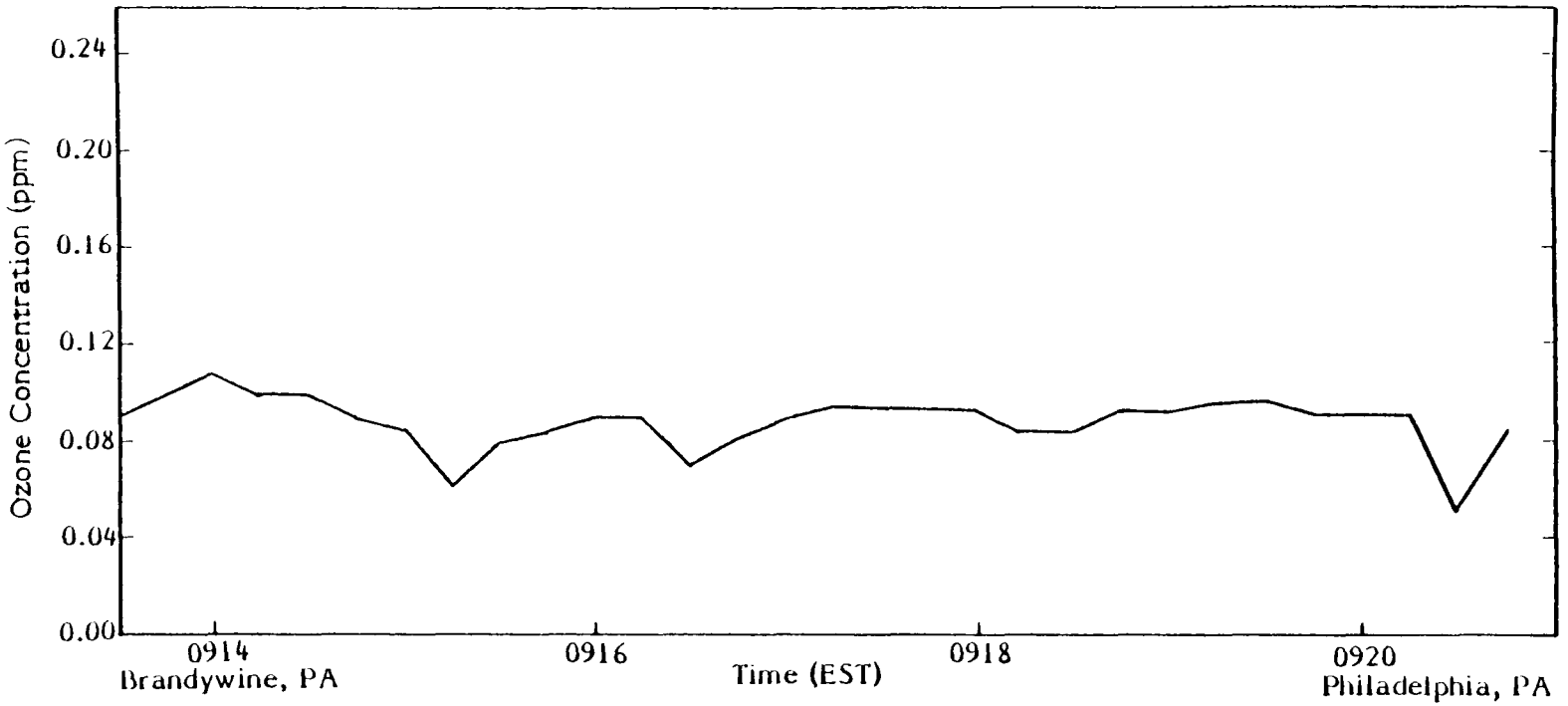


FIGURE 57. Ozone concentrations reported during helicopter transect from Brandywine, PA to Philadelphia on August 10, 1979 at an altitude of approximately 850 m MSL.

at these sites are given in Figure 58. Ozone peaks early in the day are apparent at both sites. Both sites exhibit similar ozone levels at the time of initial mixing from aloft. However, Summit Bridge concentrations continue to increase in response to transport from the southwest, but Downingtown levels do not, suggesting that little of this transport affects the western portion of the study area.

4.6.7 Hydrocarbon Species

At Franklin Institute, the hydrocarbon species type distribution showed high paraffins, mostly propane and butanes. The C_3 to C_6 olefins were slightly elevated as well. It is not clear what these should be ascribed to.

In contrast, the 0500 to 0600 EST sample at the industrial site showed a large percentage of aromatics; most of this was benzene (185 ppbC). This must be attributed to a local source but it was transitory since the 0700 to 0800 EST sample was nearly normal in distribution (20.3 ppbC benzene). Surprisingly, both samples showed six carbon olefins (1-hexene and C-2-hexene) although in this case the later sample was higher in concentration. It is difficult to explain this since we lack signatures for possible sources. To maintain perspective it must be kept in mind that these "intruders" were in no case a major part of the NMHC.

West Chester is a small city about 25 miles west of Philadelphia. A sample taken at an unspecified time on August 10 showed a high total NMHC of 907 ppbC. This was heavily weighted with light paraffins. The butanes and pentanes made up about 43% of this total. This is probably a case of gasoline vapor since minimal concentrations of higher aromatics were measured and is probably due to a local source.

An afternoon sample was taken at 1300 to 1400 EST at the industrial site. The distribution was normal with a total NMHC of 390 ppbC. It is surprising that the two aromatic olefins -- styrene and methyl styrene -- were the only olefins, except for propene, reported in this sample.

At 0621 EST on this date, a sample was taken at 488 m MSL near West Chester, Pennsylvania. Only 99 ppbC was reported in a normal pattern although neither ethylene

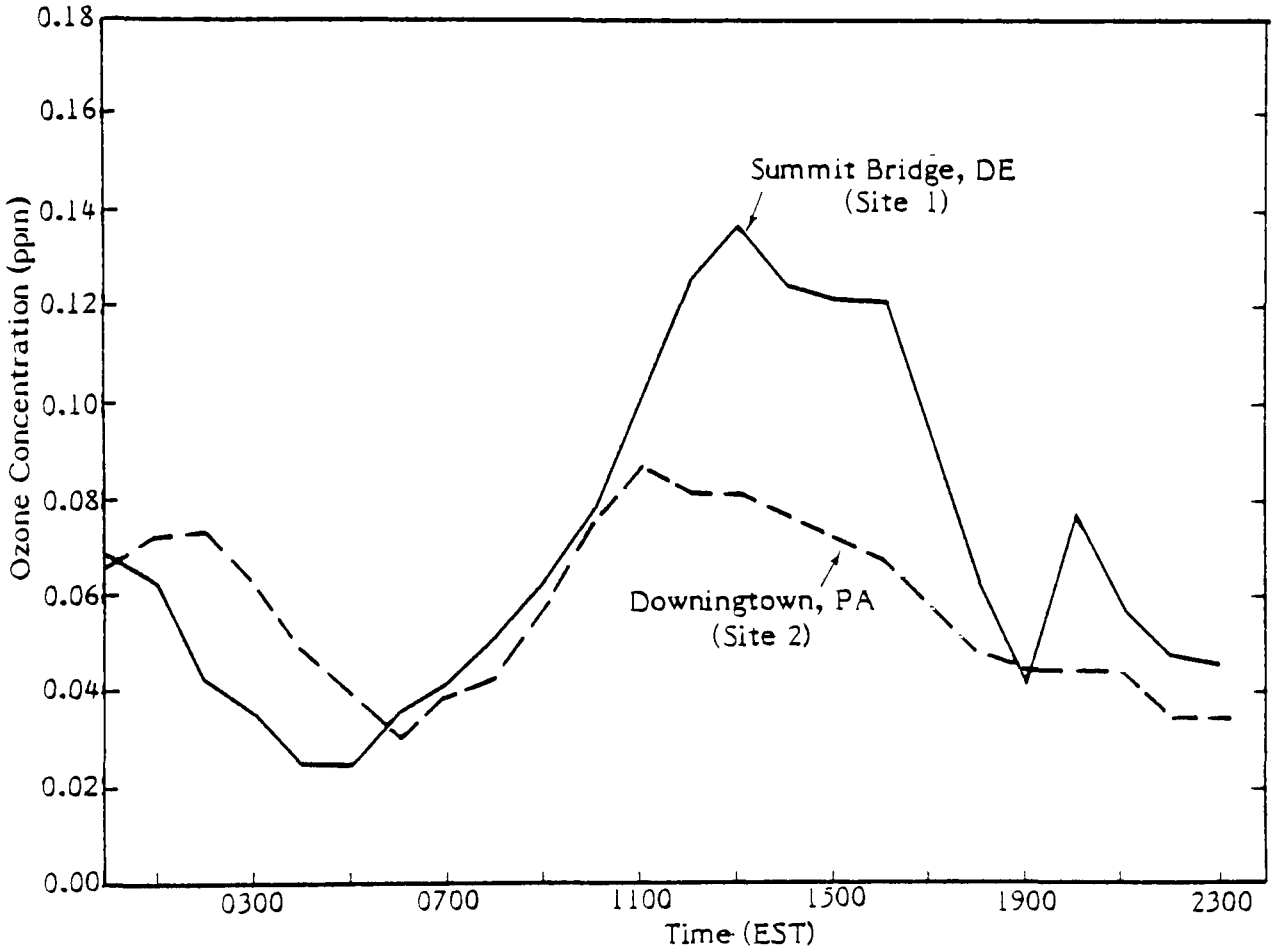


FIGURE 58. Diurnal profiles of ozone at Summit Bridge, DE (Site 1) and Downingtown, PA (Site 2) on August 10, 1979.

nor acetylene was listed. At about 0940 EST, samples were taken over downtown at two altitudes. These were similar in composition, the upper sample taken just below the mixing height of 339 m, showing 875 ppbC NMHC at 488 m MSL, and the lower sample showing 702 ppbC at 18 m MSL. Both showed high percentages of paraffin due to high propane concentrations. Propene levels were also slightly elevated.

4.7 AUGUST 22, 1979 (WEDNESDAY)

Some of the interesting features of this day were: (1) high ozone levels in Philadelphia proper, as well as downwind, (2) the evidence of significant wind shear aloft, and (3) a low-level synoptic trajectory with a long residence time over the Northeast Corridor.

The maximum ozone and NO_2 concentrations reported on August 22 were 0.140 and 0.100 ppm, respectively. Four of the fourteen operating stations reported ozone concentrations equal to or greater than 0.12 ppm and one other station reported 0.100 ppm. Seven sites reported NO_2 concentrations $\geq$ 0.05 ppm.

4.7.1 Synoptic Meteorology

The synoptic situation on this day is illustrated in Figure 59. Although, like August 10, the wind flow was predominantly from the southwest, the synoptic situation was quite different. A low-pressure center had passed through the study area from the northwest on August 21 with precipitation in the study area on August 20 and 21. On August 22, a high-pressure cell was rebuilding over the area. The center of this high pressure was over southern Quebec at 0700 EST on August 22, moving offshore toward the southeast.

The synoptic trajectory for an air parcel in the 100- to 500-m layer, shown in Figure 60, is somewhat puzzling. While surface flow over the study area was consistently from the southwest and, as will be shown later, surface study area trajectories confirmed this southwesterly flow, the trajectory of an air parcel in the 100- to 500-m layer approached from the northeast during the 12 hours preceding 1300 EST. Winds aloft data show wind shear but only at very high levels (i.e., 1500 m MSL). Prior to the erratic behavior and long residence time in the vicinity of major Northeast Corridor urban centers, the synoptic trajectory shown in Figure 46 exhibits a long, over-land, anticyclonic approach to Philadelphia. A trajectory for a parcel in the 1500- to 2000-m layer approached more directly from north-northwest.

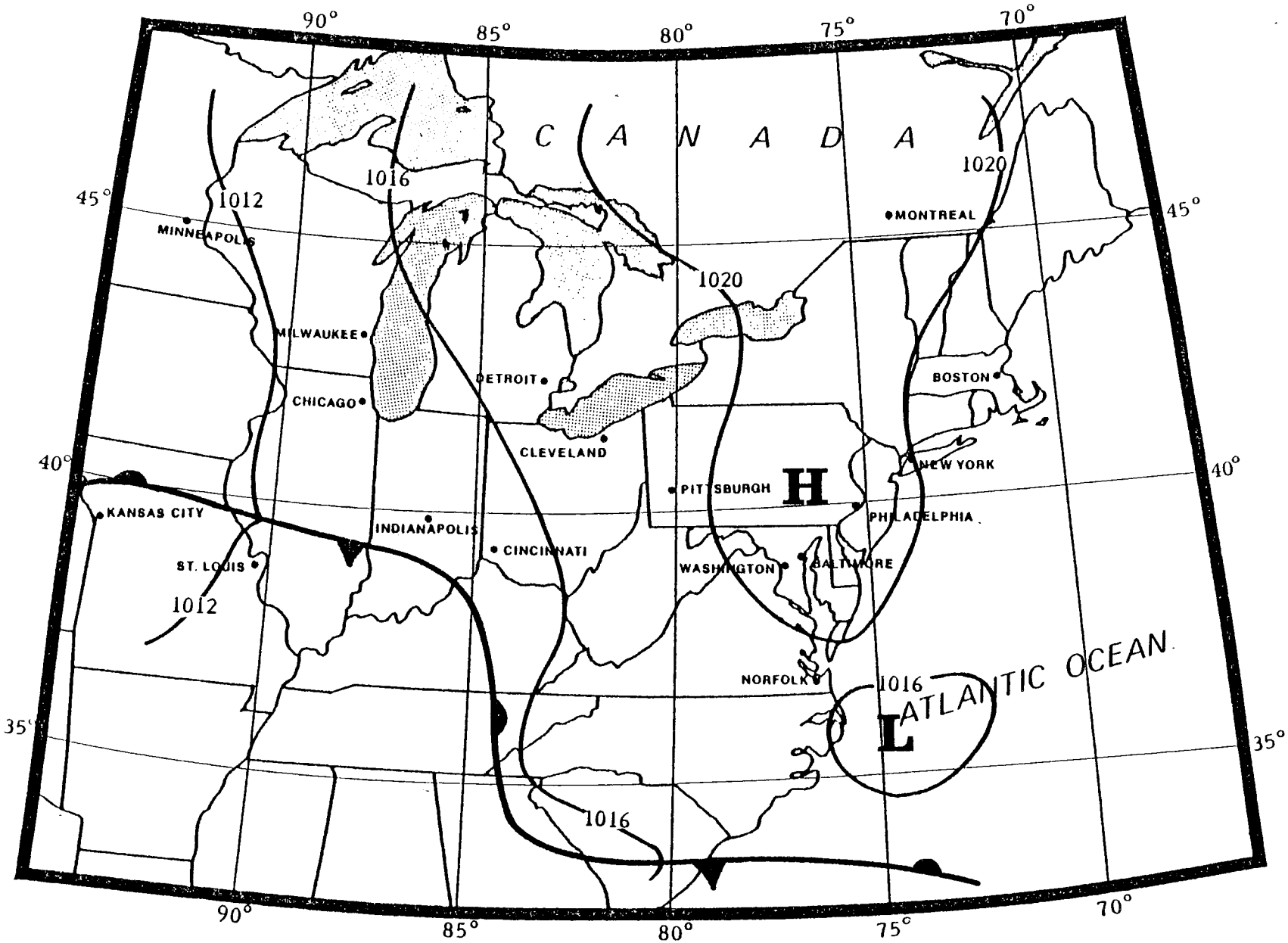


FIGURE 59. Synoptic situation, 0700 EST, August 22, 1979.

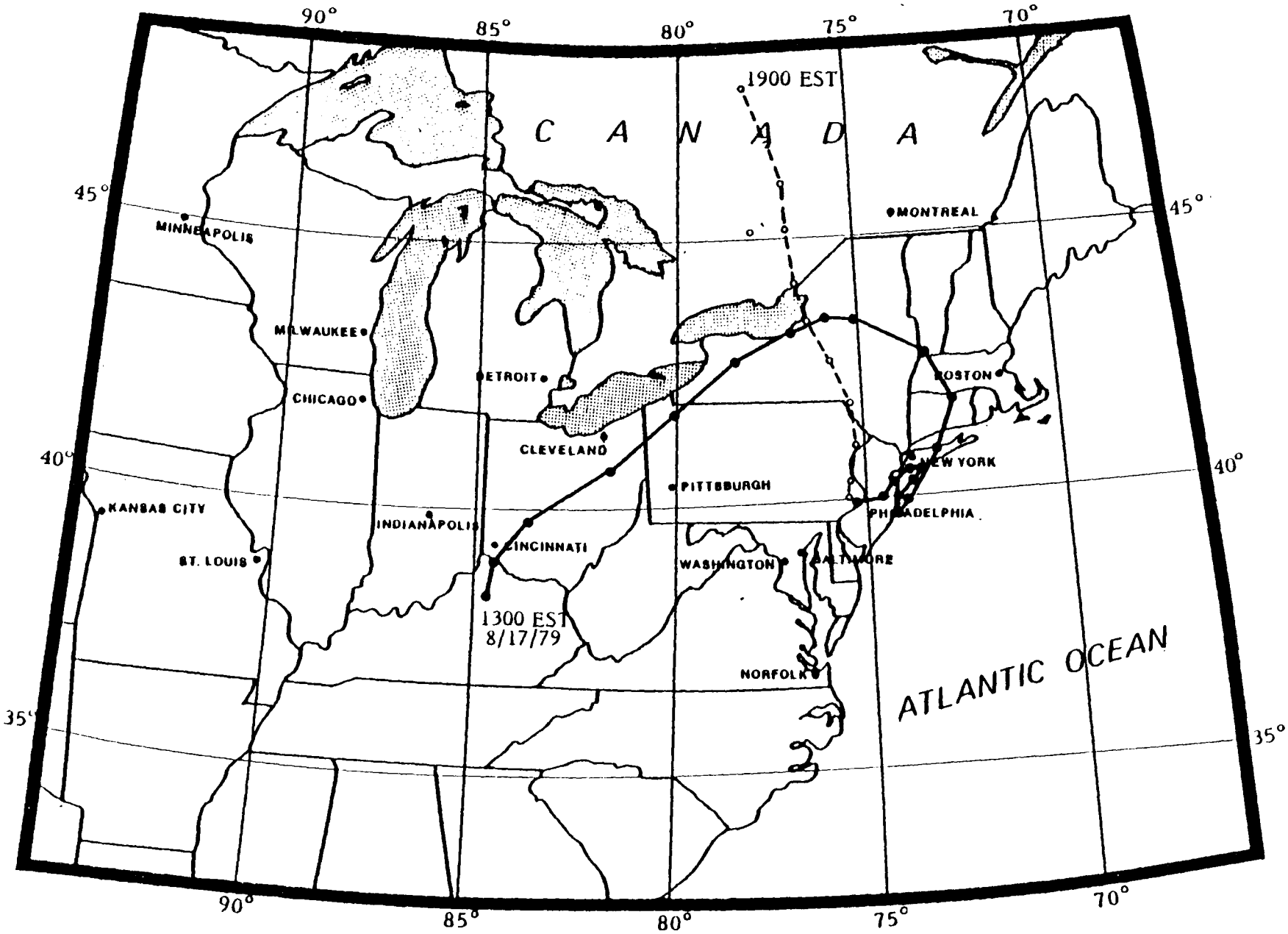


FIGURE 60. Synoptic trajectory of air parcels arriving at Philadelphia at 1300 EST, August 22, 1979. Solid line indicates parcel in the 500 to 1000-meter layer; dashed line is for a parcel in the 1500 to 2000-meter layer. Intervals are six hours.

4.7.2 Mesoscale Meteorology

The prevailing surface wind flow was generally southwesterly all day, although some variability was noted during the late morning hours, particularly at Sites 7, 8, and 21. These sites showed some tendency toward northerly winds, although the prevailing directions for the day were south to southwest. Winds aloft were northwesterly in the early morning backing to southwesterly by 1500 EST with northeast winds at 1500 m MSL.

Urban mixing heights were generally higher than on other case study days. The maximum afternoon mixing height was 1707 m MSL at 1500 EST. Rural acoustic sounder data indicate mixing through the 1000 m MSL layer by 0915 EST, with excellent vertical mixing throughout the day.

4.7.3 Precursor Patterns

The 6:00 to 9:00 a.m. LDT averages of NMHC and NO_x, along with the ratio of NMHC to NO_x, are given in Table 33 for rural and urban sites. Morning precursor levels were above average throughout the study area. The 6:00 to 9:00 a.m. LDT NO_x concentrations at all sites near the central business district were above 0.05 ppm; even Robbinsville, NJ (Site 4), experienced NO_x concentrations three times the normal average. NMHC levels were also somewhat elevated with South Broad Street (Site 12), and the AMS Lab (Site 14) reporting 6:00 to 9:00 a.m. LDT levels of 1.1 and 0.7 ppm, respectively, resulting in 6:00 to 9:00 a.m. LDT NMHC/NO_x ratios of 12.2:1 and 5.4:1, respectively. Summit Bridge, DE (Site 1), Downingtown, PA (Site 2), and Lumberton, NJ (Site 3), reported higher-than-normal NMHC concentrations -- 6:00 to 9:00 a.m. LDT averages of 0.4, 0.3, and 0.3 ppm, respectively.

4.7.4 Ozone Patterns

Peak study area ozone levels were observed at stations in Philadelphia and to the east and northeast. The AMS Lab in Philadelphia (Site 14) recorded the highest ozone concentration of the day with 0.140 ppm at 1400 EST. Figure 61 shows ozone patterns over the study area at 1400 and 1500 EST. Unfortunately, an area-wide investigation of afternoon ozone concentrations in the study area is plagued by missing afternoon data at

Table 33. 6:00 to 9:00 a.m. LDT (0500-0800 EST) AVERAGES OF NO_x and NMHC (ppm) AND THE RATIO OF NMHC TO NO_x FOR RURAL AND URBAN SITES ON AUGUST 22.

Site No.	Rural Sites	6:00 to 9:00 a.m. LDT Averages		
		NO_x	NMHC	NMHC/NO_x Ratio
1	Summit Bridge, DE	0.02	0.4	20:0.1
2	Downingtown, PA	0.02	0.3	13.5:1
3	Lumberton, NJ	0.04	0.3	7.5:1
4	Robbinsville, NJ	0.09	—	—
5	Van Hiseville, NJ	0.01	—	—
	Urban Sites			
8	Northeast Airport, Philadelphia, PA	0.07	—	—
10	Camden, NJ	0.15	—	—
12	So. Broad & Spruce Streets, Philadelphia, PA	0.09	1.1	12.2:1
13	Franklin Institute, Philadelphia, PA	0.06	—	—
14	AMS Lab, Philadelphia, PA	0.13	0.7	5.4:1

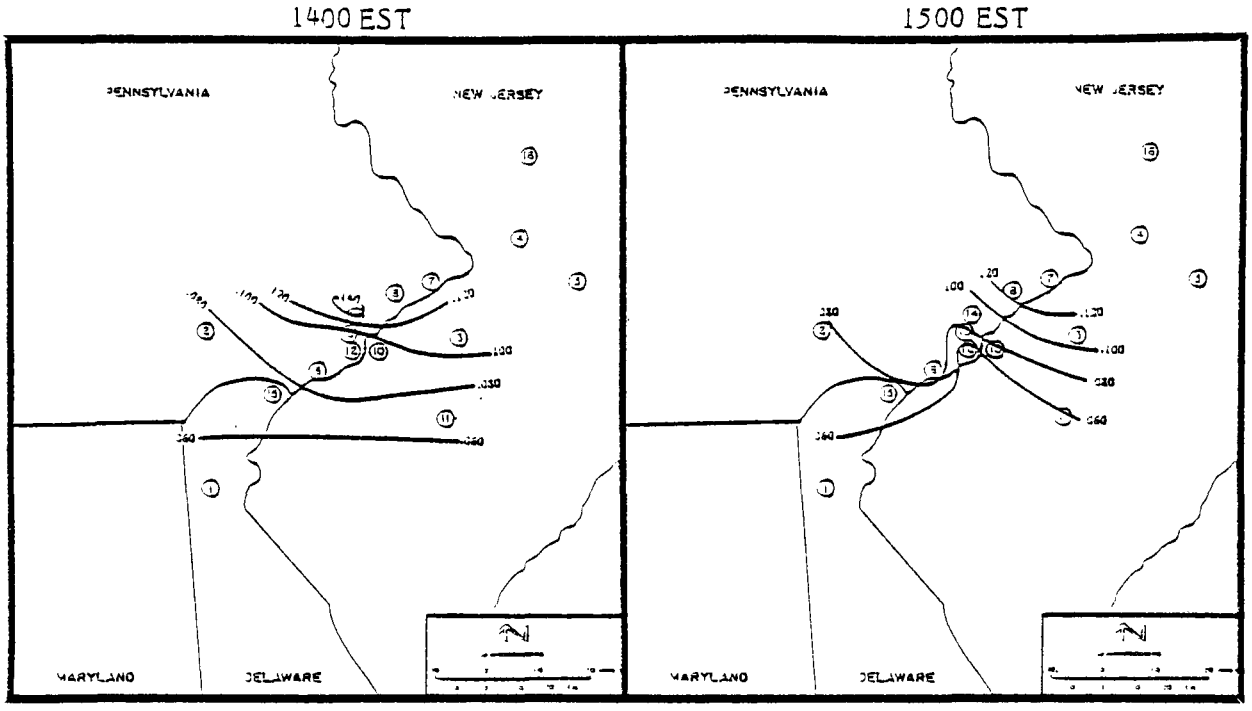


FIGURE 61. Isopleths of ozone at 1400 and 1500 EST, August 22, 1979.

most northeasterly stations. Concentrations upwind (to the southwest) are low. None of the stations to the southwest, west, or southeast of Philadelphia reported ozone levels in excess of 0.10 ppm at any time during the day.

Mesoscale surface trajectories for two air parcels of interest are shown in Figure 62. An air parcel arriving at the AMS Lab, Philadelphia (Site 14), at 1400 EST with 0.140 ppm of ozone passed through Philadelphia the previous hour and over precursor source areas along the Delaware River earlier in the morning. The 0600 EST emissions from Philadelphia's central business district were advected slowly to the northeast and were in the vicinity of Bristol, PA (Site 7), by about 1400 EST. Unfortunately, no ozone data for that site is available past 1200 EST when a concentration of 0.099 ppm was recorded. Nearby, North Philadelphia Airport (Site 8) reported 0.130 ppm of ozone at 1400 EST. The mesoscale trajectories show that surface advection was similar in direction to August 10 but wind speeds were much lower. Still, source areas other than Philadelphia, but within the study area, are again suggested as the explanation of high ozone levels.

4.7.5 NO_2 Patterns

The highest NO_2 concentrations of the day occurred in Philadelphia and Camden, NJ (Site 10), in the early afternoon (e.g., 0.10 ppm at South Broad Street (Site 12) at 1300 EST) due to the availability of both NO and ozone for NO_2 production. The peak concentration of 0.095 ppm at Camden, NJ (Site 10), occurred at 0700 EST and corresponded to a drop in NO concentration from 0.179 ppm (the highest level of the day) to 0.062 ppm and preceded a large increase in ozone levels. Other concentrations in excess of 0.05 ppm occurred in the morning at outlying sites.

4.7.6 Concentrations Aloft

Although vertical pollutant profiles aloft are lacking, some indication of early morning ozone and precursor transport aloft can once again be found by a review of surface concentrations during the first complete hour of uninhibited vertical mixing which, according to the acoustic sounder at Summit Bridge, DE (Site 1), was 1000 EST. The diurnal profile of ozone at Summit Bridge, DE, and Downingtown, PA, is shown in

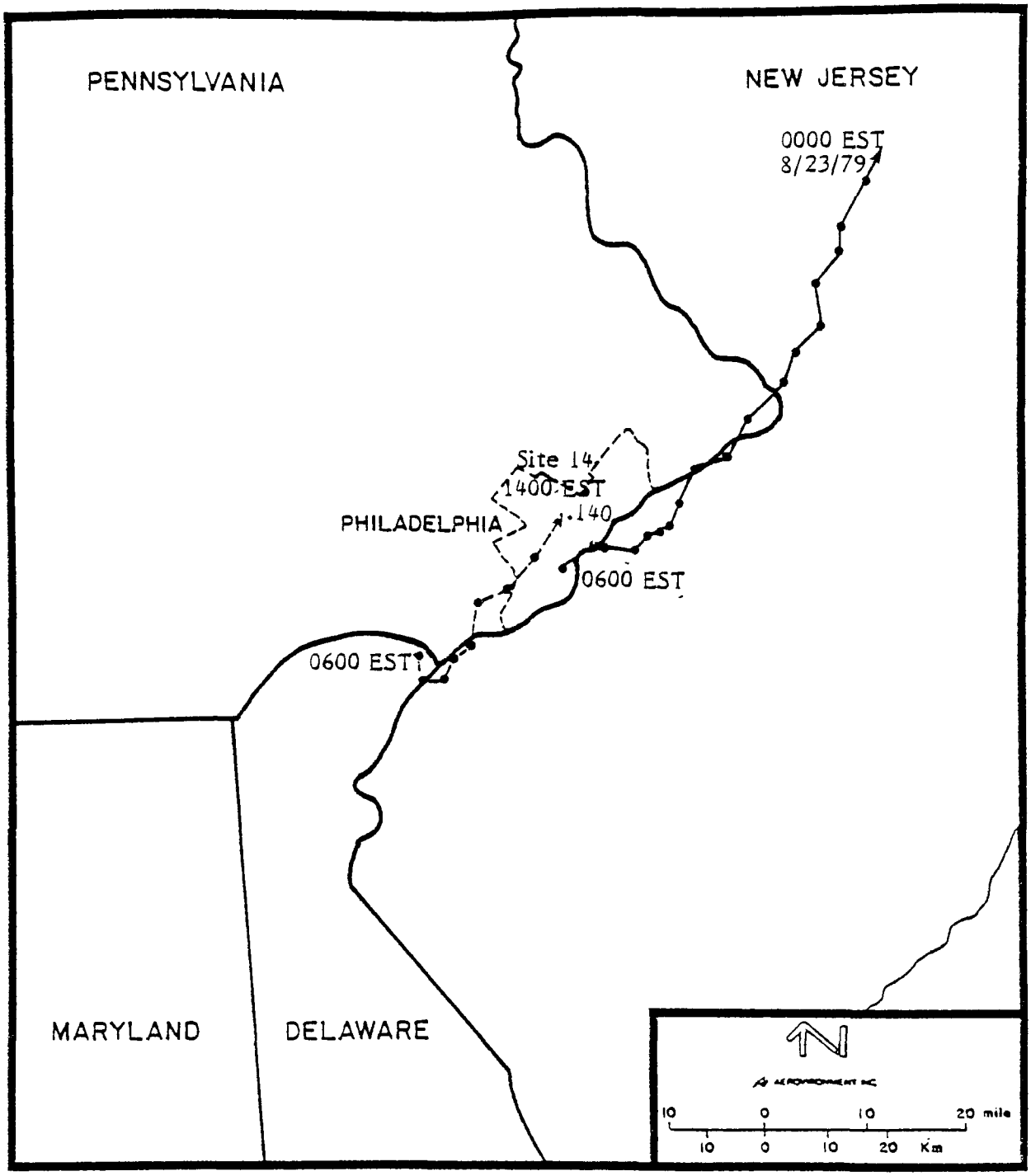


FIGURE 62. Surface trajectory for various air parcels located within the study area on August 22, 1979. Solid line indicates a trajectory beginning at downtown Philadelphia at 0600 EST; dashed lines are for parcels ending at the indicated site and time. Dots show the positions of the parcels at one hour intervals.

Figure 63. The rapid increase in ozone levels characteristic of ozone mixing down from aloft can be seen, especially at Summit Bridge. Concentrations (ppm) at these sites at 1000 EST were:

Location	Ozone	NO	NMHC
Summit Bridge, DE (Site 1)	0.077	0.000	0.50
Downingtown, PA (Site 2)	0.062	0.000	0.10

These data indicate substantial levels of ozone aloft. The 0.077 ppm ozone level observed at Summit Bridge, DE (Site 1), at 1000 EST was the maximum for the day. Although substantial NMHC is present (0.50 ppm, an unusually high level for 1000 EST), indicating at least some of the raw material of further ozone production is available, NO and NO_x are lacking. The apparently substantial levels of transported ozone and low maximum concentrations upwind of Philadelphia are puzzling. Unfortunately, no actual measurements of ozone aloft are available.

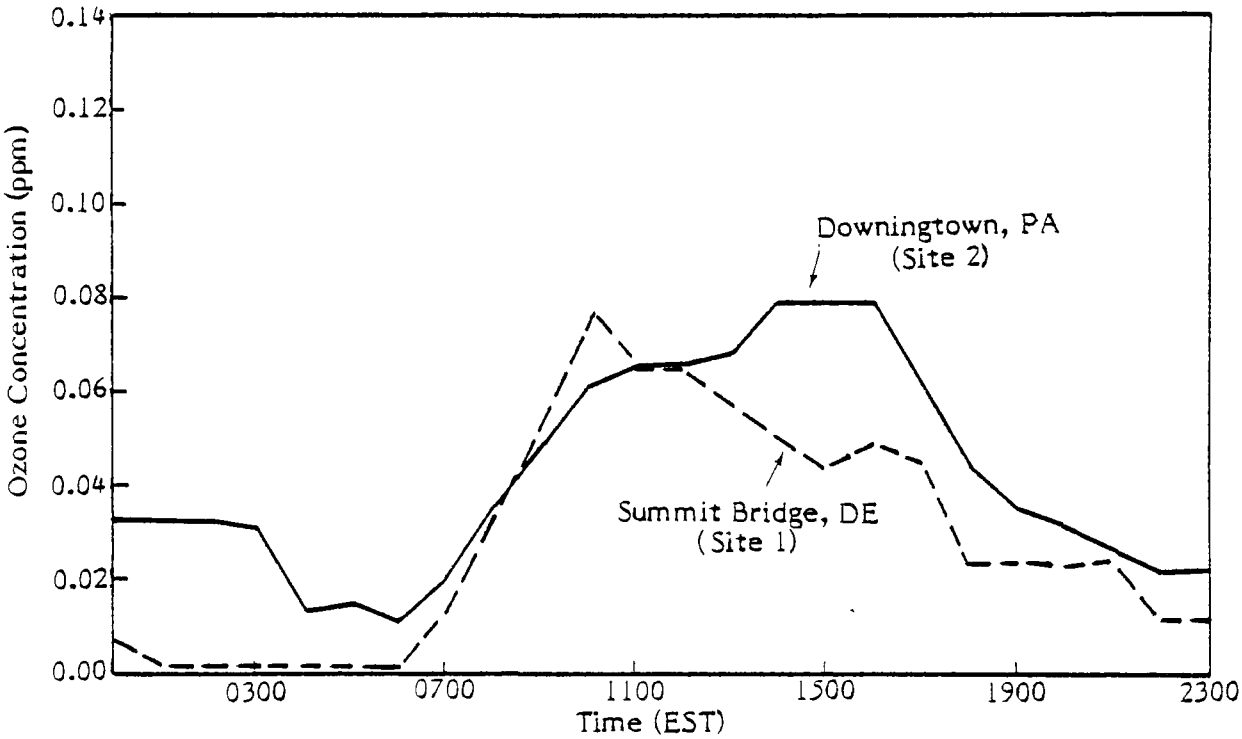


FIGURE 63. Diurnal profiles of ozone at Downingtown, PA (Site 2) and Summit Bridge, DE (Site 1) on August 22, 1979.

5. CONCLUSIONS

The analysis of the ten case study days discussed in the previous chapter has led to the following findings:

- Ozone levels aloft in the early morning on days of high surface ozone vary from 0.015 to 0.097 ppm.

- Significant nighttime ozone transport aloft can be a major cause of high late-afternoon surface ozone concentrations in urban and rural areas.

- Peak ozone levels do not always occur in the Philadelphia urban plume.

- The ozone transport phenomenon in the Northeast Corridor involves local, mesoscale, and synoptic scale transport.

5.1 MORNING OZONE LEVELS ALOFT

During the ten case study days, early morning ozone levels observed aloft were as low as 0.015 ppm and as high as 0.097 ppm. Table 34 summarizes the ozone concentrations aloft observed generally upwind of Philadelphia for the case study days. Two methods were used to estimate these concentrations aloft: (1) the actual average concentration measured aloft by helicopter above the layer of surface ozone depletion and below the top of the afternoon mixed layer; and (2) the average concentration observed at the surface during the first full hour of complete vertical mixing through the 1000-m layer, as determined by the acoustic sounder located at Summit, DE (Site 1). An assumed complete vertical mixing time of 1000 EST, based upon the average time of complete mixing on other case study days, was used for July 12, 13, and 16, due to the unavailability of acoustic sounder data. Average concentrations detected aloft ranged from 0.015 to 0.020 ppm on August 7 to 0.060 ppm on August 10. Ozone concentrations measured at the surface at the time of complete vertical mixing ranged from 0.031 to 0.047 ppm on August 7 to concentrations in excess of 0.080 ppm on July 13, 19, and August 10.

Table 34. SUMMARY OF MORNING OZONE CONCENTRATIONS (in ppm) OBSERVED GENERALLY UPWIND ON CASE STUDY DAYS.

Date	Concentrations Aloft			Surface Concentrations			
	Site Location	Time (EST)	Concen-tration	Site Location	Site Number	Time (EST)	Concen-tration
July 12	--	--	--	Summit Bridge, DE	1	1000	0.068
				Downingtown, PA	2	1000	0.075
July 13	--	--	--	Lumberton, NJ	3	1000	0.097
				Van Hiseville, NJ	5	1000	0.064
July 16	--	--	--	Lumberton, NJ	3	1000	0.049
				Van Hiseville, NJ	5	1000	0.061
July 19	--	--	--	Lumberton, NJ	3	1000	0.082
				Van Hiseville, NJ	5	1000	0.083
August 4	West Chester, PA	0930	0.060	Downingtown, PA	2	1000	0.058
				Robbinsville, NJ	4	1000	0.067
August 5	West Chester, PA	0758	0.050	Downingtown, PA	2	1000	0.058
				Robbinsville, NJ	4	1000	0.076
August 6	Pottstown, PA	0631	0.030	Downingtown, PA	2	1000	0.061
	Pipersville, PA	0555	0.030				
	Willow Grove NAS, PA	0919	0.035				
August 7	Pottstown, PA	0628	0.020	Summit Bridge, DE	1	1000	0.047
	Pipersville, PA	0577	0.015	Downingtown, PA	2	1000	0.031
	Seabrook, NJ	1020	0.020				
August 10	Summit Field, DE	0535	0.060	Summit Bridge, DE	1	1100	0.079
	West Chester, PA	0612	0.060	Downingtown, PA	2	1100	0.087
August 22	--	--	--	Summit Bridge, DE	1	1000	0.077
				Downingtown, PA	2	1000	0.062

Concentrations observed at the surface at the time of complete mixing tend to be somewhat higher than concentrations measured aloft earlier. Although the bulk of ozone production occurs during the late morning and early afternoon, some ozone is probably produced between the time of the helicopter sounding and the time of the surface concentrations shown in Table 34.

The measures of transport presented in Table 34 correspond to the geographical extent of peak ozone concentrations in the study area. High transported levels imply widespread levels later in the day. July 13, 19, and August 10 were the only case study days on which surface concentrations higher than 0.08 ppm were observed during the first hour of uninhibited vertical mixing. In addition, August 10 was the only case study day during which average ozone concentrations of 0.06 ppm were reported aloft in the early morning.

A review of peak surface ozone concentrations shows that July 13, 19, and August 10 were also the only case study days in which high ozone levels were widespread across the study area (i.e., more than five sites with concentrations $\geq$ 0.12 ppm and ten or more sites with concentrations $\geq$ 0.10 ppm). Although the sample size is limited, the implication is that significant nighttime ozone transport aloft can be a major cause of high late-afternoon surface ozone concentrations in urban and rural areas.

5.2 OZONE LEVELS IN THE PHILADELPHIA URBAN PLUME

During the ten case study days, peak ozone levels did not always occur within the urban plume. Table 35 summarizes the locations of peak ozone concentrations observed with respect to Philadelphia. On five of the ten case study days, peak concentrations were found downwind of Philadelphia under prevailing flow. On one occasion, the peak concentration occurred upwind, on one occasion in Philadelphia, and on two occasions in other areas. It should be pointed out that, while fourteen to fifteen monitoring sites were generally operating in the study area, the peak concentration due to the urban plume could have been missed, particularly when northerly flow prevailed. The frequency with which peak ozone concentrations occur outside the urban plume is surprising. Some of the conditions which contribute to this phenomenon were found to be:

Table 35. LOCATIONS OF PEAK OZONE CONCENTRATIONS WITH RESPECT TO PHILADELPHIA.

Date	Peak Ozone Concentrations (in ppm)			Other Areas
	Downwind	Upwind	Philadelphia Proper/ Camden	
July 12	0.124	0.114	0.111	0.147
July 13	0.123	0.141	0.161	0.183
July 16	0.151	0.067	0.100	0.131
July 19	0.157	0.104	0.138	0.160
August 4	0.102	0.123	0.130	0.144
August 5	0.135	0.082	0.120	0.119
August 7	0.120	—	0.122	0.129
August 10	0.129	0.170	0.137	0.124
August 22	—	0.095	0.140	0.120

- Surface advection of photochemical products from other urban centers into the study area (August 4 and 10).

- Very light or variable surface winds which cause high ozone levels in or near Philadelphia (July 13 and August 22).

- Surface transport from other high emission density areas in the study area (July 12).

Of the five days during which peak ozone levels were found downwind of Philadelphia, one day (August 7) experienced complete surface flow reversal so that no true upwind area existed. For the remaining four days, the difference between upwind and downwind ozone peaks ranged from 0.044 to 0.084 ppm. For this very small sample, this 0.04 to 0.08 ppm range represents the additive effect of the urban plume, while the late morning surface ozone levels representing ozone aloft (Table 34) were in the 0.05 to 0.08 ppm range.

5.3 MESOSCALE TRANSPORT

Mesoscale surface trajectories developed for the case study days revealed both local (0 to 50 km) and mesoscale (50 to 100 km) surface transport. Table 36 presents the locations of surface source areas for peak ozone levels and areas impacted by Philadelphia's central business district emissions. These locations were determined from surface trajectories. The central business district's emissions could be directly related to study area peak ozone levels on three days: July 15 and August 5 and August 6. (It is interesting to note that August 5 was a Sunday and August 6 a Monday. Downwind ozone levels are virtually identical for the two days.) A source region outside the study area was apparent on August 10 and suggested on August 4. High emission density areas within the study area were possible source regions on July 12 and August 22. The source areas for the remaining three case days (July 13, 19, and August 7) were rural or near rural regions. July 13 and 19 showed evidence of high ozone levels aloft, while August 7 was a puzzling case with a very pronounced flow reversal.

Table 36. SOURCE AREAS FOR PEAK OZONE LEVELS AND AREAS IMPACTED BY EMISSIONS FROM PHILADELPHIA'S CENTRAL BUSINESS DISTRICT AS DETERMINED BY MESOSCALE SURFACE TRAJECTORIES.

Date	Peak Ozone (ppm)	Location	Source Area (0600 EST)	Area Impacted by Central Business District	Approximate Ozone Concentration (ppm)
July 12	0.147	Ancora, NJ	10 km SE of Wilmington, NJ	20 km S of Robbinsville, NJ	0.12
July 13	0.183	Chester, PA	25 km ESE of Philadelphia	20 km NE of Downingtown, PA	0.12
July 16	0.151	Downingtown, PA	Central Business District	5 km NW of Downingtown, PA	0.15
July 19	0.160	Claymont, DE	15 km SE of Lumberton, NJ	10 km W of Downingtown, PA	0.16
August 4	0.144	Robbinsville, NJ	55 km NNE of Robbinsville, NJ	40 km SSW of Ancora, NJ	0.12
August 5	0.135	Ancora, NJ	Central Business District	25 km SSE of Ancora, NJ	0.14
August 6	0.136	Ancora, NJ	Central Business District	20 km SE of Ancora, NJ	0.14
August 7	0.129	Lumberton, NJ	5 km SW of Lumberton, NJ	15 km W of Chester, PA	0.12
August 10	0.170	Claymont, DE	Baltimore/ Washington, D.C.	>100 km NE of study area	--
August 22	0.140	AMS Lab, Philadelphia	Claymont, DE	5 km NE of Bristol, PA	>0.10

Ozone levels found downwind of the central business district were, in all cases, in excess of 0.10 ppm. (No data were available for August 10 during which the central business district's emissions were advected out of the study area.) On four of the case study days, peak ozone levels downwind of the central business district were more than 0.03 ppm lower than the peak level observed in the study area.

5.4 SYNOPTIC TRANSPORT

While the case study days were selected to provide a variety of prevailing flows, it is interesting to note that these flows were spawned by a variety of synoptic situations and that synoptic trajectories approached the study area in a variety of ways.

While most of the trajectories examined showed over-land paths, July 16 and 19 showed over-water paths. Six of the ten case study days demonstrated significant anticyclonic curvature in the trajectory. Two of the days examined (July 19 and August 4) demonstrated practically no relationship between trajectories in the 100- to 500-m and 1500- to 2000-m layers.

The three days on which the highest morning ozone levels were observed which suggested synoptic transport were July 13 and 19, and August 10. The synoptic trajectories, particularly low-level trajectories, showed evidence of tracks which passed upwind over or near major urban areas.

5.5 DAYS RECOMMENDED FOR MODEL VERIFICATION

To properly evaluate the effects of ozone control strategies on ozone concentrations downwind of Philadelphia, cases in which ozone levels occur downwind of Philadelphia must be selected for modeling. To give confidence to the results, the model must be validated on these types of days. Of the ten case study days analyzed, the study area peak levels occurred unambiguously downwind of Philadelphia on three days (July 16, and August 5 and 6).

To consider the effects of transported versus locally-produced ozone, July 13, 19, and August 10 are candidates for model verification. July 19 is especially suitable since

very high ozone levels were recorded downwind of Philadelphia, while significant transport aloft resulted in widespread high ozone levels.

Finally, for the most precise definition of boundary and initial conditions aloft, the days with helicopter data must be considered: August 4 through 7, and August 10.

6. BIBLIOGRAPHY

Baxter, R., G.Y. Lowe, and T. Nguyen (1978): Acoustic Radar Chart Preparation and Interpretation. AeroVironment Inc., Pasadena, California.

Chan, M.W., D.W. Allard, and I. Tombach (1979): Ozone and precursor transport into an urban area: evaluation of measurement approaches. EPA-450/4-79-039.

Code of Federal Regulations, Volume 40, Title 50, Appendix F.

Federal Register (1978): Volume 44, Page 8221-8233, February 8.

Hancock, C.W. (1978): Philadelphia oxidant study, 1978 helicopter platform data report. Northrop Services, Inc., Report No. ESG-TR-78-15.

Maynard, J.B., and W.N. Sanders (1969): Determination of the detailed hydrocarbon composition and potential atmospheric reactivity of full range motor gasolines. JAPCA 19, 7 (505-510).

Mayrsohn, H., J.H. Crabtree, M. Kuramoto, R.D. Sothern, and S.H. Mano (1977): Source reconciliation of atmospheric hydrocarbons 1974. Atmos. Environ. 11 (189-192).

Reynolds, S.D., T.W. Tesche, and L.E. Reid (1978): An introduction to the SAI Airshed Model and its usage. Systems Application, Incorporated, Report No. EF78-53R3.

Sanders, W.N. and J.B. Maynard (1968): Capillary Gas chromatographic method for determining the C_3-C_{12} hydrocarbons in full range motor gasolines. Anal. Chem. 40, 3 (527-535).

Stephens, E.R. (1973). Hydrocarbons in polluted air summary report. Coordinating Research Council Project CAPA-5-68.

Westberg, H. and P. Sweany (1980): Philadelphia oxidant data enhancement study: hydrocarbon analysis. Washington State University Chemical Engineering Department, February.

TECHNICAL REPORT DATA
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1. REPORT NO. EPA-450/4-81-011	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Philadelphia Oxidant Data Enhancement Study - Analysis and Interpretation of Measured Data		5. REPORT DATE March 1981
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Douglas Allard, Michael Chan, Chris Marlia, and Edgar Stephens		8. PERFORMING ORGANIZATION REPORT NO. AV-FR-80/588R
9. PERFORMING ORGANIZATION NAME AND ADDRESS AeroVironment, Incorporated 145 Vista Boulevard Pasadena, California 91107		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. 68-02-3332
12. SPONSORING AGENCY NAME AND ADDRESS Monitoring and Data Analysis Division Office of Air Quality Planning and Standards Environmental Protection Agency Research Triangle Park, North Carolina 27711		13. TYPE OF REPORT AND PERIOD COVERED Final
		14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

Project Officer: Norman C. Possiel

16. ABSTRACT

The Philadelphia Oxidant Data Enhancement Study was conducted to obtain a data base of ozone, precursor, and meteorological measurements in the vicinity of Philadelphia, PA. The data will be used by the U.S. Environmental Protection Agency for two purposes: 1) to verify and apply various photochemical models and to help develop guidance for their use, and 2) to better understand the photochemical and meteorological processes associated with peak ozone and NO_2 concentrations in the Philadelphia area. Philadelphia was selected for study because it is large enough to be capable of generating high ozone levels, and it may be subject to significant ozone and/or precursor transport. During the period of July 2, 1979 through September 18, 1979, AeroVironment, Inc. (AV) operated five surface monitoring stations in the vicinity of Philadelphia to collect the required data. Eleven other surface monitoring stations operated by State and local agencies collected data for inclusion in the data base. An instrumented helicopter, operated by EPA's Environmental Monitoring and Support Laboratory in Las Vegas, collected data aloft during a four-week period in July and August. In addition, upper-air meteorological measurements were obtained by Beukers Labs. This report describes the data collection efforts of AV and includes an analysis and interpretation of the field study data base. The analyses are primarily directed toward identifying the concentrations of ozone and precursors transported in the city and ozone formed in the urban plume downwind.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Ozone Measurements Non-methane Hydrocarbon Measurements Oxides of Nitrogen Measurements Transport of Pollutants Urban Plumes Trajectory Analyses		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES 187
	20. SECURITY CLASS (This page)	22. PRICE

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