

EPA 901/9-76-007

Final Report

March 1977

OZONE IN THE NORTHEASTERN UNITED STATES

By: F. L. LUDWIG and E. SHELAR

Prepared for:

ENVIRONMENTAL PROTECTION AGENCY REGION I, AIR BRANCH ROOM 2113 J. F. KENNEDY FEDERAL BUILDING BOSTON, MASSACHUSETTS 02203

Contract No. 68-02-2352



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ABSTRACT

The data from the summer 1975 Northeast Oxidant Study have been combined with routinely collected weather and pollutant data to demonstrate that oxidant and its precursors are transported for distances in excess of 100 km in the New York, New Jersey, and southern New England region. Vertical cross sections of ozone concentration clearly show urban ozone plumes. During a daytime passage of a weather front, strong ozone gradients are observed between the warm polluted air ahead of the front and the clearer, cooler air behind; at any fixed site, concentrations drop rapidly as the front passes and clean air replaces polluted. Nighttime frontal passages do not show the marked ozone gradients found during a daytime frontal passage. High nighttime ozone concentrations are associated with the simultaneous occurrence of unusual vertical mixing and an ozone layer aloft. The ozone layer aloft appears to be the remnant of daytime photochemical production in an urban plume.

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SUMMARY AND CONCLUSIONS

The premise that sources and effects always lie within the same air quality control region does not seem to be valid when applied to the ozone problem in much of the United States. The air pollutant emissions from one region move freely to another. For some pollutants this is not a severe problem, because normal atmospheric processes dilute the previously emitted materials. In the case of ozone, there are sometimes countervailing processes in operation. These are the photochemical reactions that produce oxidants, especially ozone, from the emissions of the precursors, hydrocarbons and nitrogen oxides.

Considerable evidence exists that these reactions can, under favorable conditions, more than offset the atmospheric dilution for tens of kilometers beyond a major emissions area, causing maximum oxidant concentrations to be found far from their precursor origins. Even after the point where the rate of ozone production has fallen below the rates at which it is being destroyed or diluted, urban plumes have been distinguished from the background air--at distances of hundreds of kilometers on numerous occasions.

Many of the earlier observations of ozone plumes at long distances downwind of their origins were made in the midwestern United States. During the summer of 1975, an extensive program of field measurements was conducted under EPA sponsorship by several organizations to accumulate data so that a better understanding of the ozone problem in the northeastern United States could be obtained. At the same time, other investigators were analyzing the existing, routinely collected data statistically to explore the possibility that violations of the federal ozone standard

of 80 ppb in one part of the northeast were at least partly caused by emissions in other parts of the region. This report describes new analyses of the special data and the routinely collected data by methods that are more those of the meteorologist than of the statistician. Reassuringly, the conclusions reached by the meteorological and the statistical approaches are essentially the same, i.e., there is often considerable distance between emissions and effects in this part of the country.

Briefly, the objectives of the work reported here have been:

- To determine the importance of pollutant transport to the oxidant problem in the northeastern United States.
- To determine how transport and ozone-formation processes are affected by other factors, specifically
 - The effects of weather fronts
 - The importance of weekly emissions cycles
 - The causes of high nighttime ozone readings.

As noted before, a considerable body of data was available for use in the pursuit of the above objectives. In addition to the data that were specially collected during the northeast oxidant study, hourly ozone observations were also available from routinely operated sites through the states of New Jersey, New York, Connecticut, Rhode Island, and Massachusetts. Surface weather maps at 3-hour intervals and meteorological data from higher altitudes at 6-hour and 12-hour intervals were used in the analysis. The major problem was not scarcity of data during the study period, 15 July to 31 August 1975, but developing the methods required for the proper display and interpretation of that data.

Obviously, one of the most important factors bearing on the objectives of this study is air history--where the air comes from and where it goes. The wind observations were used to calculate air trajectories for air arriving at two Connecticut sites, Groton and Simsbury. The afternoon ozone data were then classified according to where the air had

come from. It was found that high ozone concentrations (above 80 ppb) at Groton were associated with air arriving from both the New York and the Hartford areas; at Simsbury, only air from the direction of New York was associated with afternoon ozone observations above the federal standard. Although not conclusive, the data suggested that the New York emissions might be affecting ozone concentrations nearly 200 km downwind and the Hartford emissions almost 100 km away.

Analysis of the data from the airborne operations showed the frequent occurrence of regions of higher ozone concentrations, a few hundred meters above ground level These observations are most easily explained as "plumes" of ozone and ozone precursors trailing downwind from urban areas. In a few cases, observations were also available upwind for the same period as the downwind observations. These upwind cases showed generally lower, much more uniform, distributions of ozone—a fact that indicates that the higher downwind observations are the result of ozone produced in elevated, urban pollutant plumes.

Other studies had shown that high ozone concentrations were most apt to be found in conjunction with the northwestern parts of high-pressure weather systems and in the warm air ahead of weather fronts. The studies in New England showed similar relationships. The distribution of ozone concentrations during a daytime frontal passage are particularly striking. Typically, the winds are from the southwest preceding the frontal passage, a condition that is conducive to the occurrence of high ozone concentrations in southern Connecticut. As the weather front moves through, the ozone-laden air is replaced by the cooler, cleaner polar air behind the front. This causes rapid decreases in ozone concentration and strong spatial gradients.

If the front passes through at night, then there is no photochemical ozone production and fewer emissions in the air ahead of the front, so that the strong gradients do not develop. This does not mean that

nighttime ozone concentrations are never high. As noted before, the ozone plumes from the cities are often present aloft. Generally, surface cooling at night causes the atmosphere to be relatively stable, and mixing in the vertical is suppressed. This leaves the ozone elevated and isolated from the surface and the processes that would tend to destroy it. Isolated from the surface, ozone can persist for long periods without appreciable degradation. By virtue of being concentrated aloft, it will generally remain undetected by surface-based instruments unless something happens to transfer it to ground level.

Our studies of several cases of high nighttime ozone concentrations at ground level in New England showed that there was evidence of atmospheric instability in at least some of these cases. Such instability is quite likely to be accompanied by vertical motions that could bring ozone aloft down to ground level. In some cases, the areas of maximum ozone concentrations moved along the ground in a direction and at a speed consistent with winds in the lower layers of the atmosphere. In these cases, declining ozone concentrations at a series of sites marked the passage of air that left the New York area during midafternoon. There was widespread vertical motion, and the trailing edge of the high ozone area was moving through it with the wind. In at least one case, the ozone was relatively widespread, but the region of vertical motions was limited to the vicinity of a low-pressure trough that moved at a speed greater than the wind. It is apparent that the effects of long-range transport need not be confined to the daylight hours.

The findings of this study--indicating that transport of ozone and its precursors over distances of hundreds of kilometers in the north-eastern United States plays a large part in determining the observed concentration distribution in the region--will have important consequences in the development of control strategies and policies. It is obvious that there is no place in the entire region that has complete

control over the air pollutants to which it will be exposed, and there is no place that does not at times contribute to the problems of other places within the region. For this reason, oxidant-control strategies should encompass very large areas. Connecticut and Rhode Island will require the cooperation of New York and New Jersey if they are to achieve compliance with federal standards. Similarly, Massachusetts will require cooperation from Connecticut and Rhode Island. This does not mean that each place's problems always have their origins elsewhere. It does mean that such is the case often enough that solutions must involve very large-scale considerations that extend beyond the confines of the typical Air Quality Control Region.

It may never be possible to fully quantify the impacts that one area has on another. The non-linear chemical activity, the concurrent introduction, transformation and removal of ozone and precursors, and the transport and dilution are all so complicated that a simplistic identification of the source of any given amount of ozone at any particular location just isn't possible. About the best that one can do is to say that the pollutants came from a certain direction more often than from somewhere else. For this reason cooperative emissions reductions efforts will be much more effective than attempts to divide the problem into neat little pieces to be assigned to their proper jurisdictions.

I INTRODUCTION

The motivation for the research described in this report has been to answer some questions related to the development of oxidant-control strategies in the northeast United States. Recent special observational programs have provided more detailed data than have been available in the past (Washington State University, 1976; Spicer, Joseph, and Ward, 1976; Siple, Zeller, and Zeller, 1976; Wolff et al., 1975). One of the reasons why the special data collection programs were undertaken was because other studies indicated that control strategies that focused on urban areas alone might not be adequate for the achievement of federal oxidant standards (e.g., EPA, 1975).

The underlying premise of the control strategies generally has been that air quality problems and their causes are not widely separated in space or time. It follows from this premise that air quality control strategies can be applied within limited regions to control the problems in those regions. Figure 1 shows the air quality control regions into which the eastern United States has been divided. Their size is consistent with the view of the problem that has been outlined above.

The discovery that violations of the federal oxidant standard were frequent in rural areas raised questions concerning the validity of the premise that effects of pollutant emissions were limited in spatial extent. Martinez and Meyer (1976) have recently reviewed the accumulation of evidence concerning longer-range transport of oxidants and oxidant-producing primary pollutants. They concluded that an individual urban area source can affect ozone concentrations as far as 300 km downwind. This, of course, means that control strategies should have greater scope than originally supposed.



FIGURE 1. FEDERAL AIR QUALITY CONTROL REGIONS

Other evidence exists that also suggests that oxidant problems extend well beyond the confines of the typical air quality control region (AQCR). Recently Ludwig et al. (1977) used SAROAD data (System for the Automatic Retrieval Of Aerometric Data) to map the distribution of maximum-hour ozone concentrations in the eastern United States for each day during 1974. They found that the areas within which the Federal ozone standard was violated often had dimensions of hundreds of kilometers. Figure 2 shows one example of widespread high ozone concentrations in the eastern United States; the high ozone areas tend to be considerably larger than the typical AQCR of Figure 1.

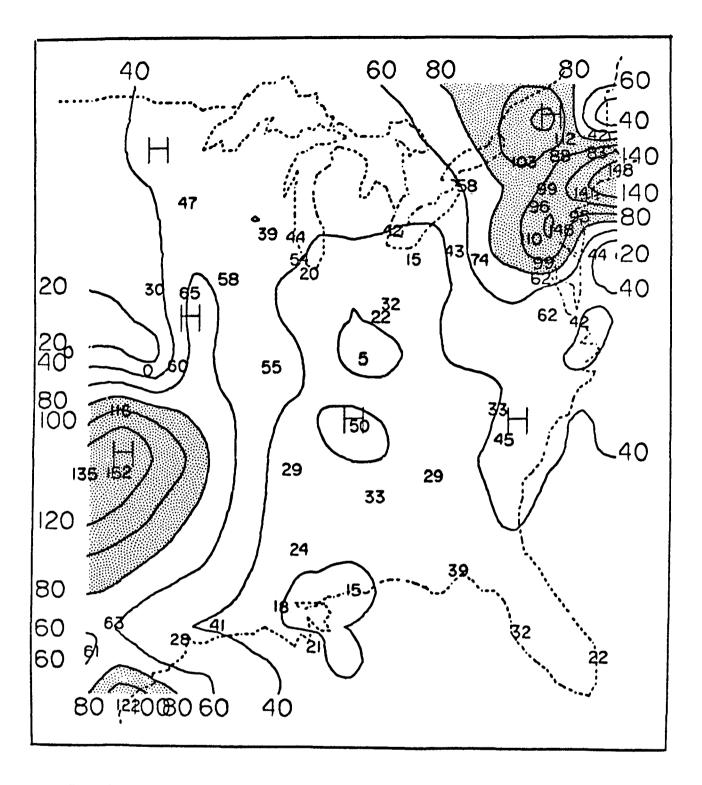


FIGURE 2. DISTRIBUTION OF MAXIMUM-HOUR ${\rm O_3}$ CONCENTRATIONS FOR THE EASTERN UNITED STATES FOR 22 MAY 1974

The region of concern for this study has been New England. If pollutant transport with its accompanying widespread violations of the federal oxidant standard has been found to be important in other areas of the United States, there is certainly no reason to expect it to be unimportant to New England. The east coast of the United States has a large number of major source areas. Figure 3 shows all the counties in the eastern United States where average annual $\mathrm{NO}_{\mathbf{v}}$ emissions exceed 75 tons mi $^{-2}$ yr $^{-1}$. There are only 124 such counties in the entire United States and Figure 3, based on data from the National Emissions Data Service (NEDS), shows that a large number of them are along the northeast coast. The importance of pollutant transport is compounded by the fact that the winds often tend to parallel the coast during the summer months when oxidant production is most pronounced. Figure 4 (United States Department of Commerce, 1968) shows the frequency of different wind directions at many United States cities. It is obvious from Figures 3 and 4 that the transport of pollutants into New England is likely to be relatively frequent.

Others have studied ozone transport in the area (e.g., Cleveland et al., 1975) and have concluded that it is an important factor in determining the distribution of ozone in New England. It is our intent to use the data from the special, summer 1975 monitoring programs cited earlier to provide more detailed descriptions of the important features of the New England ozone problem. In particular, we have been interested in:

- The transport of ozone and precursors to and from EPA Region I.
- The dimensions of pollutant plumes from urban areas.
- · The effects of weather fronts on ozone distributions.
- The causes of high ozone concentrations at night in New England.
- The differences between workday and nonworkday ozone concentrations.

Of course, we have not limited ourselves to the data collected during special studies; we have also used conventional weather data, hourly ozone data from the SAROAD system, and the findings of other investigations.



FIGURE 3. COUNTIES WITH AVERAGE ANNUAL NO $_{\rm X}$ EMISSIONS GREATER THAN 75 t mi $^{-2}$ yr $^{-1}$

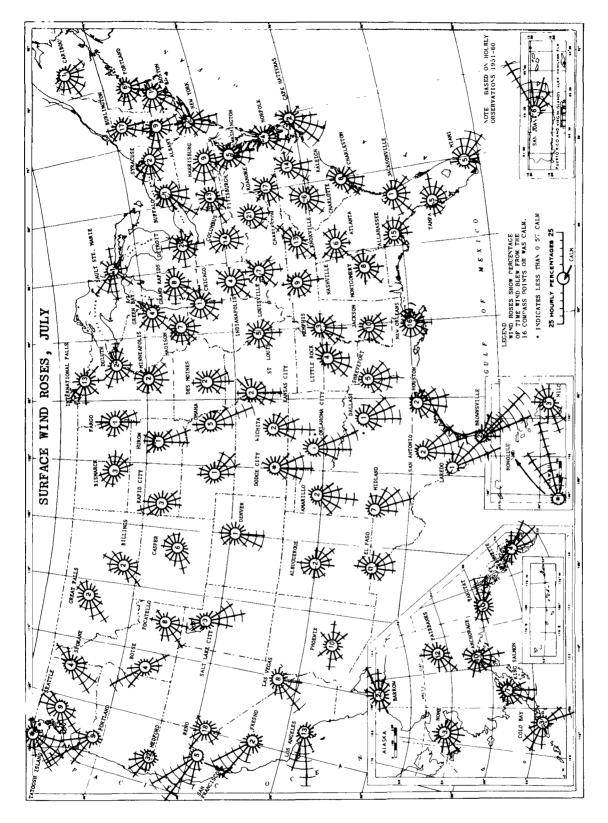


FIGURE 4. SURFACE WIND ROSES, JULY

II DATA

A. The Northeast Oxidant Study

1. General

A comprehensive field measurement program was begun in the New England area on 15 July 1975. The primary objectives of the program were to monitor ozone, ozone precursors, and meteorological parameters throughout the New England and surrounding areas. The resulting data were to be used to determine the origins of ozone levels in the New England area.

The field study involved research teams from Battelle Columbus Laboratories, Washington State University (WSU), the Interstate Sanitation Commission (ISC), The Research Corporation of New England (TRC), and EPA groups from Research Triangle Park (RTP), Las Vegas (LV), and Region I. In addition, supporting data were made available from several agencies. These data include:

- <u>Air quality data</u> from stations operated by agencies reporting to the EPA SAROAD data base.
- <u>Upper air wind measurements</u> available through the National Oceanic and Atmospheric Administration (NOAA) for calculation of trajectories.
- Standard weather data as collected by the National Weather Service (NWS); this is reported and stored at the National Climatic Center (NCC) in Asheville, North Carolina.
- Emission data collected by state and local agencies; most of this is eventually reported to the EPA NEDS data base.

- Ozone soundings were taken at the Albany (New York) airport; some 6 valid soundings during the study period were collected by NWS; Research Triangle Institute (RTI) is processing these data.
- Aircraft data collected by RTI in late July as they tracked a high-pressure system from the midwest to the Atlantic.

Intensive field data acquisition operations span the period from 15 July through 31 august, although all parties were not active the entire period. Three groups (EPA, WSU, and Battelle) operated both aircraft and ground stations. Locations of these ground stations and bases of operations are illustrated in Figure 5. WSU was located on the southern Connecticut coast near Groton; Battelle operated out of Simsbury, Connecticut (about 25 km northwest of Hartford). EPA had two groups operating out of the Boston area. The Environmental Monitoring and Support Laboratory (Las Vegas) was responsible for aircraft operations; the Environmental Sciences Research Laboratory operated the ground station. Ozone, carbon monoxide, nitrogen dioxide, nitric oxide and meteorological parameters were measured continuously at the ground station.

The Interstate Sanitation Commission (ISC) joined EPA, WSU, and Battelle in the aircraft-monitoring program. Vertical and horizontal profiles of ozone and temperature were the primary data gathered. Other parameters measured by one or more aircraft included nitric oxide, scattering coefficient, relative humidity (or dew point), and cloud-condensation nuclei. In addition, WSU and TRC conducted pibal programs from four locations, two each in Connecticut and Massachusetts.

2. <u>Summary of Ground Station Data Obtained</u> by Participating Organizations

Three ground stations continuously recorded meteorological parameters and pollutant levels for the duration of the field study.

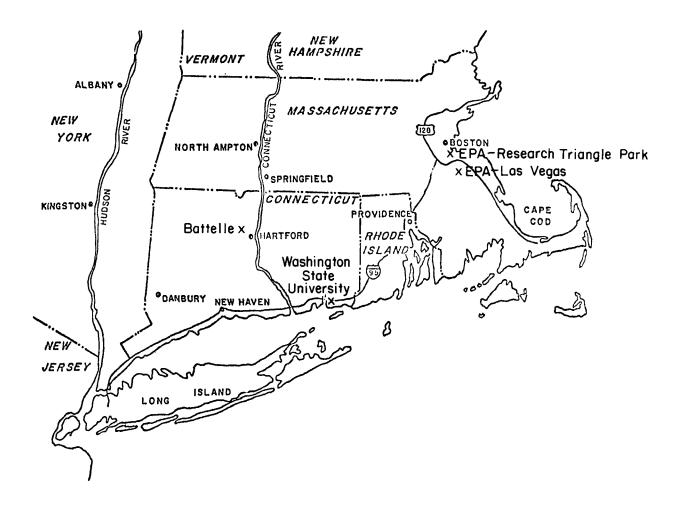


FIGURE 5. MAP OF STUDY AREA SHOWING BATTELLE, WASHINGTON STATE UNIVERSITY, AND EPA MOBILE LABORATORY LOCATIONS

Table 1 identifies the location of each of the special stations and the data measurements made at each.

3. Summary of Flight Operations

Table 2 is an index of flight operations conducted during the Northeast study. Figure 6 is an example of a flight pattern, and Figure 7 is the type of data gathered during the EPA flights. Other organizations collected similar data.

Table 1

SUMMARY OF DATA OBTAINED AT GROUND STATIONS

Battelle, '5 15 July-21 August 1975 Simsbury, Connecticut	×	××	× ×	××	×	× ×	×	× ×	×	×			×	×	×	~ ;	< >	×
Washington State U., 15 July-22 August 1975 Groton, Connecticut	×	x x	××	××	× :	×				×			×	×	× :	*	× ×	۷
EPA, 13 July-28 August 1975 Chickatawbut Hills, Mass.	X	××	××	××	X	×				:	×	×	×		×	∢ :	≺	
Unit	Ly min ⁻¹ Ly min ⁻¹	qdd qdd	mdd qdd	mdd mdd	ppt	ppt ppb	qdd	q d d	qdd	qdd		g m -3	deg.	deg.	m s_1	υ >	percent	و
Parameter Measured	Ultraviolet radiation Solar radiation	0 ₃ NO	NO ₂ CH ₄	Nonmethane hydrocarbon CO PAN	Fluorocarbon-11	Ethane	Ethylene	Propane Acetylene	o)	ne Hydrocarbons	C1-C10	Aerosol scattering (as concentration)	Wind direction	Stand, dev. wind dir.	Wind speed	Temperature	Relative humidity	Dewpoint

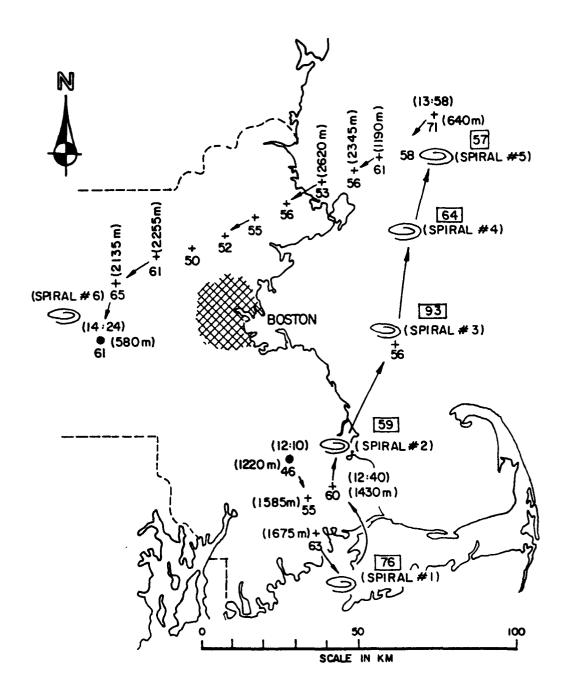


FIGURE 6. EXAMPLE OF FLIGHT TRACK DATA PROVIDED BY EPA/LV (Flight No. 3 on 11 August 1975)

Table 2 SUMMARY OF APPROXIMATE TIMES (EDT) OF AIRCRAFT OPERATIONS

	EPA, La	as Vegas	WS	 ນ	ISC	Battelle			
	Total	Vertical	Total	Vertical	Total	Tota1	Vertical		
Date	Flight	Sounding	Flight	Sounding	Flight*	Flight	Sounding		
July									
15			16-17	16					
18			13-14	14					
18			16-17	16					
18						20-22	22		
19			10-13	10,12					
19			16-19	17					
20						10-11	10		
20			15-17	15,16					
20			19-20	20					
21			11-14	12,13,14					
21			16-18	16,17		17-20	18		
22			8-9	8,9		9-11			
22			13-16	14,15		14-15			
23			8-12	9-10		9-12	11		
23			15-17	16,17		14-17	16		
24			9-12	10,12		9-12			
24			14-17	15		15-18	17		
26			10-13	10,11		9-12	10,11		
26			15-18	16,17		15-19	16,17		
27			9-12	10,11		9-13	11,12		
27			15-18	15,17		15-18	16,18		
28			10-12	11		9-11			
28			14-17	15,17		16-17			
29			9-12	10,11		9-13	10,12		
29			15-18	15,16		15-18	15,17		
30			21-23	22,23					
31						14-17			
August									
2			12-15	13,14					
2			21-23	21,22,23					
3			10-13	11,12		12-15			
5						9-10			
5			13-15	13,14		11-13	13		

Table 2 SUMMARY OF APPROXIMATE TIMES (EDT) OF AIRCRAFT OPERATIONS (Con't)

	EPA,	Las Vegas	W	su	ISC	Battelle			
	Total	Vertical	Total	Vertical	Total	Total	Vertical		
Date	Flight	Sounding	Flight	Sounding	Flight"	Flight	Sounding		
August									
5						18-20	19-20		
6			9-12	10,11,12		10-12			
6			14-17						
9			12-14	12,13		11-13	13		
9	14-15		15-18	16,17		17-20	18		
10			11-14	12,13,14	9-12				
10					9-12				
10					14-16	12-14	12,13		
10			16-19	17,18	14-16	16-18	17-18		
11	12-14	12,13,14	9-12	10,11,12	10-12	11-12			
12	10-11		9-13	12		10-12	12 -		
12	13-16	14,15	15-17	16					
13	10-13	11,12,13	9-12	10,11		10-13	11,12,13		
13	15-17	15,16,17	16-19	16,17,18		16-19	17-18		
14	12-13	12,13	10-13	11,13		10-13	12,13		
14	15-18	15	16-19	16,18		15 - 18	16,17		
15					3-6				
15			10-13	11,12,13	11-16	10-13	11,12		
15	15-18	16,17	17-19		12-17				
17	10-12	10,11,12							
18			11-14	11,13		9-10			
18						12-15	13,14		
18			20-21	20		17-21	19		
19	10-12	10,11,12	10-13	11,12	9-12				
19					10-13	10-13			
19	15-17	15	15-17	15,16	15-17	17-19	17,18		
19			19-22	20,22	15-18				
20	9-12				10-13				
20	14-16		12-15		13-16	11-18	13,16,17,18		
20			16-19		14-17				
21			9-12	11	9-12				
21					9-12	10-12	11		
21			15-17	16,17	14-17	14-18			

Table 2 SUMMARY OF APPROXIMATE TIMES (EDT) OF AIRCRAFT OPERATIONS (Con'd)

	EPA, I	as Vegas	WS	U	_ISC_	Battelle				
	Total Flight	Vertical Sounding	Total Flight	Vertical Sounding	Total Flight*	Total Flight	Vertical Sounding			
August										
21					14-17					
24	10-12	10,11,12								
26	17-18									
27	10-12	11,12								
27	14-16									
27	16-17									
28	11-12									

 $[\]ensuremath{^{\star}}$ Vertical soundings were taken approximately hourly during Interstate Sanitary Commission Flights

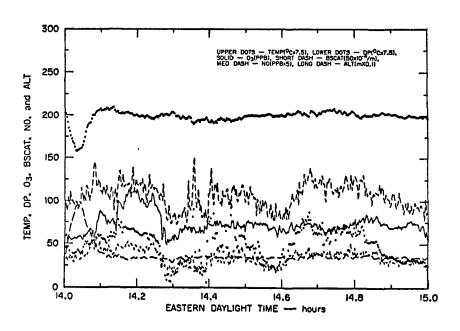


FIGURE 7. EXAMPLE OF AIRCRAFT DATA GATHERED FROM EPA/LV (Flight No. 2 on 22 August 1975)

B. SAROAD Data

Hourly, ozone concentrations at the surface were obtained for many stations in the northeast from the EPA SAROAD data base. Primarily, monitoring stations from Connecticut, Massachusetts, Rhode Island, New Jersey, and New York were included along with a few stations from New Hampshire and Vermont. Table 3 lists the monitoring stations for which hourly ozone concentrations were obtained. The table includes the SAROAD station identification, the name, and the geographic location of each monitoring site.

C. U.S. Weather Service Analyses

The primary Weather Service product used during this study was the surface weather map. Figure 8 is an example of this type of map. The map shown is from the "Daily Weather Map Series" published by NOAA. The following description is quoted from that supplied by NOAA. "The Surface Weather Map shows station data and the analysis for 7:00 a.m., EST. Tracks of well-defined low-pressure areas are indicated by chain of arrows; locations of these centers at 6, 12, and 18 hours preceding map time are indicated by small white crosses in black squares. Areas of precipitation are indicated by shading."

In addition to the "Daily Weather Map" analyses that are reproduced in Appendix A, we also had available to us surface weather maps for 3-hour intervals and upper-air maps for two times per day. These were obtained on microfilm from the National Climatic Center.

Table 3

LIST OF OZONE MONITORING STATIONS

	EPA	SAROAD	OZONE	AND OXIDANT	٥	ATA		
			15 JULY THRO	UGH 31 AUG 197	15			
	*****	*****	****	*****	*****	*****	****	****
	~****	CT 1 T		1.00		7015	LITAY	1174
	1710N ID 10060123F0		ION LOCATION SEPORT. CONN.	LON. W0731137	LAT. N411051	ZONE 18	UTMX 651	UTM
	70175123F0		JRY CONN.	W0750000	N412051	18	500	457
	7020n0n1F0		ORD. CONN.	W0720507	N415026	18	742	463
	70250123F0		ELD. CONN.	W0723420	N415954	18	701	465
	7033 <u>0</u> 004F0		WICH, CONN.	W0734156	N410437	18	609	454
	1035¢123F0		ON. CONN.	W0720137	N412304	18	748	458
	0400001F0		N. CONN.	W0725426	N412252	18	674	458
	70420123F0		FORD, CONN.	W0724001 NN. W0730821	N414618	18	693 654	462 461
	/0478001F0 /057n0n3F0		+FIELD CO+ CO _ETOWN+ CONN+	W0724428	N414021 N385130	18	696	430
	70700008F0		HAVEN, CONN.	W0725510	N411952	18	674	457
	1080123F0		ORD. CONN.	W0733215	N410334	18	622	454
	/116n123F0		INGTON. CONN.	W0730645	N414827	18	656	462
4. AO	/152000[FO	1 WINDS	SOR. CONN.	W0723947	N415107	18	693	463
	20060001F0		RST. MASS.	W0723333	N423324	18	700	471
	0240002F0		N. MASS.	M0665100	N710600	19	595	789
	0360004F0		RIDGE, MASS.	W0710400	N422210	19	329	469
	20400004F0		OPEE, MASS.	W0723718 W0705837	N420914 N423531	18 19	696 337	466 471
	2048^V0?F0 20570001F0		RS: MASS. HAVEN, MASS.	W0765428	N413812	18	341	461
-	0580004F0		RIVER, MASS.	W0710959	N414107	19	319	461
-	0620003F0		BURG, MASS.	W0714702	N423418	19	271	471
	2066n002F0		INGHAM. MASS.	W0711039	N421724	19	320	468
24. A22	20783002F0	I GREEN	FIELD, MASS.	W0723550	N423419	18	697	471
	21080004F0		L. MASS.	W0711904	N423848	19	309	472
-	21210001F0		IELD. MASS.	W0712008	N421244	19 19	307 326	467 469
-	2122n003F0 2180n004F0		DRD, MASS. Sfield, Mass.	W0710653 W0731327	N422500 N422753	18	646	470
	21880002F0		CY, MASS.	W0705833	N421452	19	336	467
	1980001F0		1. MASS.	W0705444	N423030	19	342	470
	22160005F0		NGFIELD. MASS		N420512	18	699	466
32. AZ	22340003F0		HAME MASS.	W0711532	N455508	19	313	469
	22340004F0		HAM. MASS.	W0711456	N422242	19	315	469
-	22640012F0		HESTER, MASS.	and the same of th	N420859	18	522	466
	00040007F0		IN. N. H.	W0711105	N442754	19 19	326 299	492 476
	00420009F0		HESTER, N. H. Ja. n. H.	W0712734 W0712748	N425926 N424510	19	298	473
	70430005F0 10300011F0		DENCE R. I.		N414957	19	299	463
-	10330011F0		JATE R. I.	W0713409	N414516	19	286	462
						18		
40. A4	70140003F0	1 BUPL	INGTON. VT.	w0731243	N442852	10	642	492

Table 3

LIST OF OZONE MONITORING STATIONS (Concluded)

```
18
                                                                   W0750000
                                                                                                            500
                                                                                                                   4653 .
• 43. A330480007F01 BINGHAMTON. N. Y.
                                                                                   N420210
                                BUFFALO. N. Y.
• 44. A33n66n005F01
                                                                   W0844836
                                                                                   N425237
                                                                                                    16
                                                                                                            678
                                                                                                                    4749 •
                                                                                                                    4750 .
+ 45. A33066nuc7F01
                                BUFFALO: N. Y.
                                                                   W0785250
                                                                                   N425309
                                                                                                    17
                                                                                                            673
• 46. A33188n003F01
• 47. A332020002F01
• 46. A331880003F01 ELMIRA. N. Y.
• 47. A332020002F01 ESSFX CO. N. Y.
• 48. A332480003F01 GLENS FALLS. N. Y.
                                                                                                    18
                                                                   W0764808
                                                                                   N420634
                                                                                                            350
                                                                                                                   4663
                                                                                                    18
                                                                                                            587
                                                                                                                   4912
                                                                   W0735429
                                                                                   N442154
                                                                                                                   4796
                                                                   ¥0733726
                                                                                   N431900
                                                                                                    18
                                                                                                            611
                               GLENS FALLS: N. Y. #0733726

MEMPSTEAD: N. Y. #0735513

KINGSTON: N. Y. #0735932

MAMARONECK: N. Y. #0735415

NEW YORK CITY: N. Y. #0735415

NEW YORK CITY: N. Y. #0735818

NEW YORK CITY: N. Y. #0735330

NEW YORK CITY: N. Y. #0735615

NEW YORK CITY: N. Y. #0735615

NEW YORK CITY: N. Y. #0735650

NEW YORK CITY: N. Y. #0735650

NEW YORK CITY: N. Y. #0735650
                                                                                                    18
                                                                                                            619
                                                                                   N404443
                                                                                                                   4511
◆ 49. A332900005F01
                                                                                                    18
                                                                                   N421706
                                                                                                            583
                                                                                                                   4681
• 50. A33350non2F01
                                                                                   N405558
                                                                                                    18
                                                                                                            603
                                                                                                                   4531
   51. A334100002F01
  52. A33468n003H01
53. A33468n004H01
                                                                                   N404954
                                                                                                            592
                                                                                                                   4520
                                                                                                    18
                                                                                                            599
                                                                                                                   4510
                                                                                   N404413
54. A334680005H01

55. A334680005H01

56. A334680007H01

57. A33468001H01

58. A33468001H01
                                                                                   N404606
                                                                                                    18
                                                                                                           586
                                                                                                                   4513
                                                                                                                   4525
                                                                                   N405222
                                                                                                            593
                                                                                   N403535
                                                                                                    18
                                                                                                            589
                                                                                                                   4493
                                                                                   N404422
                                                                                                    18
                                                                                                            585
                                                                                                                   4510
                                                                                  N404358
                                                                                                    18
                                                                                                            588
                                                                                                                   4509
• 59. A334680014H01
                                NEW YORK CITY, N. Y.
                                                                   W0735620
                                                                                   N404804
                                                                                                    18
                                                                                                           589
                                                                                                                   4517
• 60. A334680018H01
                                NEW YORK CITY. N. Y.
                                                                   W0735901
                                                                                  N404006
                                                                                                    18
                                                                                                           585
                                                                                                                   4502
                               NEW YORK CITY: N. Y.
NEW YORK CITY: N. Y.
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• 62. A334680034H01
                                                                   W0735752
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                                                                                                                   4512 •
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                               NEW YORK CITY, N. Y.
NEW YORK CITY, N. Y.
                                                                   W0735627
W0740011
W0785933
                                                                                                    18
                                                                                                                   4513
• 63. A33468ñ05ŋF01
                                                                                   N404601
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                                                                                                                  4508
4772
4719
                                                                                  N404315
                                                                                                    18
  64. A334680062H01
                                                                                                           584
 NIAGARA FALLS: N. Y.
66. A335680001F01 RENSSELAER: N. Y.
67. A335760004F01 ROCHESTER: N. Y.
68. A336020003F01 SCHENECTADY: N. Y.
70. A336620001F01 SYRACUSE: N. Y.
71. A336880004F01 UTICA: N. Y.
72. A310060001F01 ASBURY PARK: N. J.
73. A310100002F01 ATLANTIC CITY: N.
                                                                                                    17
• 65. A334740006F01
                               NIAGARA FALLS: N. Y.
                                                                                  N430509
                                                                                                           663
                                                                                                    18
                                                                   W0734504
W0770430
                                                                                   N423739
                                                                                                           602
                                                                                   N431000
                                                                                                                   4781
                                                                                                    18
                                                                                                           331
                                                                   W0735619
                                                                                  N424755
                                                                                                                   4738
                                                                                                    18
                                                                                                           586
                                                                   W0761040
                                                                                   N430341
                                                                                                    18
                                                                                                           404
                                                                                                                   4768
                                                                   W0760852
                                                                                   N430243
                                                                                                    18
                                                                                                                   4766
                                                                                                           406
                                                                   W0751148
                                                                                   N430559
                                                                                                    18
                                                                                                            483
                                                                                                                   4771
                                                                   W0740046
                                                                                   N401258
                                                                                                    18
                                                                                                            584
                                                                                                                   4452
                               ATLANTIC CITY. N. J.
                                                                   W0742622
                                                                                  N392127
                                                                                                    18
                                                                                                            548
                                                                                                                   4356
                               BAYONNE N. J.
BURLINGTON N. J.
  74. A310180003F01
                                                                   W0740711
                                                                                   N404052
                                                                                                    18
                                                                                                           574
                                                                                                                   4503 *
                                                                                                    18
  75. A310640001F01
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                                                                                  N400440
                                                                                                           512
                                                                                                                   4436
* 75. A310640001F01 BURLINGTON, N. J.

* 76. A310720003F01 CAMDEN, N. J.

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* 78. A310740001F01 CAMDEN, N. J.

* 79. A31030004F01 ELIZABETH, N. J.

* 80. A31030004F01 ELIZABETH, N. J.

* 81. A310620001F01 HACKENSACK, N. J.

* 83. A312320002F01 JERSEY CITY, N. J.

* 84. A313300001F01 MORRISTOWN, N. J.

* 85. A313480002F01 NEWARK, N. J.
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W0750710
W0745145
W0741252
                                                                                  N395523
                                                                                                    18
                                                                                                                   4419
4421
                                                                                                           491
                                                                                                    18
                                                                                  N39565D
                                                                                                           489
                                                                                                    18
                                                                                                                   4392
                                                                                  N394100
                                                                                                           511
                                                                                                           566
                                                                                                                   4501
                                                                                  N403943
                                                                   W0741228
                                                                                  N403828
                                                                                                    18
                                                                                                           566
                                                                                                                   4499
                                                                   W0741628
                                                                                  N40153B
                                                                                                    18
                                                                                                           561
                                                                                                                   4456
                                                                   W0740228
                                                                                                                   4525
                                                                                  N4 05256
                                                                                                           580
                                                                   W0740401
                                                                                   N404352
                                                                                                    18
                                                                                                           578
                                                                                                                   4509
                                                                   ₩0742904
                                                                                  N404745
                                                                                                    18
                                                                                                            543
                                                                                                                   4516
• 85. A313480002F01
• 86. A314140003F01
                               NEWARK, N. J.
PATERSON: N. J.
                                                                   W0741033
                                                                                  N4Q4411
                                                                                                    18
                                                                                                           569
                                                                                                                   4509
                                                                   W0740920
                                                                                  N405545
                                                                                                    18
                                                                                                           571
                                                                                                                   4531
• 87. A314160001F01
                                PAULSBORD. N. J.
                                                                   W0751427
                                                                                  N394948
                                                                                                    18
                                                                                                           479
                                                                                                                   4408
                               PENNS GROVE. N. J.
PERTH AMBOY. N. J.
                                                                   W0752813
                                                                                                                   4397
. 88. A314200001F01
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                                                                                                    18
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                                                                                                   18
                                                                                                           561
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                                                                                                   18
                                                                                                                   4503
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                                PHILLIPSBURG. N. J.
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                                                                                                           483
  91. A315060001F01
92. A315360001F01
                                SOMERVILLE N. J.
TOMS RIVER N. J.
                                                                   W0743649
                                                                                                    18
                                                                                                           532
                                                                                                                   4490
                                                                                  N403410
                                                                   W0741153
                                                                                N395713
                                                                                                           568
                                                                                                                   4422
• 93. A315400002F01 TRENTON, N. J.
                                                               W0744554
                                                                                N401312
                                                                                                                   4451
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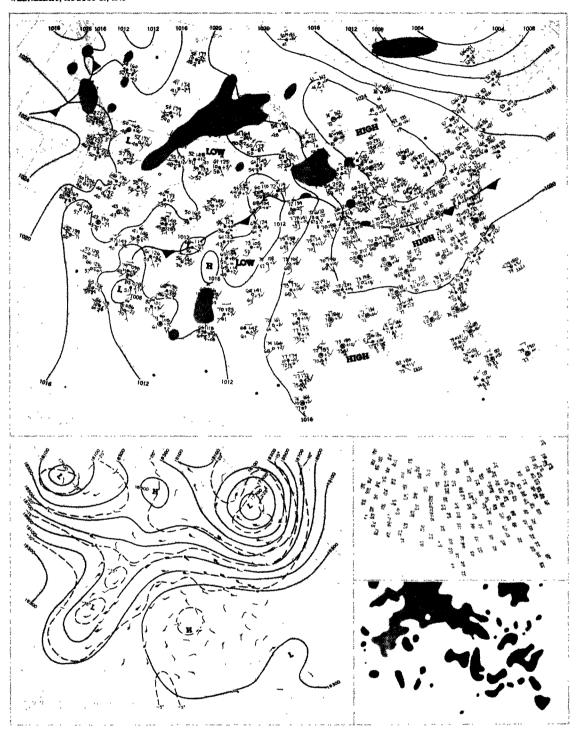


FIGURE 8. EXAMPLE OF THE DAILY WEATHER MAP SERIES

III ANALYZING AND INTERPRETING THE DATA

A. Tracing the History of the Air

One method used to study the transport of pollutants into and within a region is to trace the air movements, based on wind observations in the area of interest. The history of air containing ozone or its precursors can be studied by calculating such trajectories. This enables one to locate the various source areas over which the air passed before arriving at a specific locale. For this study, the computer program used to calculate trajectories is a version of Heffter and Taylor's (1975) model that was provided to us by Mr. Dale Coventry of EPA, Research Triangle Park, North Carolina.

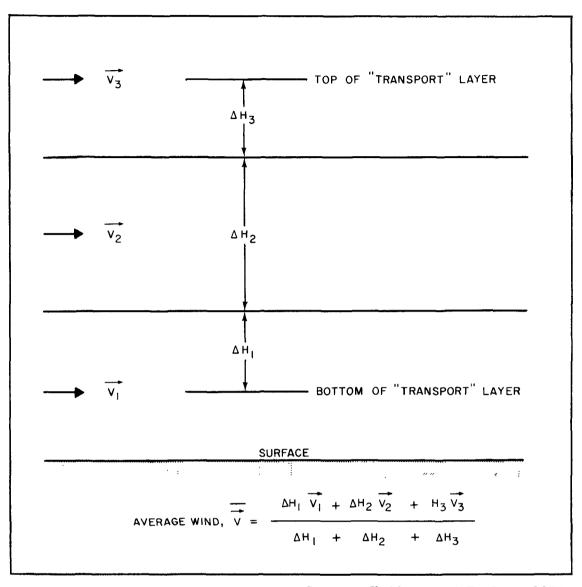
For these applications, the model has used observed winds within a "transport" layer to calculate the trajectories. Figure 9 illustrates the observed winds above a point for a specific example; the general form is:

$$\vec{v} = \sum_{\Sigma} \frac{\Delta H}{\Delta H} \vec{v}_{i},$$

where \overrightarrow{V} is the vector average wind throughout the transport layer; \overrightarrow{V}_i is the measured wind vector through the i^{th} layer; and H_i is the depth of that part of the i^{th} layer that lies within the transport layer.

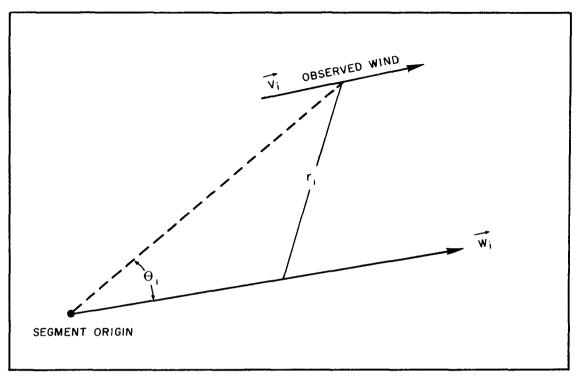
The trajectory segments are calculated from the transport layer winds according to the following formula:

$$\vec{S} = \frac{\sum_{i}^{R} D_{i} A_{i} \vec{W}_{i}}{\sum_{i}^{R} D_{i} A_{i}} ,$$



Source: Heffter and Taylor, 1975

FIGURE 9. SCHEMATIC DIAGRAM OF WIND AVERAGING SCHEME USED IN THE TRAJECTORY CALCULATION MODEL



Source: Heffter and Taylor, 1975

FIGURE 10. PARAMETERS USED BY THE HEFFTER AND TAYLOR TRAJECTORY CALCULATION MODEL

where:

 \overrightarrow{S} = trajectory segment.

 D_{i} = distance weighting factor

 $= 1/r_i^2$.

 $A_{i} = alignment weighting factor$

= 1-0.5 $\sin \theta_i$.

 \overrightarrow{W}_{i} = 3-hour displacement for \overrightarrow{V}_{i} .

r = distance between W and wind observation point (see Figure 10).

 θ_i = angle between \overrightarrow{W}_i and line connecting the trajectory segment origin and the wind observation point (see Figure 10).

 Σ indicates a summation over all observation points within a distance, R, of the segment origin; following the example of Heffter and Taylor, R was set equal to 300 nautical miles.

The lower bound of the transport layer has been taken to be 300 m. The top of the transport layer was taken to be 1000 m, the average of morning and afternoon mixing heights for this area, according to Holzworth (1972). The measurements also showed this to be a typical height to which ozone was mixed.

Application of the trajectory model along the east coast presents some difficulties because of the lack of data over the Atlantic Ocean. In such a situation, the winds that are interpolated for calculating the trajectory will be based on observations to the west of the site. Usually, this is not too serious, but when there are sharp gradients in the wind field it can cause problems. In particular, when a weather front approaches from the west, the trajectory calculation will begin to reflect the shifted winds behind the front well before it arrives. Appendix B shows the calculated trajectories of air arriving at Groton and Simsbury, Connecticut, during the study period. Of course, the reliability of these trajectories is increasingly suspect at the earlier times. For the preceding 12 hours or so the trajectories probably represent air positions within a few tens of kilometers of the "true" path.

B. Graphical Data Displays

1. General

Several different kinds of graphical data display have been used in the presentation of results in the following sections. We feel that these displays aid the interpretation considerably, but they may be somewhat unfamiliar to many readers. For this reason we have provided the brief descriptions that follow.

2. Isopleth Maps of Ozone Concentration

Two types of isopleth maps were used to show the distribution of ozone concentrations near ground level. Figure 11 illustrates the first type. It shows isopleths of the maximum, hour-average ozone concentration for the day and isochrones to indicate the time that maximum concentration occurred. Isopleth maps similar to Figure 11 were also drawn to show the distribution of 03 concentration at a specific hour. The isopleth maps help define pollutant patterns and make it easier to see how these patterns relate to the meteorochemical processes involved. In all the figures of this type, lines of constant ozone concentration are labeled in parts per billion (ppb). The isochrones indicate the hour of maximum concentration in Eastern Standard Time (EST). Appendix C presents the maximum-hour ozone maps for each day of the study period.

3. Weather Maps

Time of frontal passage and prevailing meteorological conditions were determined from surface weather maps from the U.S. Weather Service. These maps have been described in Section II-C.

4. Vertical Cross Sections

Vertical cross sections showing the distribution of ozone in a vertical plane were used to identify the effects associated with weather fronts and their movement through an area and to show graphically the urban plume structure. The presence of elevated 0_3 layers is also seen easily in this kind of display. Figure 12 is an example of a vertical 0_3 cross section showing the meanings of the symbols used.

Vertical cross sections are comparable to the ozone maps discussed earlier except that the plane in which the concentrations are

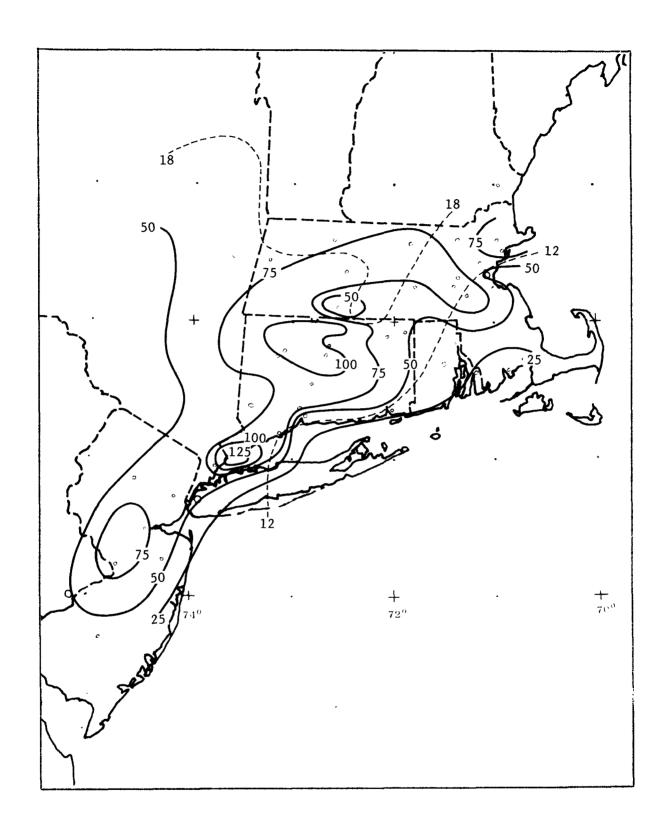


FIGURE 11. EXAMPLE OF OZONE ISOPLETHS AND ISOCHRONES

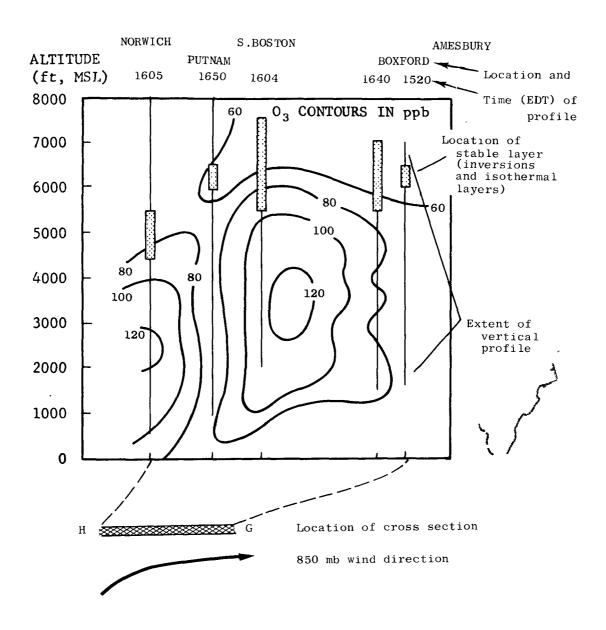


FIGURE 12. EXAMPLE OF AN ${\rm O_3}$ VERTICAL CROSS SECTION USED IN THIS STUDY

measured is oriented perpendicular to the ground surface, as opposed to being the ground surface itself. In the figures presented later in this report, the line above which the cross section applies is shown on a map of the region. The basic data were obtained from aircraft measurements of ozone. The points at which the vertical ozone profiles were measured are shown on the map, and the vertical extent of those measurements is indicated by vertical lines on the cross section itself. The presence of stable layers is indicated by stippled bars. Often the wind directions at the 850 mb level (about 1500 m) are indicated by arrows-streamlines--on the map. Times (EST) of the measurements are given above the diagram. Those cross sections that were not used in the text of this report are shown in Appendix D.

5. <u>Time Sections</u>

Time section analyses of ozone were carried out for two sets of monitoring stations during periods of frontal passage. One series of stations extended in a line from Greenwich, Connecticut, to Fairhaven, Massachusetts. The other extended from Bridgeport, Connecticut, to Amherst, Massachusetts. Figure 13 is an example of a horizontal time section offset from its corresponding geographic position. The two axes of the time section are time and distance (along the line of stations being used for the analysis). The isopleths in the analyses in this report are ozone concentrations (ppb).

The components of the ozone gradient parallel to the time axis represent the rate of change of concentration. The gradient in the direction of the space axis is the rate of change with distance along the measurement line. We have also plotted the passage of weather fronts on these diagrams. The heavy line marking the front shows its time of passage for each point along the line.

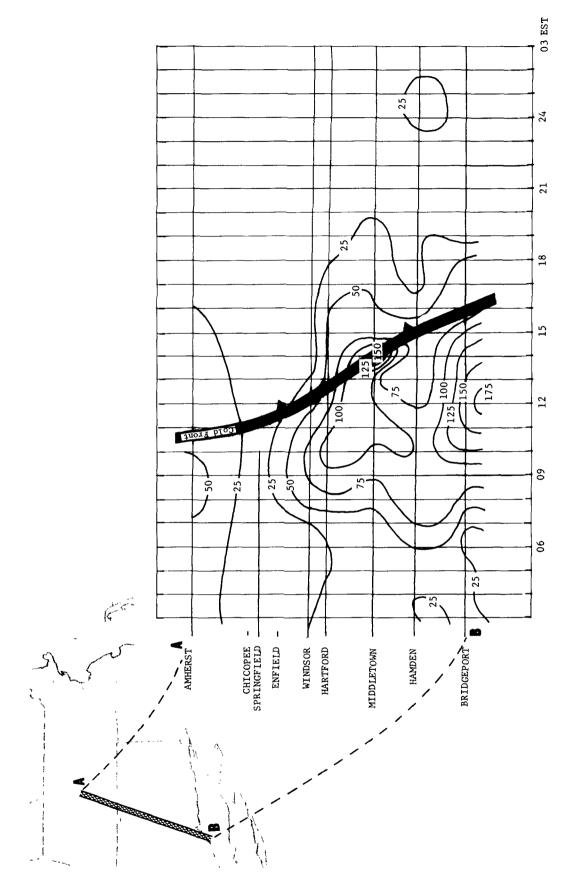


FIGURE 13. EXAMPLE OF A TIME SECTION

IV RESULTS

A. <u>Photochemical Pollutant Transport</u> in the New England Area

1. Background

In essence, the basic question to be answered by this study concerns the distance that ozone precursors from some large source area will travel before their contribution to ozone concentration falls to a level where it cannot be distinguished from the contribution of other sources. Recently, Martinez and Meyer (1976) reviewed data collected around a number of U.S. cities. They found that the increase in ambient ozone from individual urban areas could be detected nearly 300 km downwind, with maximum concentrations found anywhere from 8 km to 135 km downwind.

Ludwig et al. (1977) examined the question from a different viewpoint. They examined the trajectories followed by air arriving at different rural locations and then examined the statistical relationships among the emissions and meteorological conditions along the trajectory and the ozone concentrations at its end point. They found significant correlation between 03 concentration and NO emissions as many as 36 hours earlier. Most of the variance in the ozone data could be explained in terms of air temperature and emissions during the last 12 hours of the trajectory. They found that when ozone concentrations exceeded 80 ppb, the air movement was most often less than about 200 km during the last 12 hours of the trajectory and less than about 500 km during the last 36 hours. These studies suggest that the effects of large area sources on ozone concentration can persist for at least several hundred kilometers.

The effects of the New York metropolitan area emissions on surrounding areas have been studied by Cleveland et al. (1975a). They compared maximum daily ozone concentrations measured during the summer of 1974 at numerous New England monitoring sites with the wind directions during the same day. Briefly, they showed that the highest ozone concentrations occurred with wind directions from New York at stations throughout Massachusetts and Connecticut. Even Boston, nearly 300 km from New York, showed the effect. They only considered days with well-defined wind directions and temperatures above 70°F at Hartford.

The emissions of precursors clearly affect ozone concentrations in downwind areas. The degree to which the effects are manifested depends on the meteorological conditions. Several studies (e.g., Ludwig et al., 1977; Bruntz et al., 1974) have found that there are certain meteorological conditions that are consistently associated with high ozone concentrations. These are high temperatures, light winds, and strong insolation. Ludwig et al. (1977) have also reported that light, southerly through westerly winds are more often associated with high ozone concentrations in the areas that they studied than are winds from other directions.

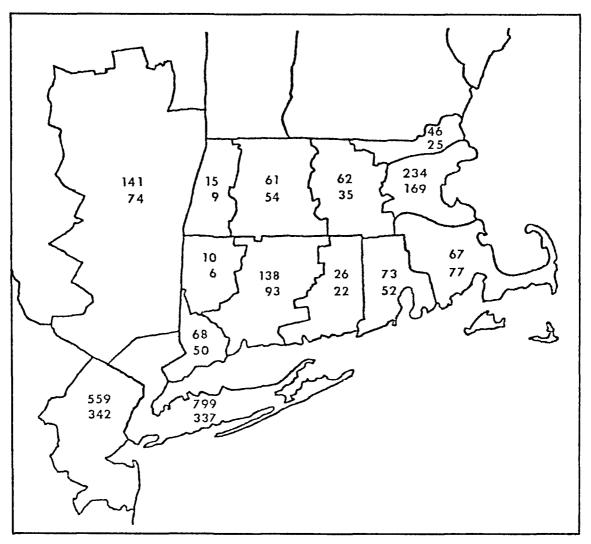
The above discussion can serve to define the areas where we might look for ozone-transport effects and the conditions under which those effects are likely to be most pronounced. In general we should expect to find the strongest evidence of ozone transport downwind of the areas where hydrocarbon and oxides of nitrogen emissions are greatest. The effects should increase with downwind distance for a few kilometers or tens of kilometers and then decrease with distance beyond that. Past studies also have shown that high daytime ozone concentrations are found most often in anticyclones (high-pressure cells), especially in their western parts. Another preferred location for high ozone concentration is the warm air near a weather front.

Following the clues provided by the above information we examined the spatial distribution of ozone concentrations to see what evidence there might be of transport from the major emissions areas. We studied in detail particular incidents where transport seemed probable, emphasizing anticyclonic and prefrontal cases. We also examined several nighttime incidents of relatively high ozone concentrations to determine their causes.

2. Statistical Evidence

Figure 14 from Cleveland et al. (1975) shows the emissions of ozone precursors in various parts of the region of interest. The figure shows that the New York City-Northern New Jersey areas are far and away the most important sources of the ozone-producing primary pollutants, with the Boston and Hartford areas providing less important source regions.

Figure 15 shows the observed maximum-hour ozone concentrations at seven sites during the study period. The sites are arranged from bottom to top in order of increasing distance from the New York City area--ranging from Bridgeport at about 80 km to Boston at about 300 km. Each asterisk represents one observation; if more than one observation had approximately the same value, then the plotted numeral shows the number of cases. The data have been divided into two categories, weekdays and weekends. For each location, the weekend values are plotted just above the weekday values. This kind of plot makes the tendency toward decreasing ozone concentrations with increasing distance from New York quite apparent. The conclusion that can be drawn from a visual examination of the figure can be verified statistically. The Spearman rank correlation (Langley, 1970) between the upper decile ozone concentrations and the distance from New York shows that there is a negative correlation that is significant at the 3% level. The upper decile values



Source: Cleveland et al, 1975

FIGURE 14. EMISSIONS OF HYDROCARBONS (upper number) AND OXIDES OF NITROGEN (lower number) IN THOUSANDS OF TONS PER YEAR

were chosen for the test because the effects should be greatest for the high ozone cases, e.g., the top 10%.

As already mentioned, Cleveland et al. (1975) found that higher ozone concentrations were most common at a wide variety of New England locations when the observed wind directions indicated air motions from New York. We have used the trajectories shown in Appendix B to examine this same phenomenon for Groton, Connecticut. The trajectory calculations

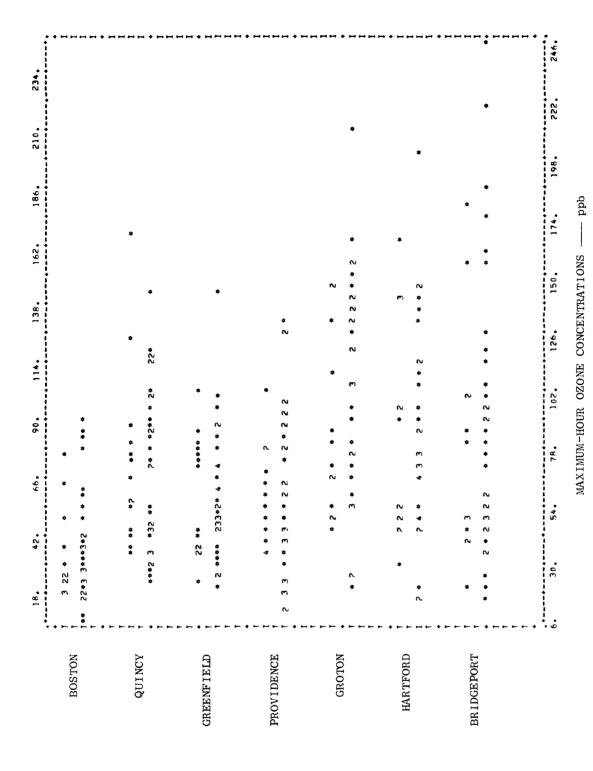


FIGURE 15. OBSERVED MAXIMUM DAILY OZONE CONCENTRATIONS AT SEVEN NEW ENGLAND SAMPLING SITES

should provide a better indication of the air's past history than do low-level wind measurements made at single locations in the area. We have limited our investigation to those days when no weather fronts passed through the area because the presence of fronts in the area reduces the reliability of the trajectory calculations, as noted in Section III of this report. The importance of weather fronts is treated in detail in a following section of this report.

The work of Ludwig et al. (1977) has shown that weather conditions are important determinants of ozone concentration apart from the effects of emissions. We have tried to isolate the emissions effects by selecting a data set of relatively uniform weather conditions and subdividing it into two classes: those cases where the air has passed near the New York-New Jersey area and those cases where it has not. Only those days when the air came from directions between southeast and west were used. By limiting ourselves to these wind directions, reasonably similar meteorological conditions should have prevailed. When the air had moved to Groton from a direction between southeast and southwest it would not have been influenced by New York or other major emissions areas; air arriving at Groton from directions between southwest and west would have been influenced by New York emissions. The 1900 EST Groton ozone concentrations were significantly greater when the air had come from the New York area than for other directions of arrival. For the ten cases influenced by New York, the average was 80 ppb and for the five non-New York cases, 26 ppb. According to the Wilcoxon sum of ranks test (Langley, 1970) there is less than a 1% chance that the two sets of data could have been drawn from the same population.

For air arriving at Groton at the other hours for which the trajectories were calculated (0100, 0700, 1300 EST), the differences were not significant. This reflects the fact that the New York effects will be most pronounced when the photochemical production of ozone can

proceed to operate on early morning emissions through most of the daylight hours.

If we use the data from both Groton and Simsbury, we can make comparisons that illustrate the effects of both New York and Hartford. Figure 16 shows ozone concentrations at Groton on the nonfrontal days plotted against the direction from which the air has come during the preceding 6 hours. Figure 16a shows ozone concentrations observed at 1300 EST and 16b those measured at 1900 EST. The directions to New York and Hartford are marked in the figure. It should be noted that in each case most of the ozone concentrations above 80 ppb occurred in air that had passed over either New York or Hartford. If it were possible to remove the emissions from one or the other of these cities, we could get some idea of how much effect they have on ozone in surrounding areas.

Obviously it isn't possible to actually remove the cities, but if we look at conditions just upwind of one of them, it should provide much the same information. Figure 17 is the same as Figure 16 except the data are from Simsbury, located northwest of Hartford. Figure 17 shows that the only high concentrations that were observed at Simsbury were found in air that had come from New York. Even though the frequency of trajectories from directions between 288° and 325° is about the same at Simsbury as at Groton, there was but one instance when the concentration exceeded 80 ppb in air arriving from those directions. The major reason for this lack of high concentrations at Simsbury is the fact that the Hartford area emissions that are present in the Groton air are not in the Simsbury air from those directions.

3. Case Studies

a. Selection of Cases

In most of the discussions in this report, we deal with data selected from the entire period when special studies were under way

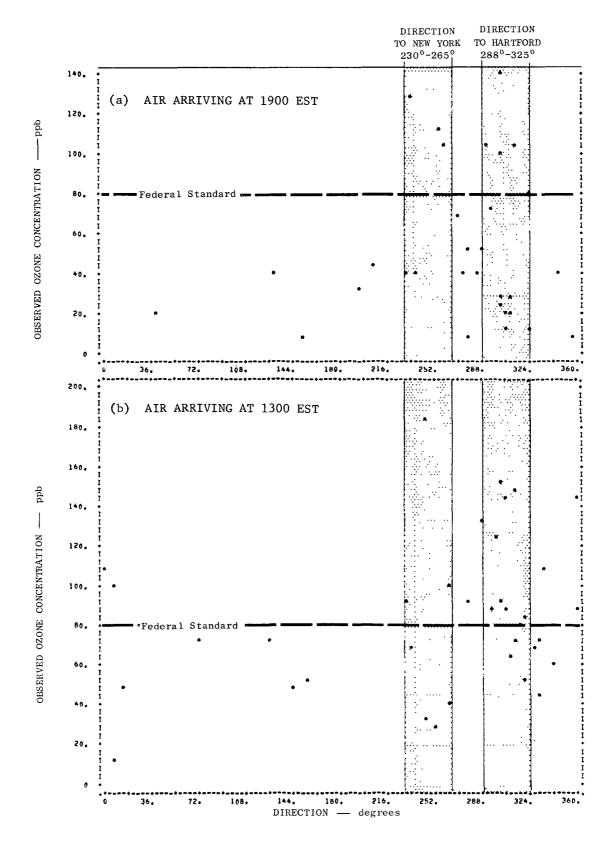


FIGURE 16. OBSERVED OZONE CONCENTRATIONS AT GROTON VERSUS THE DIRECTION FROM WHICH THE AIR CAME DURING THE PRECEDING 6 HOURS ON DAYS WITHOUT FRONTAL PASSAGES

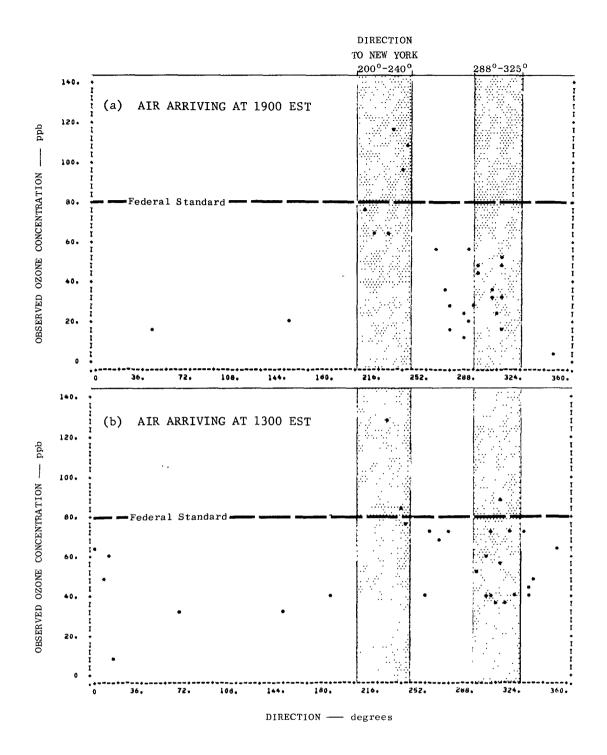


FIGURE 17. OBSERVED OZONE CONCENTRATIONS AT SIMSBURY VERSUS THE DIRECTION FROM WHICH THE AIR CAME DURING THE PRECEDING 6 HOURS ON DAYS WITHOUT FRONTAL PASSAGES

in the Northeast during 1975, that is from mid-July until the end of August. The following case studies have all been taken from that limited period when the airborne activities of the four participating groups were most intensive, from about 10 August to 21 August, because this is the only period for which the vertical cross sections could be constructed. The vertical cross section has proved to be a most useful tool for showing the anatomy of the urban plume. This method of analysis provides several quite interesting examples of ozone downwind of the major urban centers. Because the highest concentrations are often aloft, the vertical cross sections tend to provide a better picture than the more conventional surface analyses, such as were used by Rubino, Bruckman, and Magyar (1975) to show transport from New York to Connecticut.

b. <u>Interpretations</u>

10 August 1975 was a day of weak pressure gradients and light winds in the southern New England area as can be seen from the weather map shown in Figure 18. The pressure gradient should cause the general surface air flow to be from the west or west-southwest. The winds at 850 mb, approximately 1500 m altitude, shifted during the day from west-northwest to west-southwest. We can expect the pollutants from the urban areas to travel generally toward the east or east northeast through the day. Using this as a guide, we know about where to look for the urban plumes.

Figure 19 shows the distribution of the maximum observed values of hour-average ozone concentration on this day. The figure shows that concentrations exceeded 150 ppb along the south coast of Connecticut. Although the lack of data from eastern Long Island prevents confirmation, it appears that the highest concentration probably occurred over Long Island or Long Island Sound. The hours at which the highest values were observed along the Connecticut coast were in the early afternoon, around 1300 or 1400 EST.

FIGURE 18. WEATHER MAP, 10 AUGUST 1975, 0700 EST

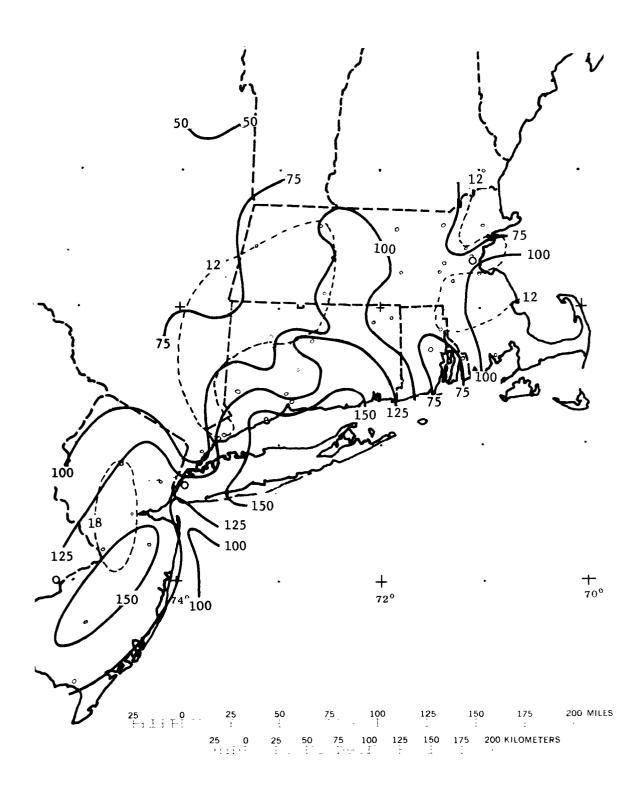


FIGURE 19. MAXIMUM HOUR-AVERAGE OZONE CONCENTRATIONS (ppb) 10 AUGUST 1975

Several of the organizations participating in the northeast northeast oxidant study conducted coordinated aircraft observations on this day, allowing use of vertical cross sections to analyze the data. Figure 20 shows the ozone distribution in a vertical plane, along a line that is nearly north-south. The analysis shows that the highest concentrations are at an altitude of about 300 m above Bridgeport. There are probably two mechanisms contributing to this elevated plume. First is the buoyancy that may come from the heat that is usually associated with pollution-generating processes. The second is the difference in the chemical reactions between ground level and the more elevated layers. At ground level the ozone-producing reactions are to some extent being offset by competing ozone-destroying reactions. In particular, NO released near ground level will quickly combine with the ozone. Eventually the NO, produced by this reaction may result in increased ozone, but on the shorter term the net result is a reduction in ozone concentrations near ground level.

Figure 21 shows two cross sections based on data collected later in the day. In this figure we have also drawn the streamlines for the 850 mb winds that were observed at 1900 EST. The cross sections are based on data collected between 1545 and 1715 EST. These two analyses show the presence of elevated ozone layers. Concentrations over Bridgeport, Connecticut, exceed 180 ppb and over western Long Island Sound they exceed 140 ppb. If the 850 mb streamlines shown in the figure represent the air motions affecting the ozone transport around this time, then the air that passed over Bridgeport also will have passed over Groton. If so, the two cross sections show a decline in the ozone concentrations from values above 180 ppb to about 125 ppb.

At the south end of the cross section over Groton in Figure 21 there are very high concentrations aloft, in excess of 230 ppb. The air reaching this area had passed over the Newark-Jersey City region

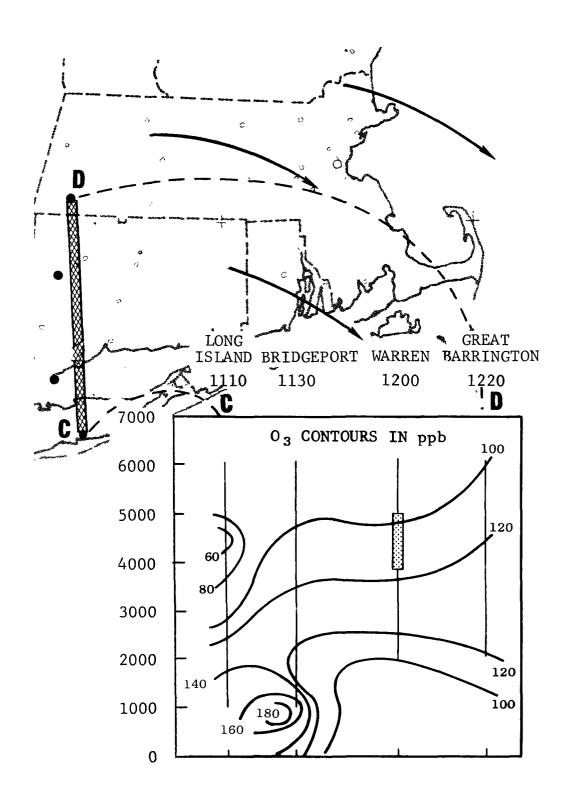


FIGURE 20. VERTICAL CROSS SECTION OF OZONE CONCENTRATION OVER WESTERN CONNECTICUT AND LONG ISLAND, 1110—1220 EST, 10 AUGUST 1975

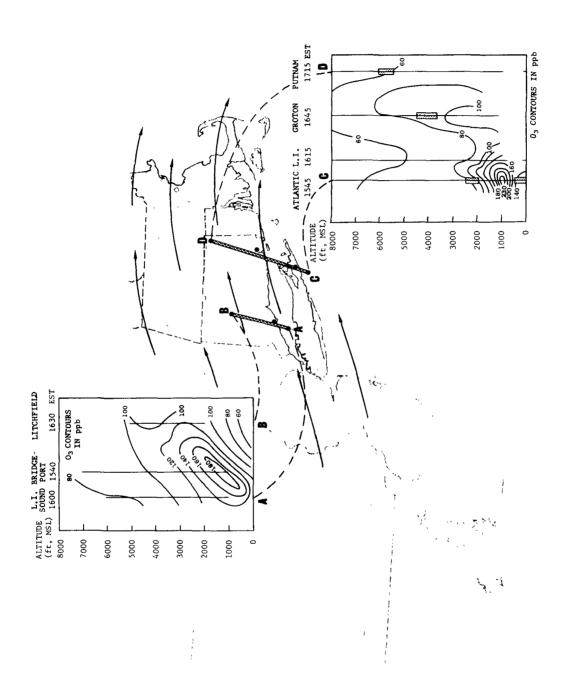


FIGURE 21. VERTICAL CROSS SECTIONS OVER CONNECTICUT 1545-1715, 10 AUGUST 1975

of New Jersey, then over the south tip of Manhattan and the Queens-Brooklyn areas. The high ozone concentrations aloft seem very likely to have had their genesis in emissions from those upstream regions.

There even seems to be a region of lower concentrations separating the high concentrations in the air that passed over the New York-Newark complex from those associated with the air that traveled along the populated Connecticut coast. Although no vertical profile is available to fully substantiate the lower concentrations in the air that traveled the length of Long Island Sound, a horizontal flight at 1000 feet shows that concentrations reached a minimum over the Sound and hence the analysis shown in the figure can be justified.

Even outside the plumes, the ozone concentrations exceed 80 ppb. This suggests that rather high concentrations of ozone may already be present in the air before it reaches these urban areas. This was confirmed by the ISC observations (Wolff et al, 1975) on this day. Concentrations as great as 160 ppb were observed in vertical profiles above upwind areas over New Brunswick and Trenton, N.J.

11 August 1976 is an instructive example because it illustrates some important meteorological effects when taken in conjunction with the preceding case. Figure 22 is the morning weather map for this day. In many respects it is similar to the preceding day, but there is a low-pressure trough in the New England area. The 3-hour weather maps shows that this trough moved slowly from west to east during the day. It was accompanied by generally unstable air; convective clouds gave evidence of mixing taking place through relatively deep layers.

Figure 23 shows two cross sections for the morning of this day. The effects of the emissions from the New York area can be seen in the lower levels of the western cross section. The plume of high concentrations in this case is much nearer the surface than the day before. This

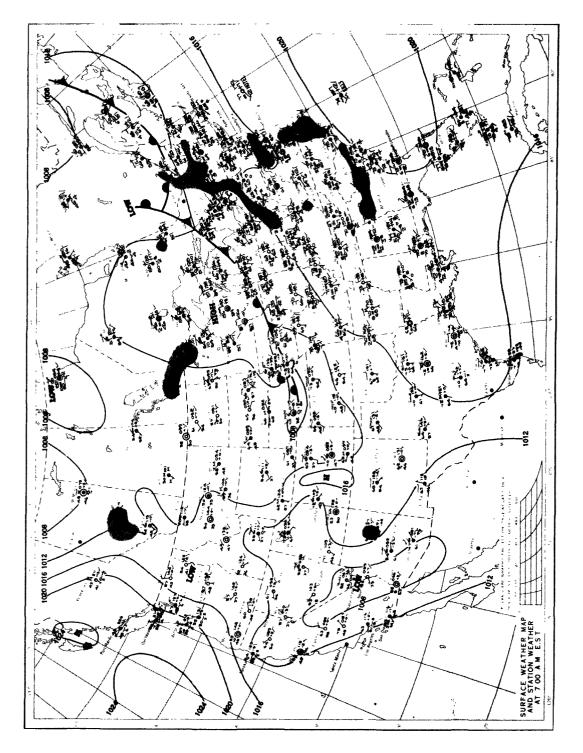


FIGURE 22. WEATHER MAP, 11 AUGUST 1975, 0700 EST

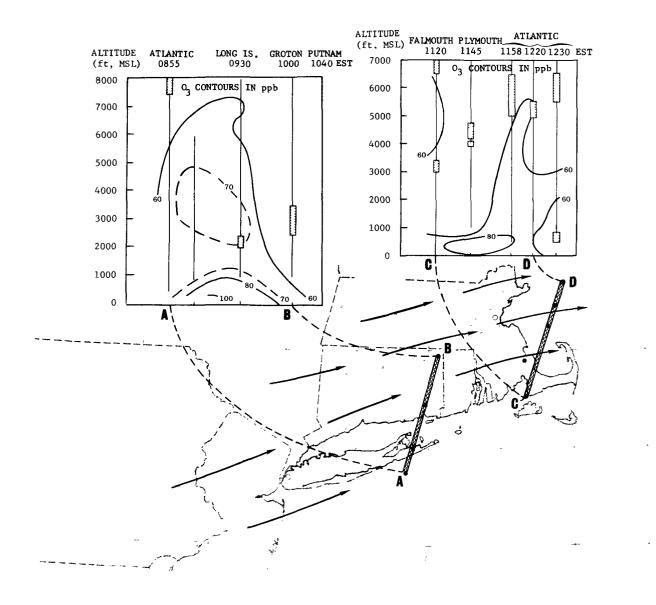


FIGURE 23. VERTICAL CROSS SECTIONS OF OZONE CONCENTRATIONS OVER EASTERN CONNECTICUT AND EASTERN MASSACHUSSETS, 0855—1230, 11 AUGUST 1975

probably is a reflection of two effects. First, the greater vertical mixing on this day has probably brought material to the surface from aloft and caused somewhat more uniform vertical profiles. Secondly, the air intersecting the cross section has had a recent passage over Long Island Sound where there were no NO emissions to lower the ozone concentrations at the surface.

The cross section off the east coast of Massachusetts gives slight evidence of a plume, perhaps from the Providence area. The northern end of this cross section does not show much evidence of transport from the Boston area. This may be because of a seabreeze that developed during the day. Figure 24 shows the maximum-hour ozone concentrations in the New England area on 11 August 1975. There are areas where concentrations during the day exceeded 125 ppb on either side of Boston, both to the northwest and to the southeast. The minimum concentrations over Boston, between the two higher areas, are probably the result of NO scavenging of ozone in the city. The 3-hour weather maps show that the surface wind at Boston switched from light WNW to a light wind from the SE between 0700 EST and 1000 EST. It may be that the pollutants were first carried to the east, and then returned westward with the onset of the seabreeze. The seabreeze had begun before the time of the cross section shown in Figure 23 so the fact that an identifiable plume from Boston is not found is not too surprising.

Figure 25 shows a cross section parallel to the morning 850 mb wind direction. The vertical profiles and surface measurements used to prepare this figure show the plume to be elevated over the urbanized area. The relatively high concentrations aloft drop below 80 ppb over the eastern parts of Long Island. This cross section provides evidence that the plume becomes diffuse rather quickly when there is good mixing, at least during the morning hours. Zeller et al (1976) have analyzed data for this day and they were able to identify an O₃ plume 50-km downwind of the Boston area in the early afternoon.

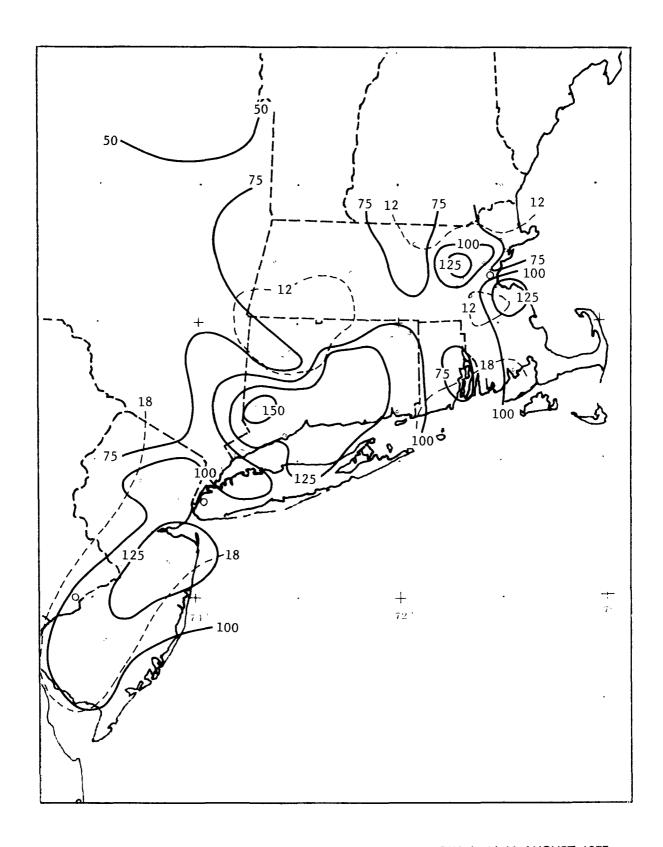


FIGURE 24. MAXIMUM HOUR AVERAGE OZONE CONCENTRATIONS (ppb) 11 AUGUST 1975

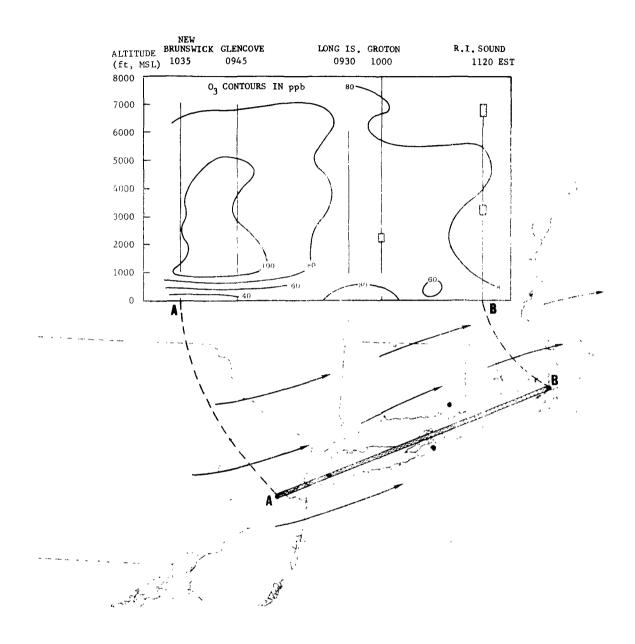


FIGURE 25. VERTICAL CROSS SECTION OF OZONE CONCENTRATION (ppb)
PARALLEL TO 850 mb WINDS, 0930—1120, 11 AUGUST 1975

21 August 1975 provides an example of the behavior of urban plumes when the area is under the influence of a large anticyclone (high-pressure cell) to the east. According to EPA (1975) and Ludwig et al. (1977) this is one of the favored meteorological situations for ozone formation. Figure 26 is the morning weather map for this day, showing the high-pressure area centered just off the coast.

Vertical cross sections based on data collected during the morning of this day show high ozone concentrations aloft that are almost certainly the result of urban emissions. Although the two cross sections in Figure 27 are reasonably close together, the line that is more to the northwest is based on data collected upwind of, or above, the major urban centers. Ozone concentrations over Trenton and New Brunswick exceed 80 ppb, but no values as great as 100 ppb were found. In general, concentrations are quite uniform with height, but tend to decrease toward the northeast at all altitudes. This uniformity with height is indicative of a well mixed body of air that can be considered to represent "background conditions."

The other cross section has a very different appearance. Ozone concentrations as great as 140 ppb are observed in a layer between 1500 and 2000 feet, even though the measurements were made in mid-morning, well before the time when one would expect maximum photochemical production of ozone. On the basis of the 850 mb morning wind patterns shown in the figure, it appears that the high concentrations observed aloft over the Atlantic ESE of Sandy Hook could be explained by emissions in the Newark-New York area. The vertically uniform low concentrations at the northeast end of this line, where it is very close to the other line, show much the same "background" conditions seen in the other cross section.

FIGURE 26. WEATHER MAP, 21 AUGUST 1975, 0700 EST

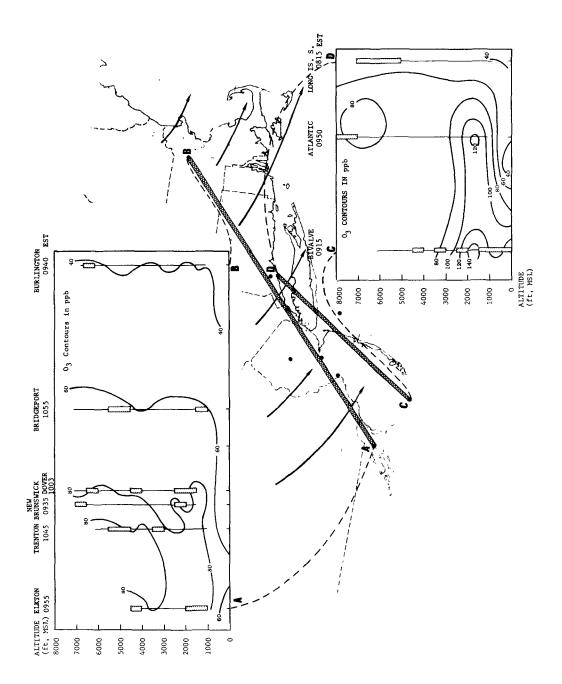


FIGURE 27. VERTICAL CROSS SECTIONS OF OZONE CONCENTRATION (ppb), 0815-1055, 21 AUGUST 1975

The high values above Bivalve (Point C in the figure), in Southern New Jersey are more difficult to explain. The only metropolitan area lying to the WNW, the direction from which the 850 mb winds were blowing, is Wilmington, Delaware. Another possibility is that these concentrations are the northern edge of a plume from Baltimore. This would require that the air motions had a component from the south. The surface weather maps show light winds from the south-southeast, so it is possible that the net transport at 2000 feet has the necessary direction to bring pollutants from Baltimore over Bivalve.

One final comment is in order concerning these cross sections. It is quite reasonable to ask why there is no evidence of a plume of high ozone concentration downwind of Philadelphia. The lack of such evidence is because no vertical profiles of concentration were made between Bivalve and the location ESE of Sandy Hook. It seems quite likely that such measurements, had they been made, would have revealed evidence of Philadelphia's effects.

Figure 28, based on data collected during the early and mid-afternoon hours displays a very complex pattern of ozone aloft that is quite difficult to interpret. Concentrations at 4000 feet above Bridgeport, Connecticut, were nearly 200 ppb. Concentrations of ozone in excess of 140 ppb are found over New Jersey and over Martha's Vineyard. Some of the difficulty that arises in the interpretation of these patterns probably comes from the rather large time span covered by the data, from 1325 to 1550 EST. Presumably, the patterns would have been somewhat more organized had the measurements been made at more nearly the same time. However, the observed complexity is more likely the result of the very light winds that prevailed in the area. The pressure gradients at the surface and 850 mb were very weak, a condition that is usually accompanied by light, variable winds. According to Wolff et al. (1975), the early morning winds were light and from the

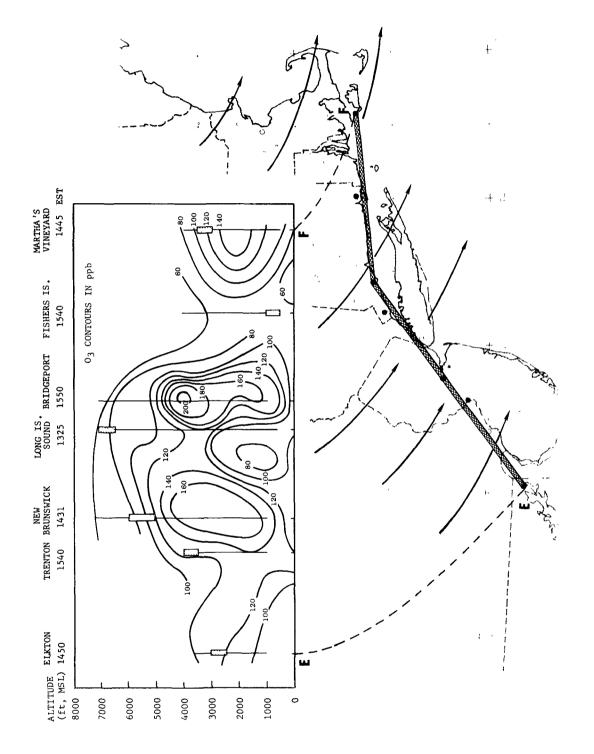


FIGURE 28. VERTICAL CROSS SECTION OF OZONE CONCENTRATION (ppb), 1325-1550 EST, 21 AUGUST 1975

north to northeast, but shifted to southwest in the afternoon.

Wolff et al (1976) have analyzed the events of this day extensively. They have concluded that ozone and precursor emissions from urban areas, such as Philadelphia, Baltimore and Washington, had accumulated during a period of light winds that lasted from late evening on 20 August until the early morning hours of the following day. These accumulated pollutants were calculated to have moved to the northeast during the afternoon of 21 August. By late evening the movement was quite rapid. The extended period of pollutant accumulation during the period of light and variable winds, followed by the long travel distances, could easily account for the complicated distribution of ozone seen in the crosssections of Figure 28. It may be, as Wolff et al (1976) have suggested, that the ozone observed later this day had come from as far away as Washington, D.C. Zeller (1976) believes that the plumes seen in Figure 28 may have come from Philadelphia, New York and Hartford, having traveled to the southwest in the morning and then returned toward the north later in the day.

No attempt has been made to discuss all the available cross sections. Others are presented in Appendix D. The reader will see in many of them the same kinds of patterns discussed above, but there are also other examples that are rather plain and "uninteresting." Of course, the upwind cross section shown for the morning of 21 August 1975 would also have been rather uninteresting had it not been for the availability of a downwind cross section with which it could be contrasted to show the presence of the urban plumes.

The three days that were discussed here illustrate several of the more important factors influencing ozone concentrations. The

effects of urban emissions, of transport by moderate and by weak winds, the effects of vertical mixing, and of scavenging by NO are all illustrated. Most important is the fact that the urban plume is clearly discernible in many of the cross sections at considerable distances downwind of the source. Also quite important is the fact that the center of the urban plume is often well above the surface. This separation from the surface may have important consequences under some special nighttime conditions where mixing downward from aloft could lead to increased concentrations of ozone at the surface.

B. Special Situations

1. Frontal Passages

a. General

In the preceding sections, it has been shown that ozone concentrations in southern New England can be affected significantly by precursors emitted elsewhere. Winds that are aligned with the generally southwest-northeast orientation of the source areas can collect large amounts of precursors and transport them into New England. If the other conditions are right, considerable ozone can form during the journey. Reviewing, the conditions that are favorable to the transport of precursor emissions to New England from the New York-New Jersey areas and to the formation of ozone along the way include:

- winds from the southwest or west during the daylight hours
- Warm, sunny conditions.

The typical weather front passing through the area will produce the conditions listed above, provided that its time of passage through New England is in the afternoon or early evening.

Ludwig et al. (1977) have analyzed the distribution of maximum daily ozone concentrations for every day of 1974. Among those analyses are numerous examples showing the formation of high ozone concentrations over New England in the warm air ahead of an approaching weather front. Four examples are shown in Figures 29 through 32. In each case the morning weather map (0700 EST or 1200 GMT) shows a frontal system approaching New England with high ozone concentrations preceding it.

Behind the front, there is a relatively fresh mass of polar air. This air has usually traveled from the northwest over areas that have few major emissions, so the cold-air side of the front should be relatively clean. Figures 29 through 32 show this effect. An observer at a fixed location would see ozone concentrations rise as the front approached and then fall rapidly as it passed.

In the following sections, five case studies are presented to illustrate the effects associated with frontal passages through the area of interest. The SAROAD data for Connecticut, Rhode Island, and Massachusetts have been used to provide detailed distributions of ozone at 3-hour intervals. The analyses of Figures 29 to 32 show only maximum-hour concentrations and not how the concentrations change with the frontal passage. Also Ludwig et al. (1977) used more smoothing in the preparation of their analyses than is done in the more detailed case studies that follow. The frontal positions were determined directly from the 3-hour weather analyses of the U.S. Weather Service.

b. Case Studies

25 July 1975 was a day that illustrates the importance of the direction of the air movement ahead of the front and of time when the front passes through the area. Figure 33 shows the weather maps for the eastern United States for 0700 EST on 25 July and 26 July. The ozone

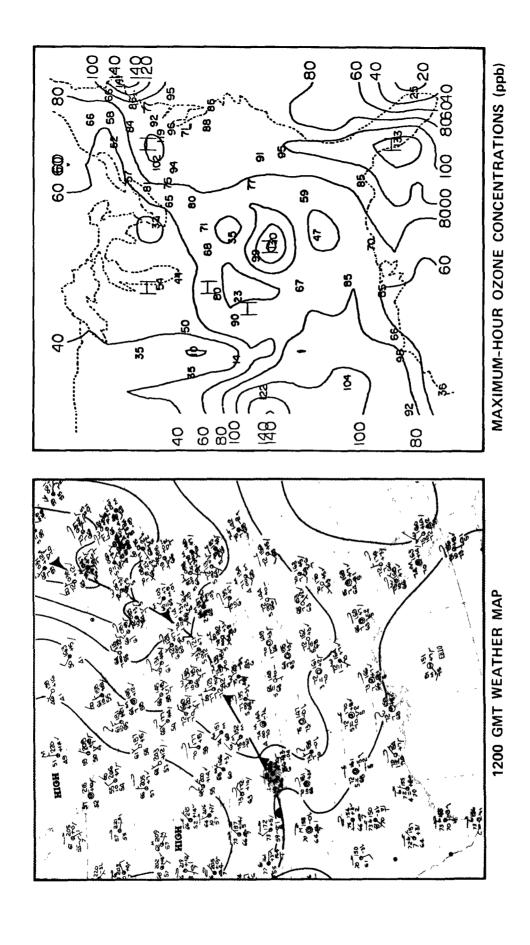


FIGURE 29. EXAMPLE OF HIGH NEW ENGLAND OZONE CONCENTRATIONS AHEAD OF A WEATHER FRONT, 15 JULY 1974

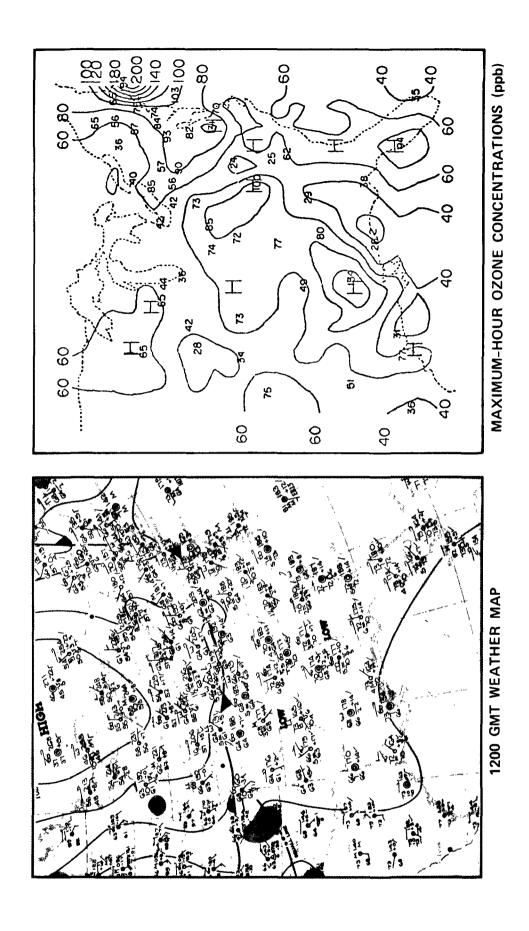


FIGURE 30. EXAMPLE OF HIGH NEW ENGLAND OZONE CONCENTRATIONS AHEAD OF A WEATHER FRONT, 14 AUGUST 1974

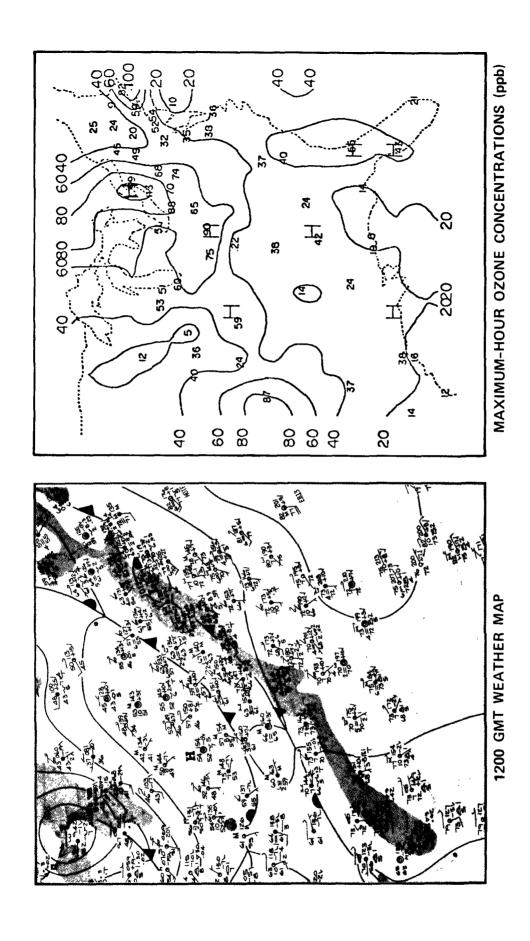
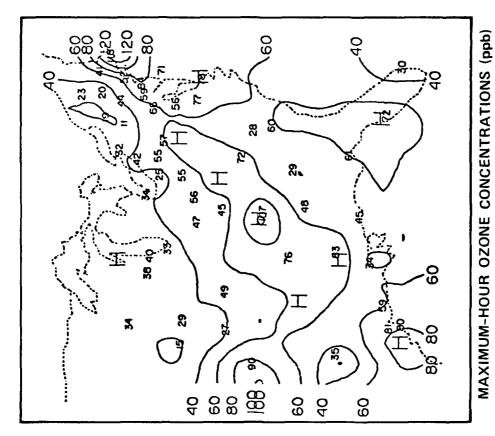
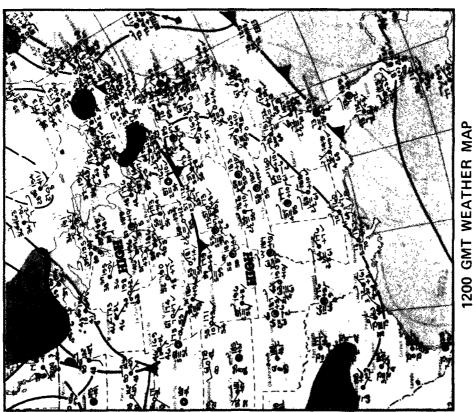
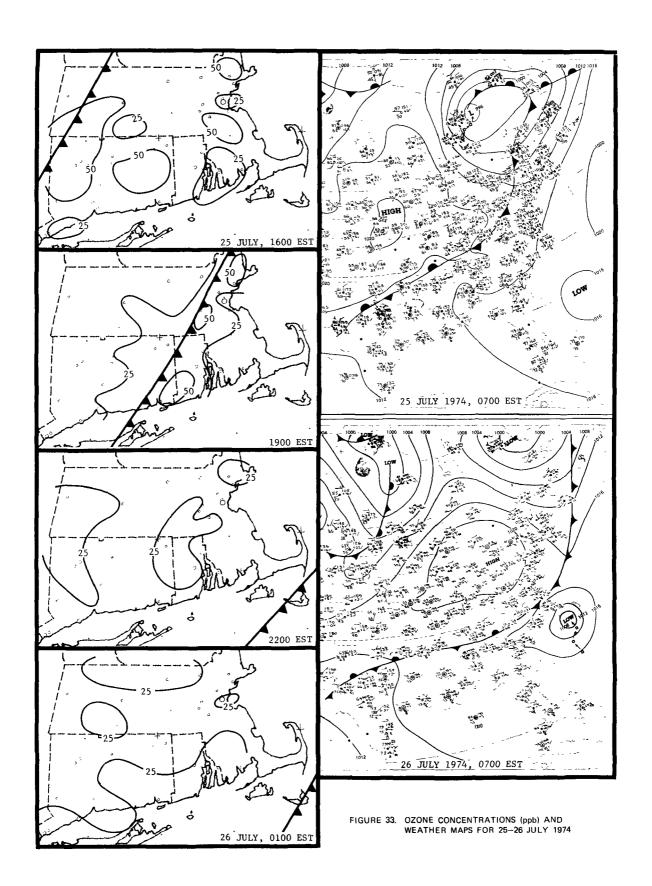


FIGURE 31. EXAMPLE OF HIGH NEW ENGLAND OZONE CONCENTRATIONS AHEAD OF A WEATHER FRONT, 30 AUGUST 1974







concentrations and frontal positions are shown at 3-hour intervals from 1600 EST on 25 July to 0100 EST on 26 July. As the front approaches the area at 1600 EST, the ozone concentrations are not very high, generally less than 60 ppb. Three factors contributed to the relatively low concentrations:

- (1) The area had been overcast for most of the day, suppressing photochemical 0_3 production.
- (2) The air arriving in the region had passed north of the major emissions areas (see Figure 34).
- (3) The time was past the period of peak photochemical activity.

With the already low concentrations, it is not surprising that the frontal passage does not produce any pronounced effects. About the only evidence of the type of frontal passage described earlier, with high ozone concentrations in the warm air ahead of it, is the line of 0_3 concentrations above 50 ppb that lies just ahead of the front at 1900 EST.

28 July 1976 was a day when ozone patterns behaved much closer to the idealized situation described earlier. Figure 35 shows the ozone patterns from 1300 to 2200 EST and the 0700 EST weather maps for 28 and 29 July 1976. Skies were clearer on this day than in the first case and the front arrives just past midday at a time when the photochemical activity should still be quite high. Although the air ahead of the front has come from the west and passed north of the area of maximum emissions, the wind speeds were lower, allowing more time to accumulate the emissions. Furthermore, during the morning rush hour the air ahead of the front had been over the Hudson River Valley. Although not ideal, the conditions ahead of the front in this case were more conducive to ozone production than they were in the preceding case.

As the front moves through the area, the highest concentrations stay just ahead of it until about 1900 EST when the front appears

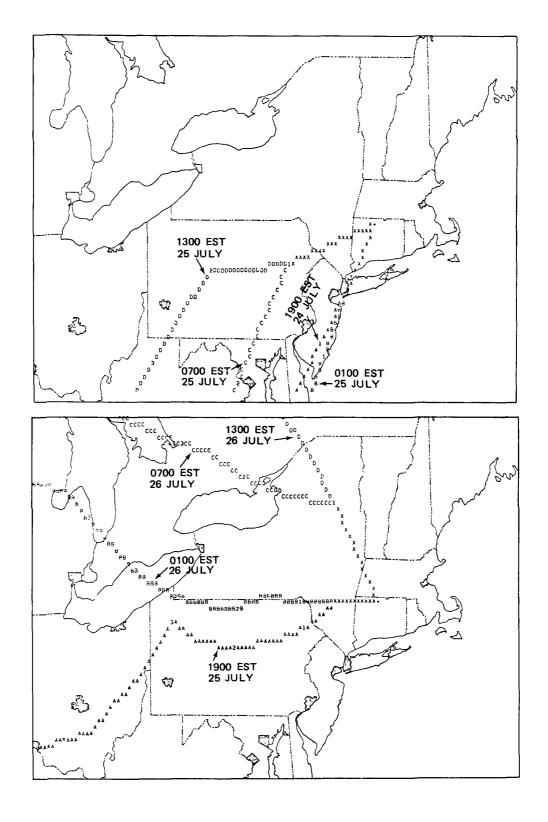
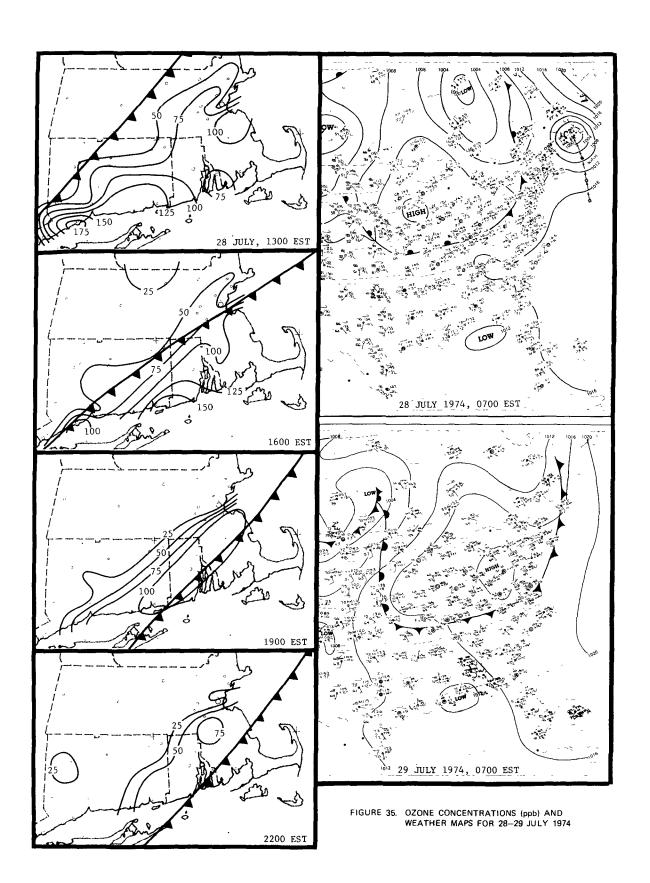


FIGURE 34. AIR TRAJECTORIES ARRIVING IN NORTHERN CONNECTICUT, 24—26 JULY 1975



to have overrun them. The frontal position shown in Figure 35 was taken directly from the Weather Service analyses. It appears from the 0_3 concentration that the actual frontal position at the time may have been about 30 km northwest of the analyzed position.

Time section analyses of the passage of this front through the area are shown in Figures 37 and 38. The map in Figure 36 shows the location of the stations used for these analyses. The approximate time that the front passed each location along the time section lines is shown in the figures along with the time-space ozone distributions. The buildup of ozone before the front arrives is evident in the figures, as is the rapid replacement of the ozone-laden air ahead of the front with the cleaner, polar air behind it.

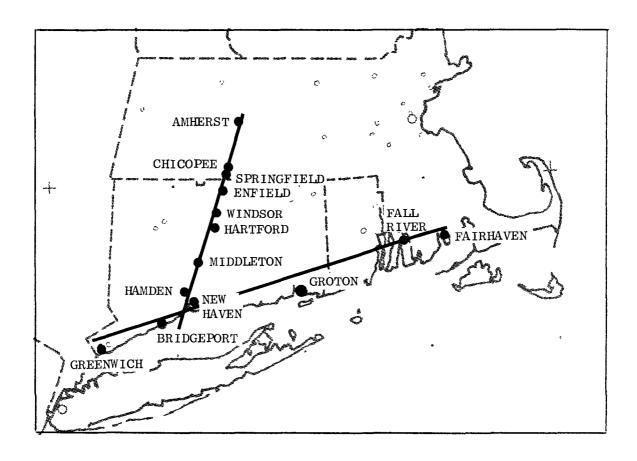


FIGURE 36. LOCATION OF TIME SECTION LINES

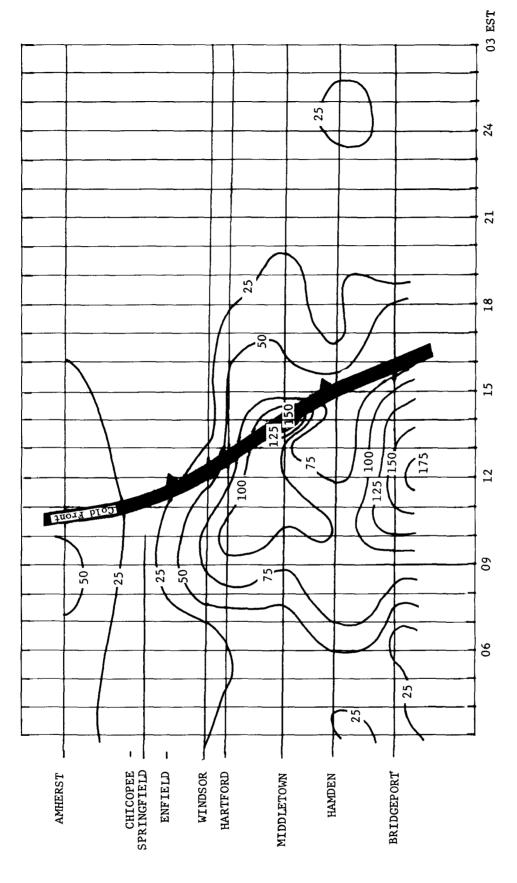


FIGURE 37. OZONE TIME SECTION ALONG LINE FROM BRIDGEPORT TO AMHERST, 28 JULY 1975

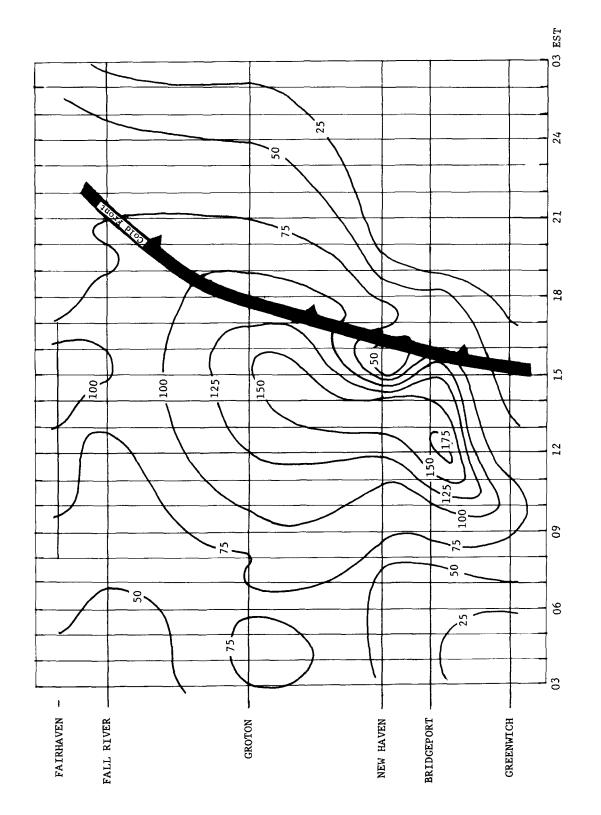


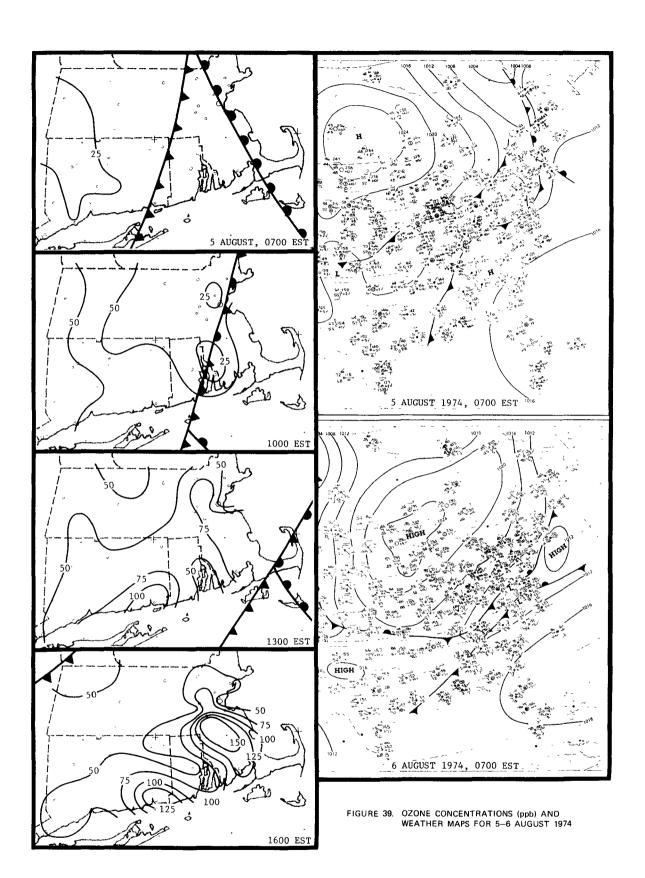
FIGURE 38. OZONE TIME SECTION ALONG LINE FROM GREENWICH TO FAIRHAVEN, 28 JULY 1975

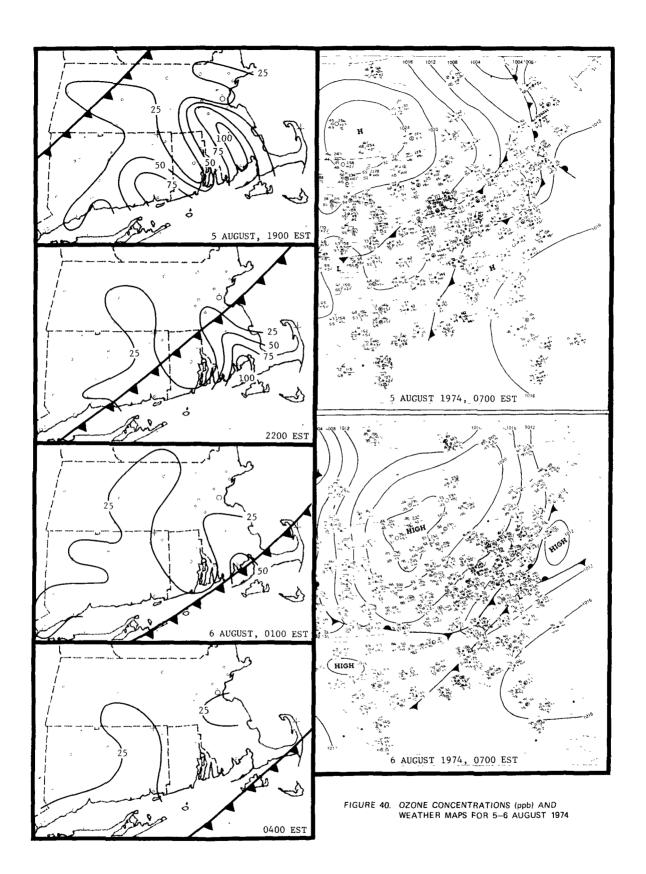
5 and 6 August 1975 were rather complex meteorologically in the New England area. Figure 39 shows the ozone concentrations from 0700 through 1600 EST on 5 August. As shown on the maps, an occluded frontal system passed through the area during the morning. Contrary to the discussion to this point, the maps show a buildup of ozone after this front rather than before it arrived. This was a rather weak front with little precipitation associated with it. The Weather Service analyses showed it to be followed by a stronger system. There was some fog behind the first front, but it had generally cleared by 1000 EST. Because the first front arrived in the area during the early morning, it is not surprising that it was not preceded by high 03 concentrations.

Figure 40 shows the ozone patterns from 5 August at 1900 EST to 0400 EST of the next day. The arrival of the second front during the late afternoon allowed the ozone concentrations to build up during the daylight hours as can be seen in the figure. The trajectory analyses show this to be a somewhat anomolous case in that the air motions leading to the high concentrations are generally from the north-northwest, which may explain why the centers of highest midafternoon 0_3 concentrations are located approximately downwind of Boston and Hartford.

As the second front moved through the area, the $\mathbf{0}_3$ concentrations fell rapidly. This is probably the result of two processes, the general decline in $\mathbf{0}_3$ at night when the photochemical processes are no longer active and the flushing of the area by the newly arrived polar air behind the front. Figures 41 and 42 are time sections that show more clearly that much of the decline in ozone concentration had already taken place before the second front arrived.

14 August 1975 is a day when a slow-moving cold front passed through the area during the daylight hours. Figure 43 shows that the front was well into the area by 1000 EST, but moved very little during the next 3 hours. By 1600 EST, the front was nearly to the Connecticut-Rhode Island





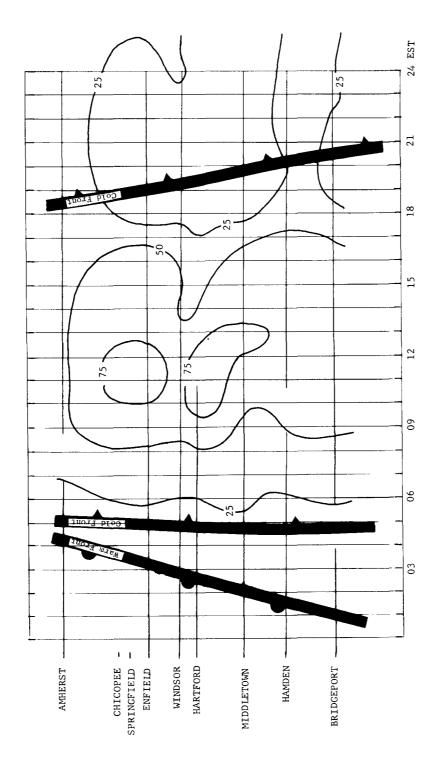


FIGURE 41. OZONE TIME SECTION ALONE ALONG LINE FROM BRIDGEPORT TO AMHERST, 5 AUGUST 1975

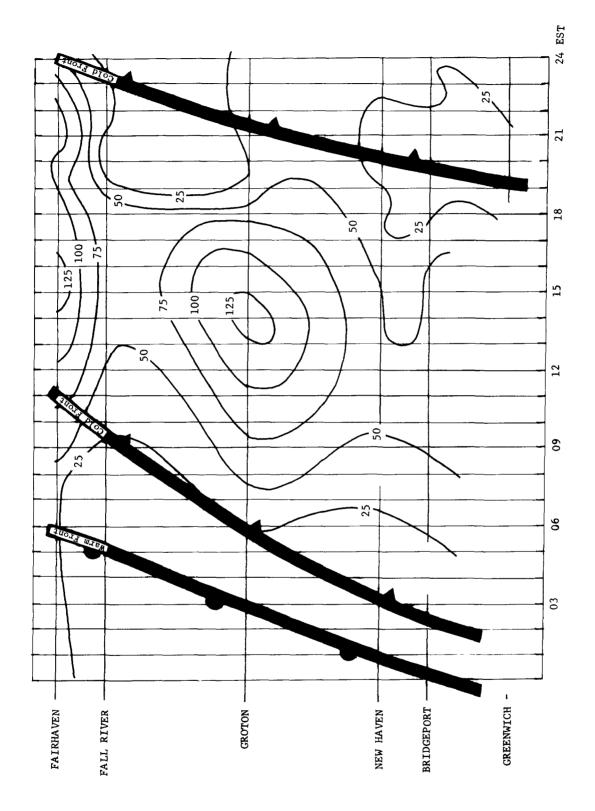
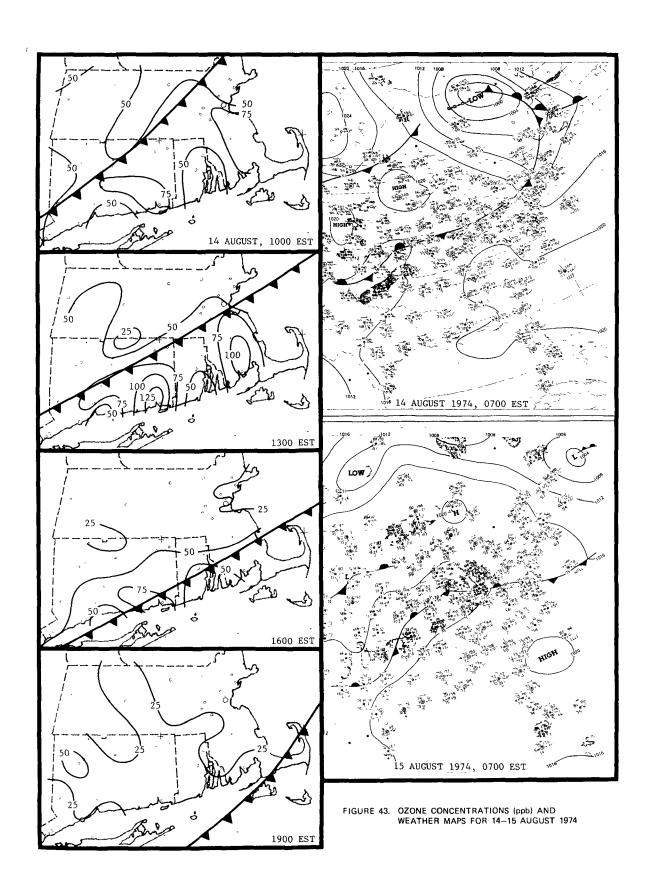


FIGURE 42. OZONE TIME SECTION ALONG LINE FROM GREENWICH TO FAIRHAVEN, 5 AUGUST 1975



coast, and the ozone-heavy air that had been there earlier was replaced with the cleaner, polar air behind the front. In this case the decrease in ozone as the front passes is clearly caused by the incoming clean air, because midafternoon is an unlikely time for the decrease to have been caused by declining photochemical activity.

Figures 44 and 45 are time sections showing the frontal passage through the area. The time section in Figure 44, along the line oriented nearly north and south (Figure 36) gives only slight evidence of the front, because the cleaner air replaces the polluted air before the ozone concentrations have had much chance to build up. The time section in Figure 45, along the coast line (Figure 36), shows the frontal passage quite clearly.

As shown in Table 2 (Section II), EPA Las Vegas, Washington State University, and Battelle all operated aircraft and measured vertical ozone profiles on this day, so it was possible to construct vertical cross sections. This is one of the few instances when aircraft data were collected during a frontal passage. Figures 46 and 47 show the cross sections and the approximate location of the front during the time when the data were collected. In both cases the front intersected the line of the cross section and the higher ozone concentrations ahead of it are apparent. The later cross section (Figure 47) shows quite clearly the sharp gradient in concentration that is associated with the front. It also shows that the high concentrations extend upward to about 2000 feet. Some of the gradient probably is caused by the difference in the time that the two easternmost soundings were taken, but frontal effects were almost certainly responsible for much of it.

18 August 1976 was quite similar to the case just discussed except that the front moved through the area somewhat more rapidly.

As shown in Figure 48, the front had entered the region of interest by

1000 EST. It was cloudy, but not overcast in the warm air ahead of the

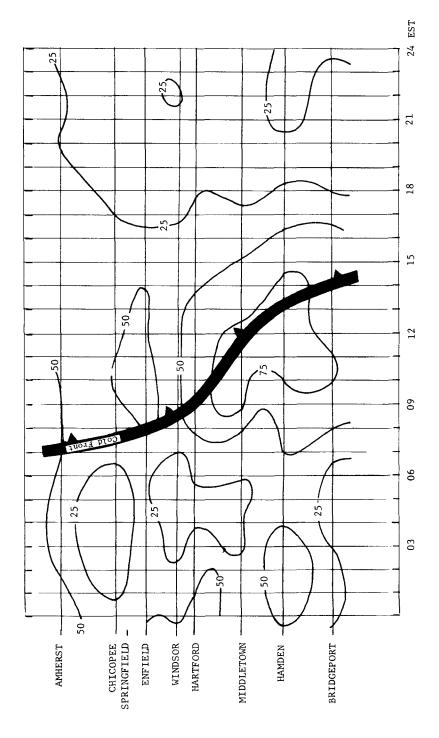


FIGURE 44. OZONE TIME SECTION ALONG LINE FROM BRIDGEPORT TO AMHERST, 14 AUGUST 1975

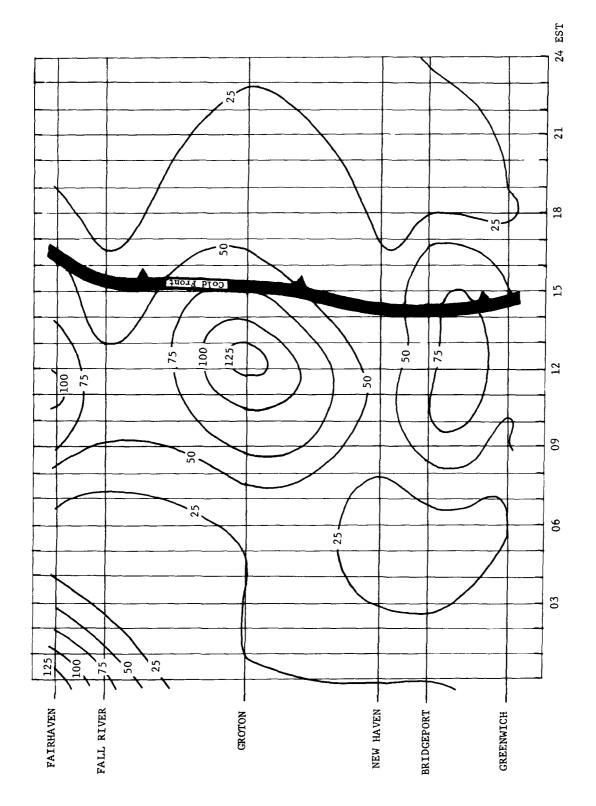


FIGURE 45. OZONE TIME SECTION ALONG LINE FROM GREENWICH TO FAIRHAVEN, 14 AUGUST 1975

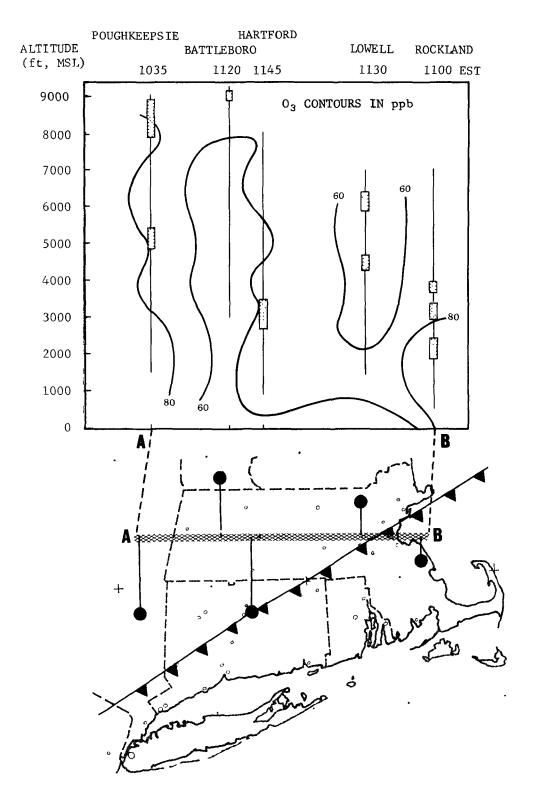


FIGURE 46. CROSS SECTION OF OZONE CONCENTRATION BASED ON DATA COLLECTED BETWEEN 1035 AND 1145 EST, 14 AUGUST 1975

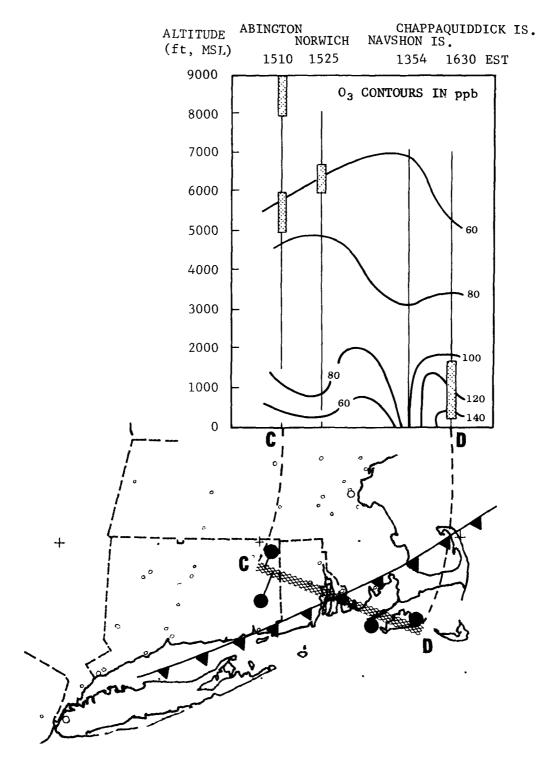
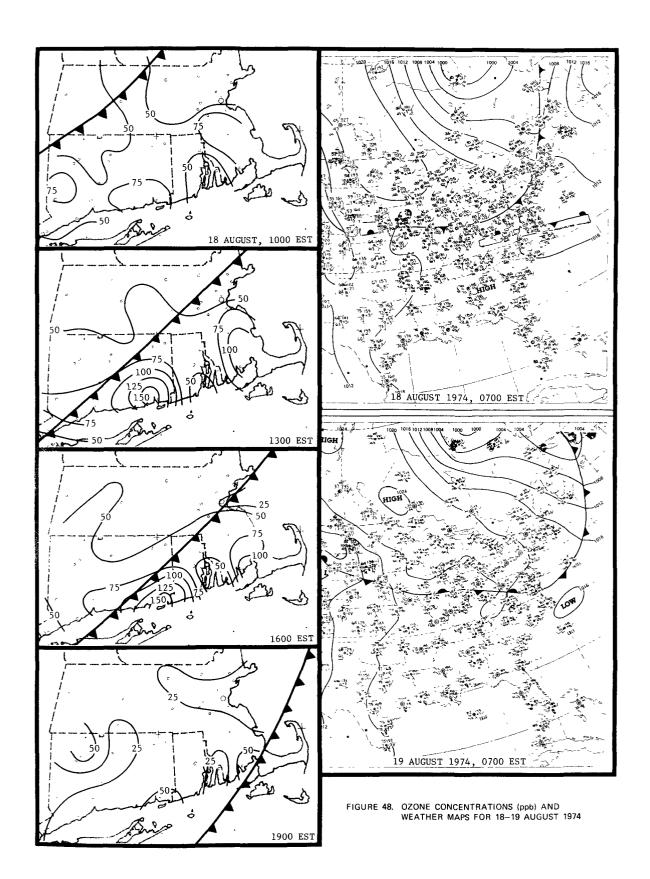


FIGURE 47. CROSS SECTION OF OZONE CONCENTRATION BASED ON DATA COLLECTED BETWEEN 1354 AND 1630 EST, 14 AUGUST 1975



front so the 0₃ concentrations ahead of the front rose with the photochemical activity during the morning and early afternoon. Concentrations in excess of 150 ppb were reached along the Connecticut coast ahead of the front. These dropped to about 50 ppb with the passage of the front between 1600 and 1900 EST. The time section shown in Figure 49 for the line along the Connecticut coast clearly shows the rapid decrease in ozone concentrations as the front moves through.

c. Recapitulation

The preceding case studies illustrate the conditions under which high ozone concentrations are likely to be found ahead of weather fronts in southern New England. Briefly these conditions are:

- The weather front must pass through the area during the daytime so that photochemical activity can take place in the air ahead of the front.
- It must not be too cloudy in the warm air so that there is sufficient sunlight for ozone production.
- The front must be oriented more-or-less southwest to northeast so that the low-level winds ahead of the front will carry precursors from the highemissions areas into southern New England.

Obviously there will be exceptions to the above "rules," such as occurred in the case of 5 and 6 August with its complex pair of fronts. Nevertheless, frontal passages during the summer that meet the above criteria are quite likely to be preceded by high ozone concentration in Connecticut and Rhode Island.

2. Occurrences of High Nighttime Ozone Concentrations at Ground Level

a. Background

Before discussing the reasons for high concentrations of ozone near ground level at night, the more common case--low nighttime

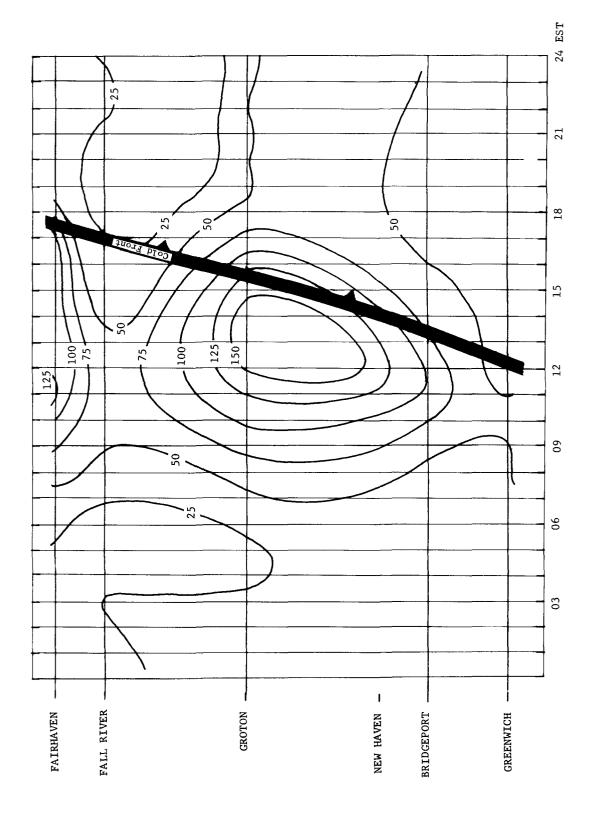


FIGURE 49. OZONE TIME SECTION ALONG LINE FROM GREENWICH TO FAIRHAVEN, 18 AUGUST 1975

concentrations--should be discussed. By sundown, of course, the photo-chemical production of ozone has ceased, but the destruction processes will continue. The most effective destruction processes occur at the ground where the surface provides sites for ozone destruction and where most emissions of nitric oxide are found. When the sun is low, or has set, the surface cools and a surface-based inversion forms so that vertical mixing is inhibited. The ozone is quickly destroyed in the lowest layers and whatever ozone may still exist at higher layers is effectively isolated.

During the daytime there is continual formation of ozone throughout the mixed layer, and the destruction processes near the surface are offset by formation and by mixing downward of ozone from aloft. Even though the ozone formed during the daytime may persist aloft at night, usually it will not be mixed downward to be measured at the surface. However, if for one reason or another, there should be vertical mixing at night then we might expect that any ozone plumes that were aloft would be brought to ground level where they could be observed. The above discussion indicates there are two conditions that must be met if high nighttime ozone concentrations are to be found at ground level. These are:

- (1) There must be a reservoir of ozone aloft.
- (2) There must be sufficient vertical mixing to bring ozone from that reservoir to ground level.

The first condition usually will be met if conditions during the preceding day were conducive to ozone formation and if the winds have been such as to transport ozone and its precursors from source areas to the observing site. The second condition requires either that the atmospheric dynamics be favorable to vertical motions, as they often are near low-pressure troughs, or that the cooling of the air in the

lowest layers be inhibited. Low-level cooling is subdued during overcast sky conditions, or when the air passes from a cooler to a warmer surface.

As we have seen in earlier sections of this report, urban ozone plumes aloft are not uncommon in the summer. There are meteorological "symptoms" that identify cases of nighttime mixing in the vertical. These symptoms are strong winds and warm temperatures at ground level. The surface acts as a sink for heat at night. It is also a sink for momentum through friction losses. If there is good mixing, momentum and heat will be transferred to the ground from aloft, and temperatures and wind speeds at the surface will remain relatively high. Hence, warm temperatures and strong winds are symptomatic of vertical mixing.

Following the example of preceding sections of this report, case studies will be used to illustrate how the factors outlined above can be used to explain at least some of the occurrences of high nighttime ozone concentrations at ground level.

b. <u>Case Studies</u>

13-14 August 1975 provides one of the most clear-cut examples of the processes operating to produce high ozone concentrations at night. Figure 50 shows average hourly values of ozone, Freon-11, wind speed, and temperature measured by Washington State University (1976) at their Groton, Connecticut, site. The figure shows an abrupt rise in ozone concentrations beginning around 1800 to 1900 EST, a time of day when photochemical processes have largely ceased and there is normally a decrease in ozone concentrations. The anthropogenic origins of this ozone are confirmed by the concurrent rise in Freon-11 concentrations.

The importance of downward mixing in this case is shown by the increase in wind speed at the onset of the higher pollutant concentrations. The increase in temperature somewhat later, and at the time of normal temperature decrease, also indicates vertical mixing.

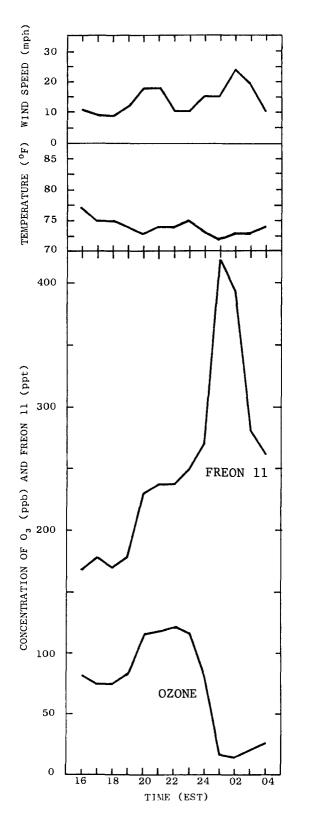


FIGURE 50. SELECTED POLLUTANT AND METEOROLOGICAL OBSERVATIONS AT GROTON, CONNECTICUT, DURING THE NIGHT OF 13-14 AUGUST 1975

The Weather Service surface weather map for 1900 EST shows a trough along the western borders of Connecticut and Massachusetts; the trough is accompanied by overcast skies and signs of convection such as recent showers and cumulus clouds. The weather map supports the other evidence of vertical mixing; we can feel confident that the sudden increase in ozone around sunset was caused by an onset of vertical mixing.

Between 2300 and 0100 there is a sharp drop in ozone concentration. This cannot be explained by a cessation of mixing because Freon-11 concentrations and wind speeds actually increase during the same period and temperature remains relatively constant. All this points to continued mixing, as do the Weather Service analyses showing the trough passing over Groton during the same period. If our list of requirements for high nighttime ozone at ground level is complete, then we must assume that the supply of ozone aloft has disappeared, although other anthropogenic pollutants—as represented by Freon-11—continue to affect the Groton site.

Suppose we hypothesize the following:

- (1) The New York-Newark area is a major source of the pollutants reaching Groton.
- (2) Pollutants emitted from that area after about 1600 EST will not undergo sufficient photochemical activity to produce large amounts of ozone.

The first point of the hypothesis can be tested by constructing air trajectories from New York. Figure 51 shows an approximation of a swath of pollutants that left the New York area about 1600 EST. The approximate positions of the pollutants at subsequent hours is also shown. It can be seen that the 1600 EST New York pollutants passed Groton at just about the same time that the ozone-concentration decline began.

The hypothesis can be further tested by looking at the hourly ozone concentrations at other locations. Figure 52 shows the time

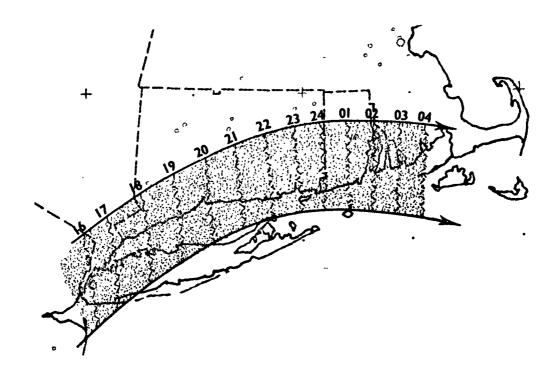


FIGURE 51. LATER POSITIONS OF AIR THAT LEFT NEW YORK AT 1600 EST, 13 AUGUST 1975

histories of ozone concentration at several other monitoring stations. The hatched bars in the figure mark the time at which the pollutants that left New York between 1400 and 1600 EST should have passed each of the sites. It is apparent that these sites did not show the sharp drop found at Groton when the 1600 EST New York air passed by. They did show marked decreases in concentrations beginning two to three hours before, corresponding to the passage of air that left the New York area earlier in the afternoon. The second part of our hypothesis should be revised to indicate that pollutants emitted later than about 1400 EST do not undergo sufficient photochemical activity to achieve the oxidant concentrations that are produced from precursor emissions earlier in the day. The measurements at Groton, upon reexamination, show a leveling off of ozone concentration when the air that had left New York at 1300 to 1400 EST passed the site. The measurements at Hartford, being generally outside the plume, show no pronounced indications of its passage.

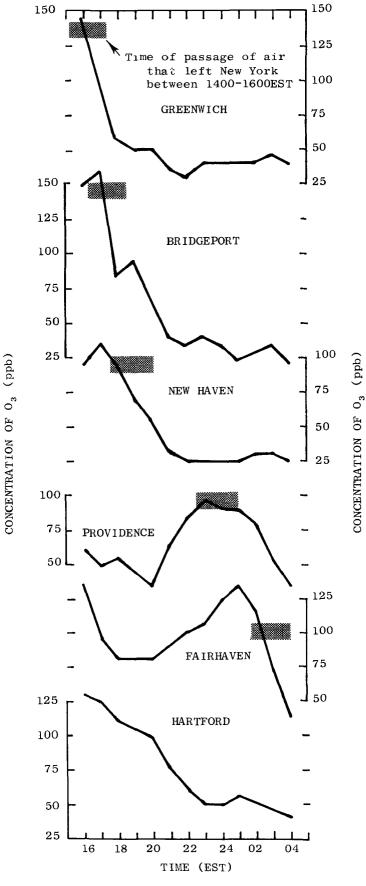


FIGURE 52. OZONE CONCENTRATIONS AT SEVERAL SOUTHERN NEW ENGLAND SITES DURING THE NIGHT OF 13-14 AUGUST 1975

21 August 1975 was another occasion with nighttime ozone concentrations in excess of the federal standard, but the causes are not quite so clear as in the preceding case. Vertical mixing appears to have been present, at least to some degree. Figure 53 shows the wind speed, temperature, and freon and ozone concentrations during the evening of this day and the following morning at Groton and through late evening at Simsbury. (The Simsbury records end at the time shown in the figure.) Judging by the wind records, the onset of vertical mixing was around 1800 EST. Some shower activity began in the area between 1900 EST and 2200 EST, providing further evidence of vertical mixing after this time. However, the Groton records show that ozone concentrations began to decline by 1900 EST and the Simsbury values increased, but did not reach very high levels. This suggests that there may not be a very strong reservoir of ozone aloft at these two sites.

Air movement in the area indicates that Groton and Simsbury were at opposite edges of the swath of air that passed over the New York area during the afternoon. Figure 54 shows the movement of the air that left the New York area at about 1600 EST. The Groton and Simsbury records can be used to establish the presence of vertical mixing in the area; records from other locations have to be used to determine whether the same kinds of things happen to ozone concentrations on this day as were found in the preceding case study.

Figure 55 shows the ozone concentrations at four locations along the path of the air from New York. Again, the shaded bars show when air passed that had been over New York between 1400 EST and 1600 EST. Qualitatively, the behavior is similar to the preceding case, but the declines are less abrupt and they begin later relative to the passage of air that left New York during the latter part of the afternoon.

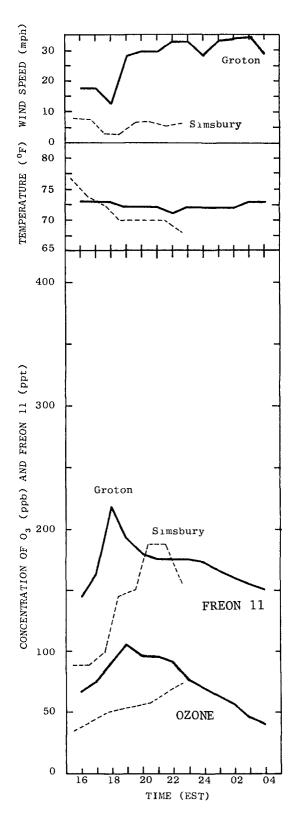


FIGURE 53. SELECTED METEOROLOGICAL AND POLLUTANT OBSERVATIONS AT GROTON AND SIMSBURY DURING THE NIGHT OF 21-22 AUGUST 1975

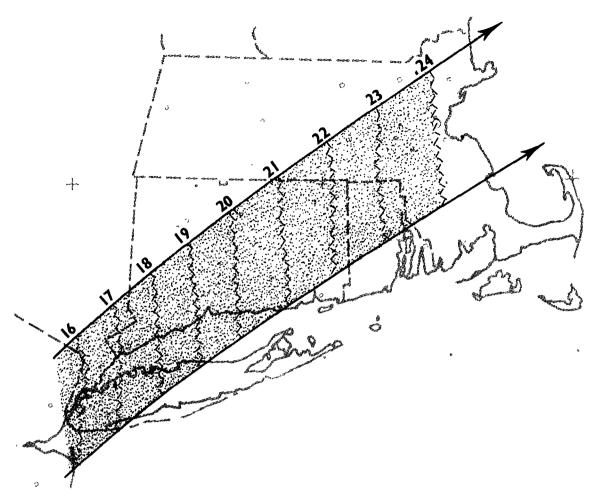


FIGURE 54. LATER POSITIONS OF AIR THAT LEFT NEW YORK AT 1600 EST, 21 AUGUST 1975

This day is probably more typical, because there should not be an abrupt change from air that was subjected to photochemical processes and air that was not; the decline should be more gradual through the afternoon. Superimposed on this gradual change in photochemical activity are changes in emissions rates and the effects of turbulent diffusion, both of which further blur the end of the ozone for the day. The data do fit the general hypothesis presented earlier to explain observed nighttime ground-level ozone concentrations.

18 July 1975 illustrates how meteorological factors can cause misinterpretation of observed ground-level ozone concentrations.

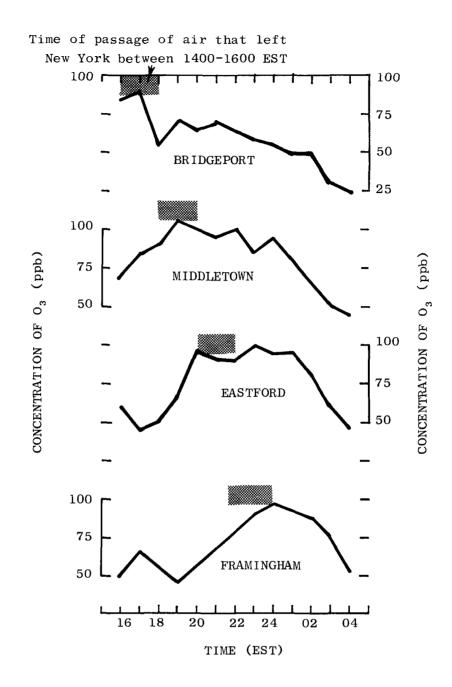


FIGURE 55. OZONE CONCENTRATIONS AT SELECTED STATIONS DURING THE NIGHT OF 21–22 AUGUST 1975

Figure 56 shows the observed ground-level ozone concentrations at three different times during the late afternoon and night of 18 July 1975. The apparent motion of the center of high ozone concentration is from southwest to northeast at about 35 km hr⁻¹ during the 6-hour time span covered in the figure. Air trajectory calculations in the area and during the same general time period indicate a somewhat slower 25 to 30 km hr⁻¹ in about the same direction, as shown in Figure 57. Figure 58 shows the ozone histories at several stations generally along the direction of air movement. The peak concentration at Middletown, Connecticut, is separated from the peak at Salem, Massachusetts, by about 4 hours and 190 km. If we assumed that the onset of declining ozone concentrations at night always corresponded with the arrival of midafternoon emissions from the major upwind source area, then we would estimate a speed of motion of nearly 50 km hr⁻¹.

In the two case studies discussed in the preceding sections, vertical mixing was quite widespread and the onset of the nighttime decline in ozone concentration did correspond to the passage of the last photochemically affected air from New York. In this case it appears that the opposite situation prevailed—an area of vertical mixing moved rapidly through the area while high ozone concentrations aloft were still quite widespread. The National Weather Service weather map for 1600 EST shows a trough in the surface pressure field. Subsequent maps have dropped this feature from the analysis, probably because the sparsity of weather observations off the east coast makes its detection difficult, if not impossible.

If we assume that the trough persisted for at least a few more hours and moved eastward at a reasonable rate, then it might have moved more-or-less as shown in Figure 59. Low-pressure troughs are often accompanied by instability and enhanced vertical mixing. A trough moving as shown in Figure 59 would easily explain the ozone traces shown in Figure 58.

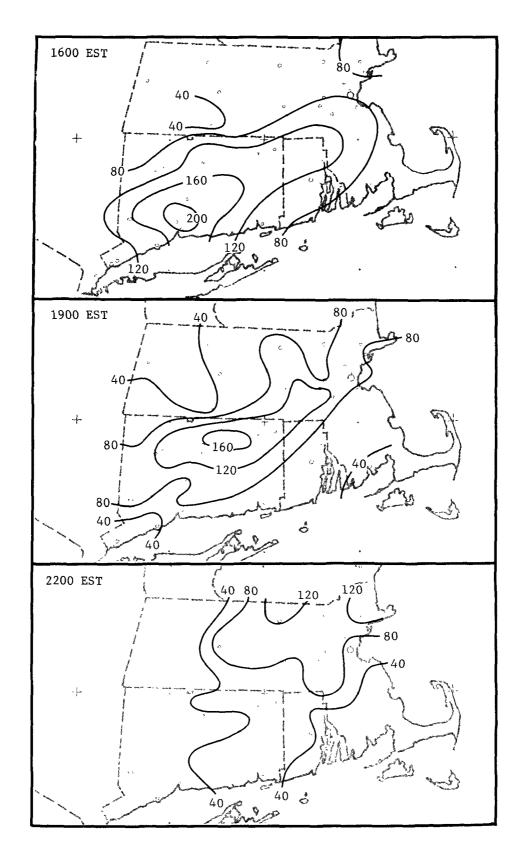


FIGURE 56. OZONE CONCENTRATIONS (ppb) ON 18 JULY 1975

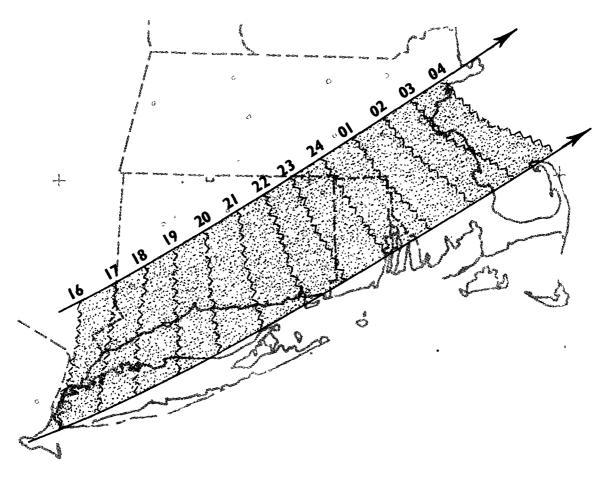


FIGURE 57. LATER POSITIONS OF AIR THAT LEFT NEW YORK AT 1600 EST, 18 JULY 1975

The above explanation is further supported by the more detailed observations at Groton and Simsbury, shown in Figure 60. If correct, the trough should have passed Simsbury at around 1800 EST to 1900 EST and we might expect to see just the kind of behavior that is seen in the ozone concentration. Unexplainably, the wind speed and temperature histories are not much like what would be expected. At Groton, there are slight indications of a trough passage in all traces at about the right time, circa 2200 EST.

c. Further Discussion

The three cases of high nighttime ozone concentrations at ground level have illustrated the importance of the simultaneous

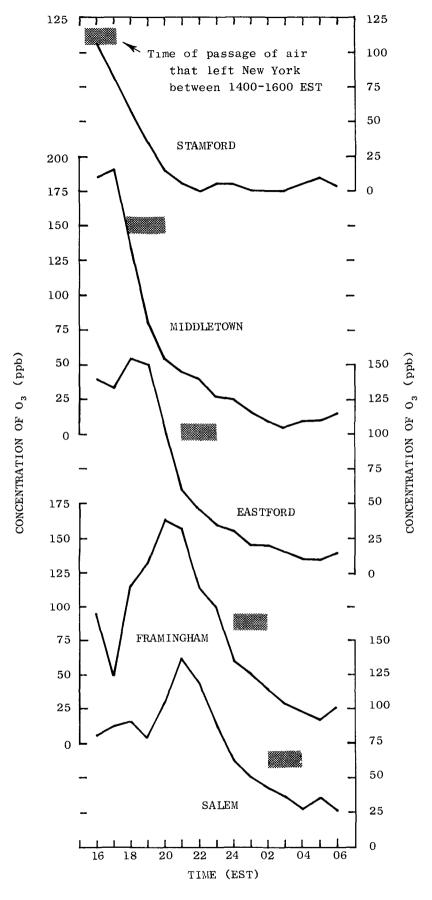


FIGURE 58. OZONE CONCENTRATIONS AT SELECTED NEW ENGLAND SITES DURING THE NIGHT OF 18-19 JULY 1975

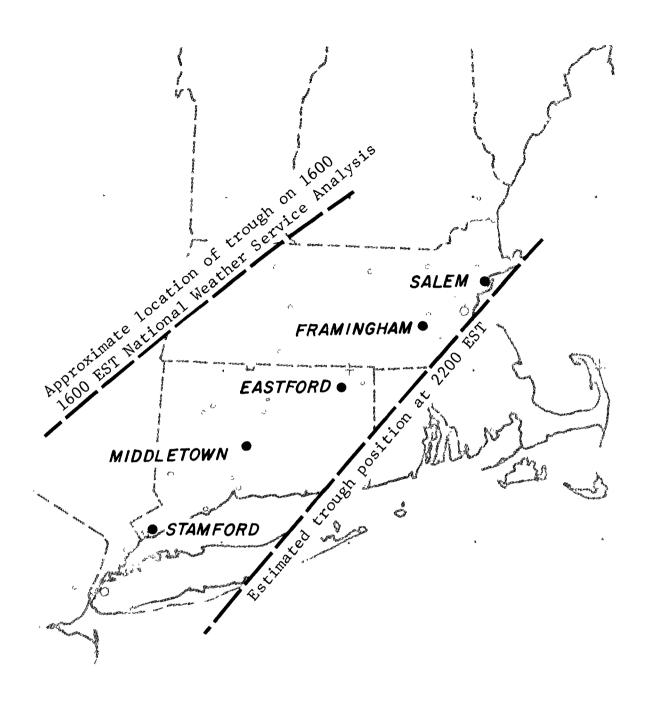


FIGURE 59. ESTIMATED TROUGH POSITIONS, 18 JULY 1975

occurrence of two factors--vertical mixing and a reservoir of the pollutant aloft. In two cases, declining ozone concentrations at a series of stations marked the passage of the trailing edge of the ozone reservoir aloft.

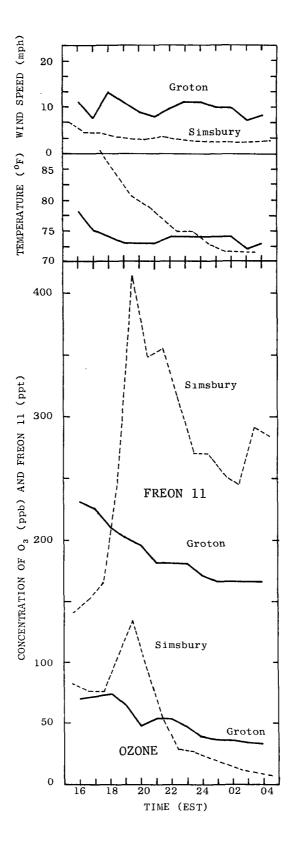


FIGURE 60. SELECTED METEOROLOGICAL AND POLLUTANT OBSERVATIONS AT GROTON AND SIMSBURY DURING THE NIGHT OF 18-19 JULY 1975

In the third case, it appears that a line of atmospheric instability—with its associated vertical mixing—passed through the area. It caused a rise and fall of ground—level ozone concentration as ozone was transferred to the surface from the layer aloft. Of course the passage of the trough through the area would have gone unreflected in the ozone observations had it happened later at night, after the ozone aloft had been advected beyond the region.

If high nighttime ozone concentrations are a product of vertical mixing and ozone aloft, then it would be worth speculating where these conditions might be found in combination. The cases presented show their joint occurrence downwind of a major source area during periods of atmospheric instability. Certain geographic features can also produce the necessary transfer of ozone aloft to ground level. One obvious example would be on a mountain where the ground surface is at the level of the ozone layer. In their discussion of transport and mixing, Coffey and Stasiuk (1975) present data from Whiteface Mountain in New York state that seem to illustrate this effect.

Although no examples are available to illustrate the point, it seems quite possible that any place where the surface tends to be warmer then its surroundings at night might cause enhanced vertical mixing that could bring ozone down to ground level. Large urban "heat islands" and bodies of water are two possible examples. Under some circumstances it seems possible that the warmer city surfaces and the increased mechanical mixing over the urban area might lead to higher nighttime ozone readings than in the surrounding countryside, provided that there is a layer of ozone aloft to be mixed groundward.

3. Weekday and Weekend Ozone Concentrations

Cleveland et al. (1975b) have found that the average ozone concentration between 0500 EST and 1300 EST is significantly higher on

Sundays than on workdays. However, they also found very little difference between the two types of day when maximum hour-average ozone values were compared. Figure 15 summarizes the data that we have examined on this project in an attempt to differentiate between weekday and weekend ozone values. A casual examination of this figure indicates little systematic difference between the weekend maximum daily ozone readings (the upper line of points for each location) and the weekday values (the lower line of points). The data sets for each of the locations were tested for significant differences. Although the mean values of weekday maximum ozone concentration exceeded those for the weekend at five of the seven sites, no site showed a difference that was significant at the 5% level. Wilcoxon's sum of ranks test (Langley, 1970) was used. It is a nonparametric test that should be quite suitable for data such as these that do not have a normal frequency distribution.

Cleveland et al. (1975b) have explained the tendency toward higher Sunday average ozone concentrations as a reflection of reduced scavenging by NO. Scavenging is reduced because there are fewer emissions of NO during Sundays, at least in urban areas. In rural areas, where the differences in NO emissions between weekdays and weekends might be expected to be smaller, the differences in scavenging should also be smaller. If the ozone in these same rural areas is the product of emissions transported from cities, then higher weekday concentrations might be expected, a result that is at least hinted at by the data from five of the seven stations analyzed, the exceptions were Providence and Quincy. This is a hypothesis that might be tested with a larger data sample.

V LIMITATIONS TO THIS STUDY AND RECOMMENDATIONS FOR FURTHER RESEARCH

At the same time that the analyses described here were being conducted, another project was archiving the data from the Northeast Oxidant Study in a computer-compatible form. This second study was not completed in time for automated data processing techniques to be applied to these initial studies. As a result, we feel that we have not been able to use the rich body of data provided by the Northeast Oxidant Study as fully as possible.

Another limitation to this work is the geographical area studied. It has been limited to the southern New England states, plus New York and New Jersey. The original concept of the project recognized the importance of northern New England, but time, data, and funds have not been sufficient to treat this area adequately. The studies that have been completed indicate that the states of Maine, New Hampshire, and Vermont may often be "the end of the line," at least within the United States, for the pollutant-transport processes along the northern part of the east coast, and hence they have an importance that has not been fully reflected in this report.

Our examination of weekday versus weekend ozone concentrations was based on a data sample that was too small to provide conclusive results. Cleveland et al. (1975b) have pointed out that the differences in emissions between Sundays and workdays constitute an experiment of sorts to demonstrate the effects of changes in emissions and emissions schedules. This experiment represents too valuable a source of information to neglect-particularly because the preliminary, inconclusive results given here

suggest that control strategies may be more effective well downwind of the locale in which they are enacted than they are within the controlled area itself.

Although further research in this area is clearly desirable, field studies are not warranted at this time. In some instances, the analysis of larger collections of routinely archived data--from 1974 and 1976, as well af from 1975, or from a more extensive geographical area--should be sufficient. In other instances, more efficient reexamination of the data already analyzed will provide valuable new information. Four tasks are strongly recommended to take full advantage of the existing data base:

- Develop and use automated data analysis techniques to provide better descriptions and better understanding of the elevated urban ozone plumes.
- Extend the geographical area of the study to include northern New England so that we will know the extent to which it is influenced by emissions from elsewhere and also to provide information on the behavior of ozone plumes in areas with relatively few anthropogenic emissions.
- Examination of more instances when ground-level ozone concentrations were high at night so that we can study transport and surface destruction of ozone under conditions when there is no photochemical production to obscure the transport and removal processes.
- Use a larger data base to study the "weekend effect" to be able to relate changes in emissions to the resulting changes in the distribution of ozone concentration, a relationship that has obvious strategic implications.

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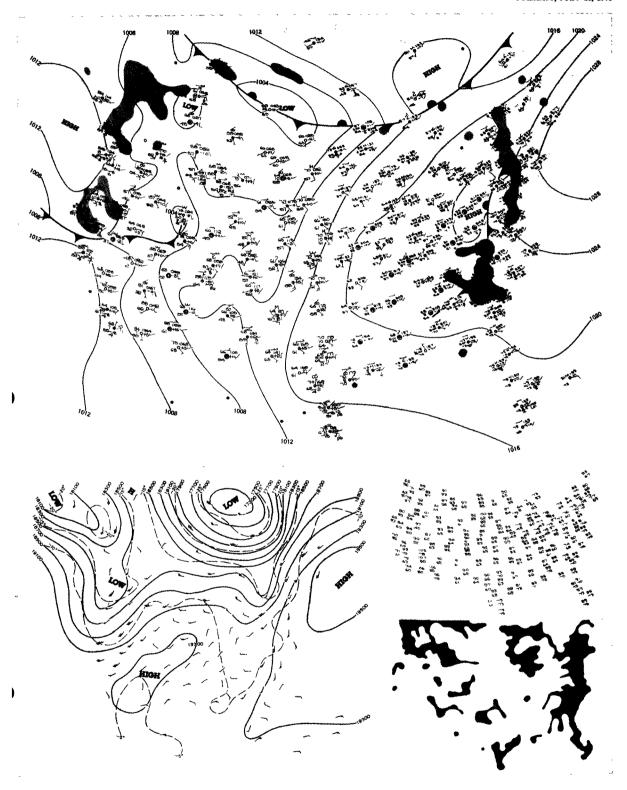
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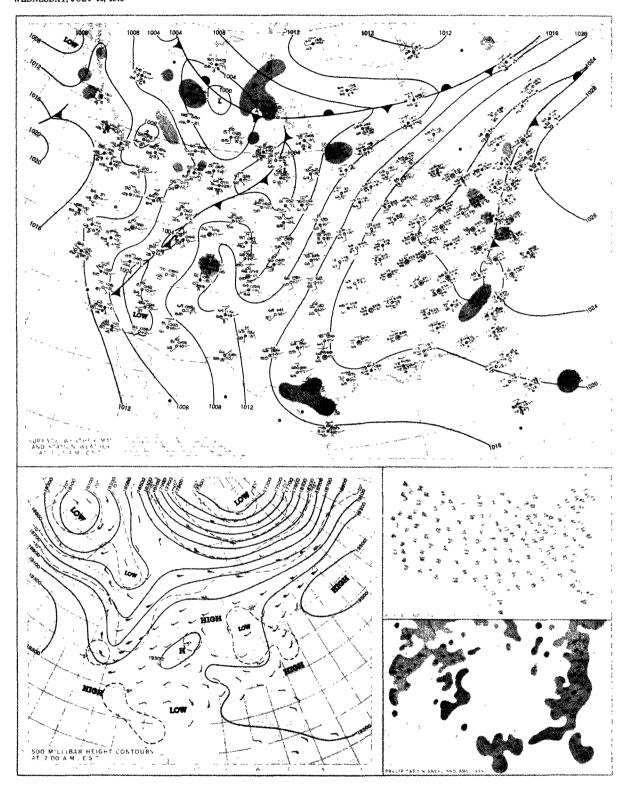
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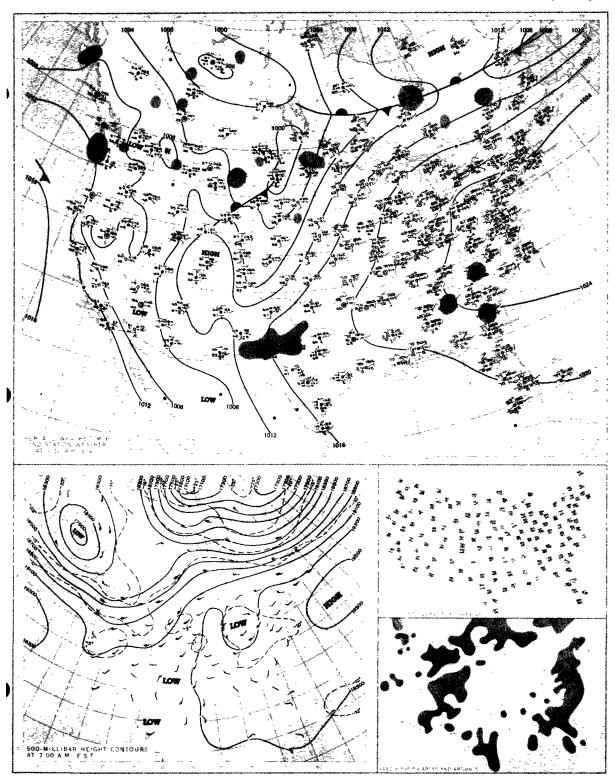
Appendix A

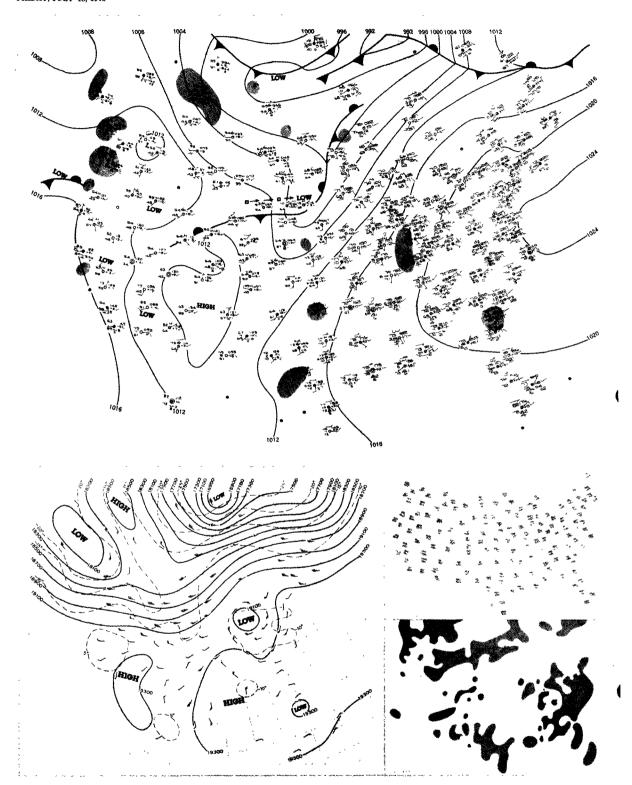
DAILY WEATHER MAPS

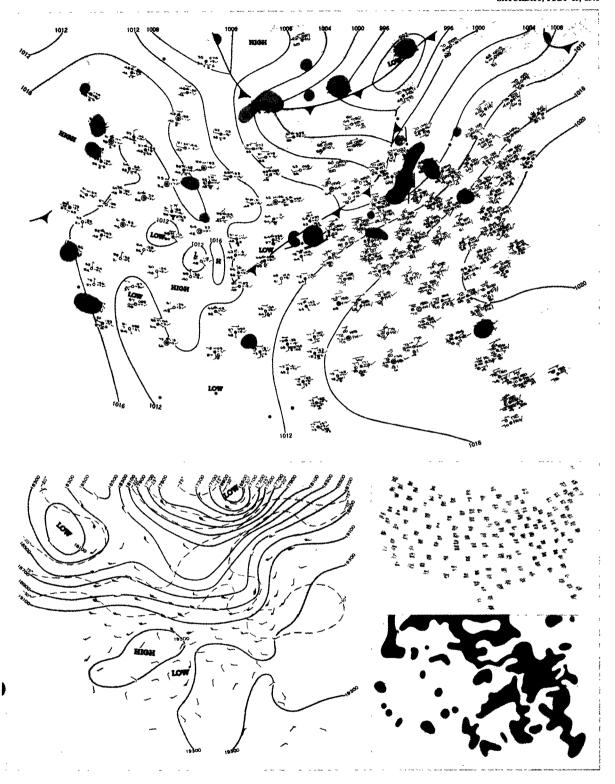
The daily weather maps given in this appendix have been copied from the National Oceanic and Atmospheric Administration's "Daily Weather Map" series. One map is presented for each day during the period 15 July to 31 August 1975. They represent conditions prevailing at 1200 GMT, or 0700 EST.

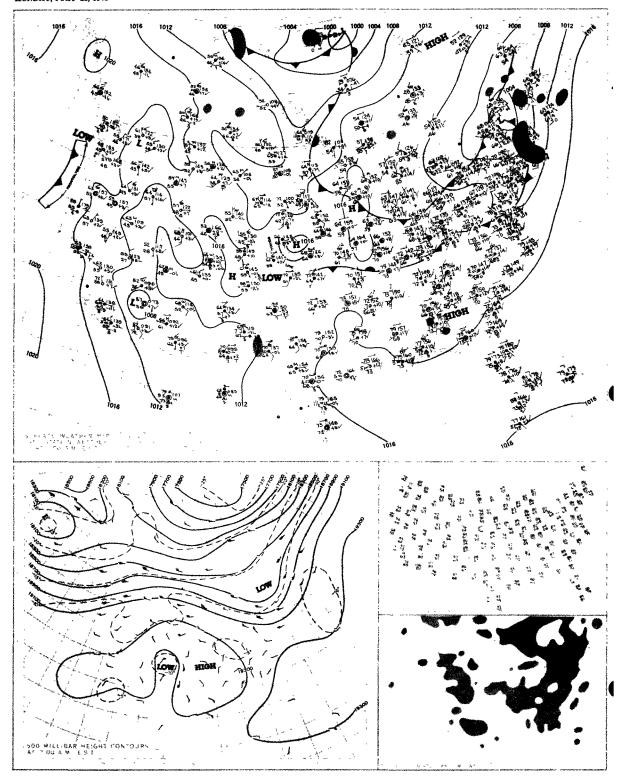


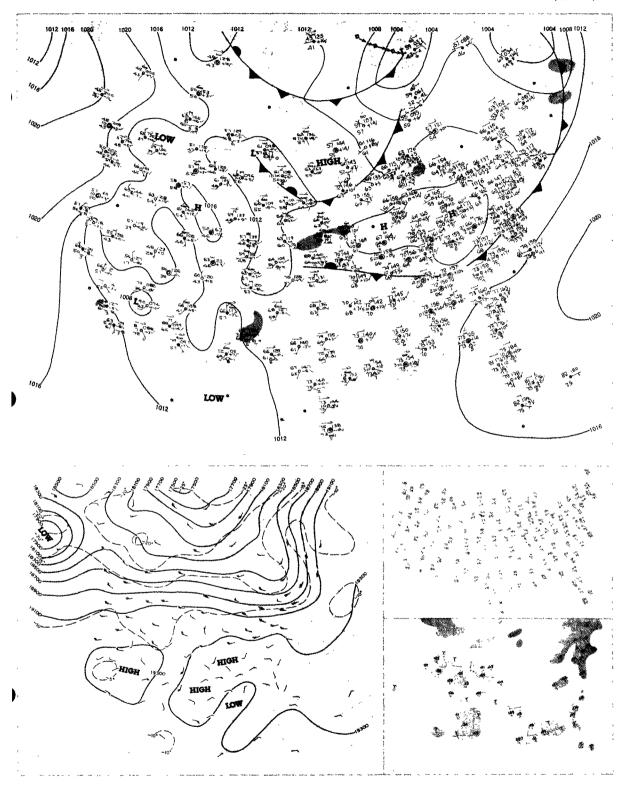


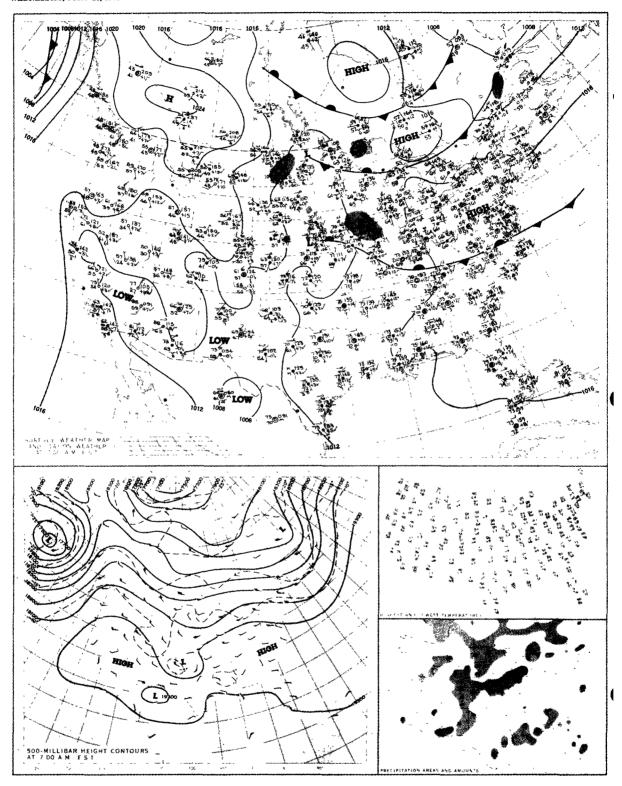


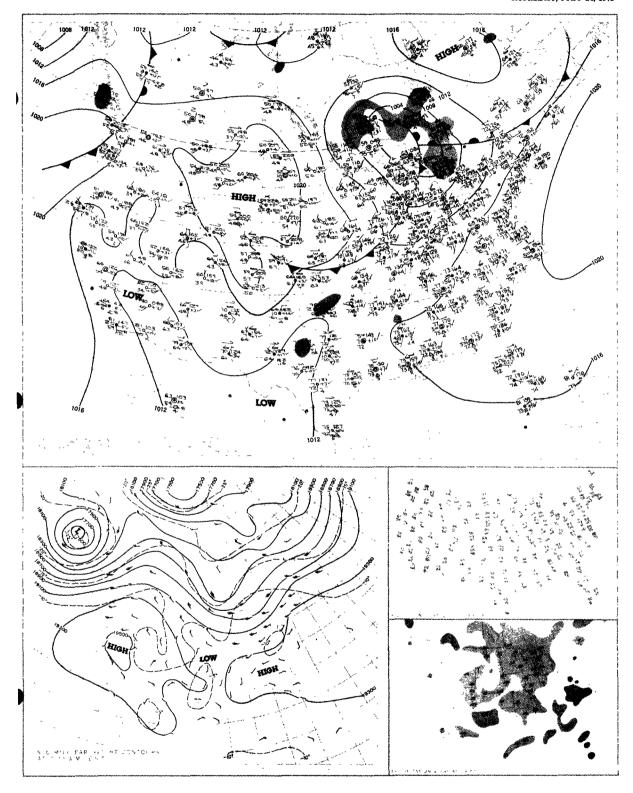


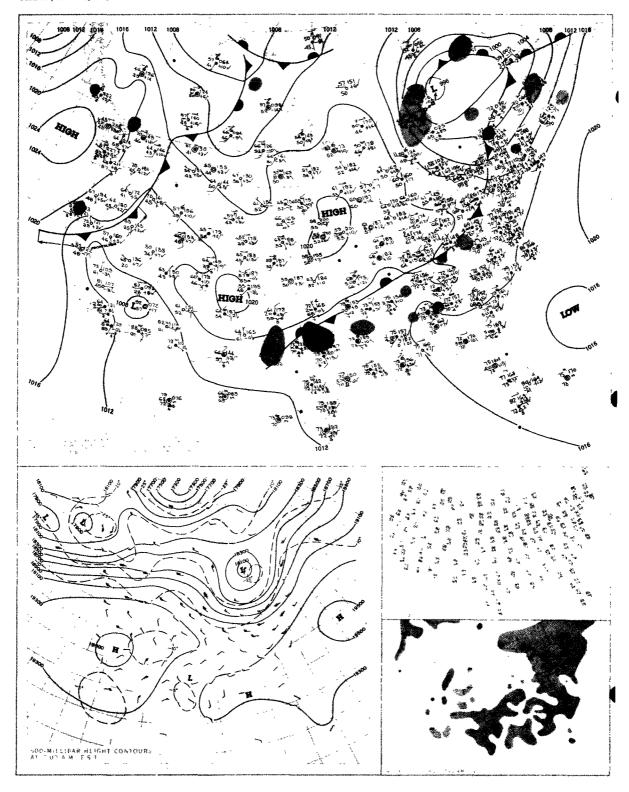


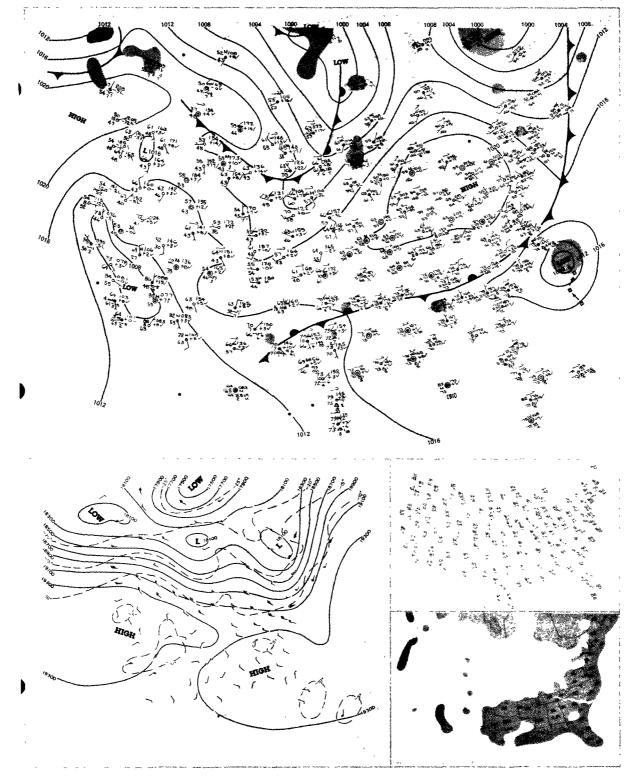


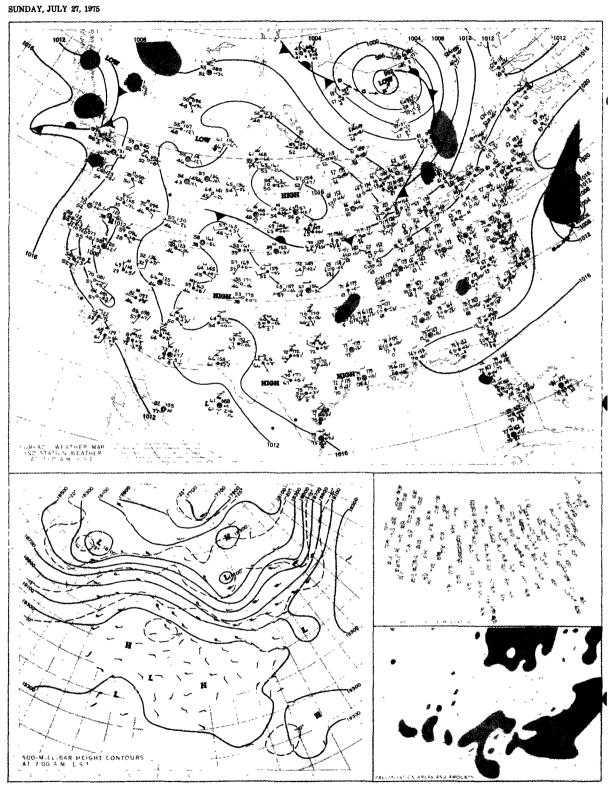


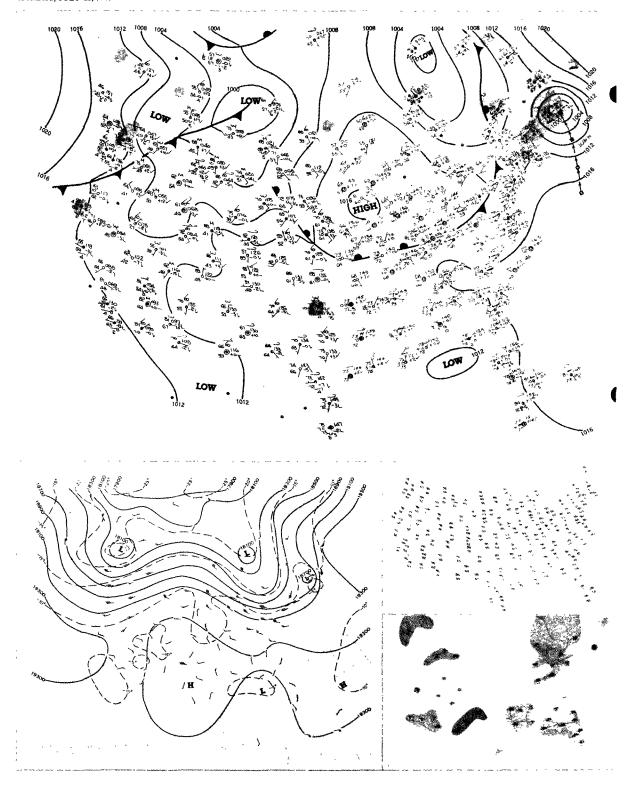


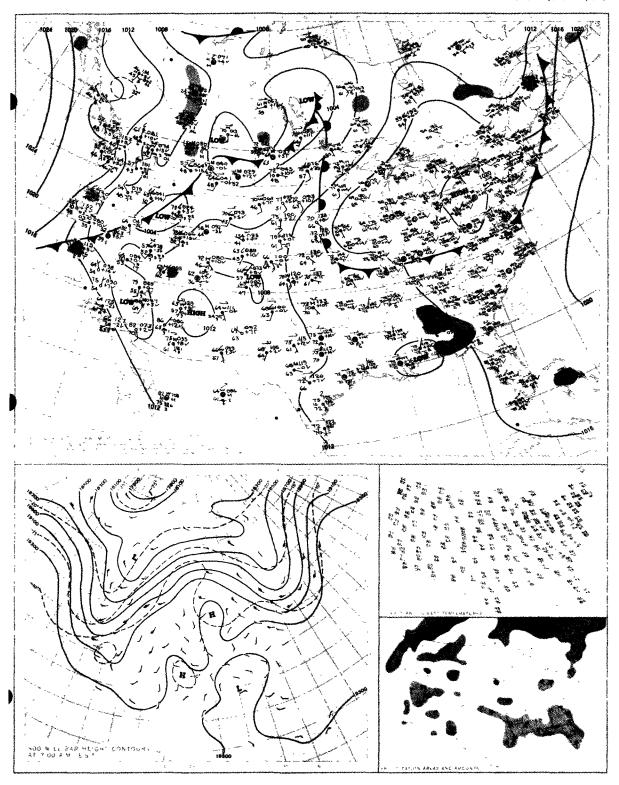


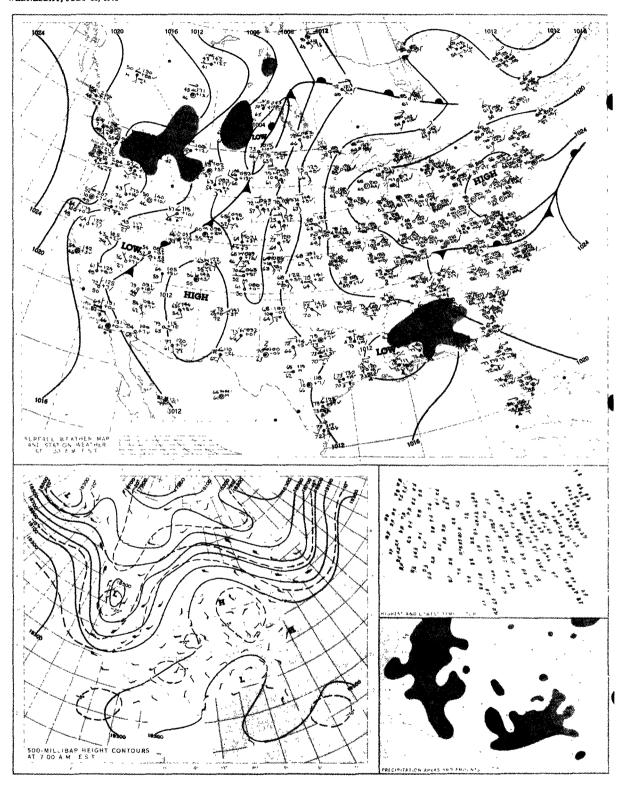


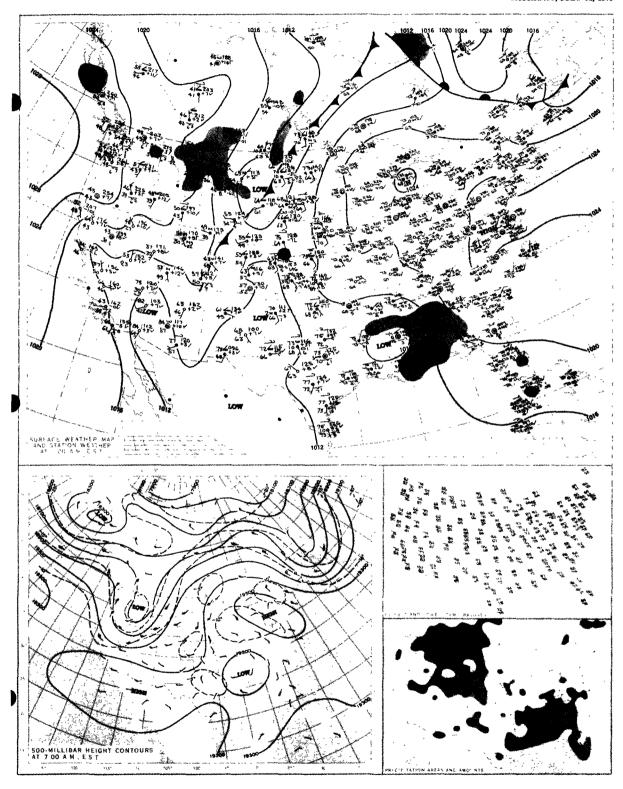


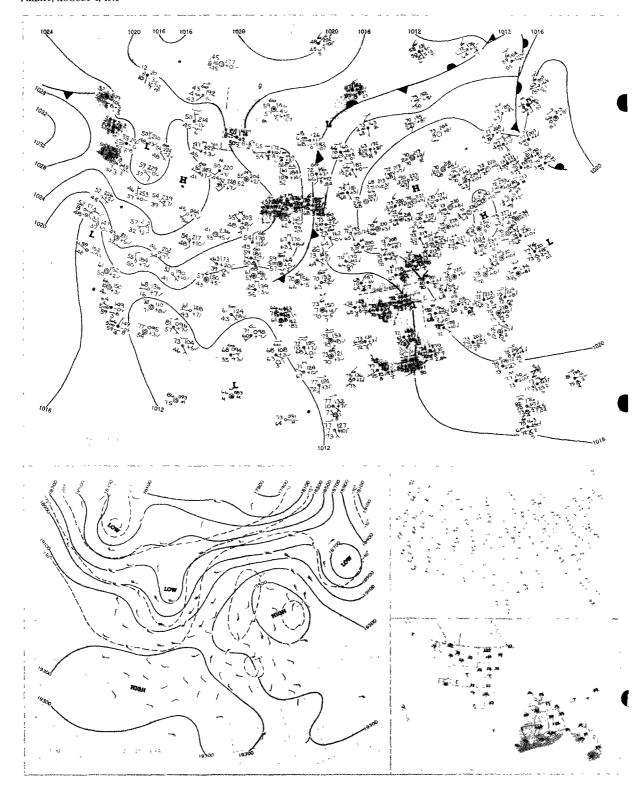


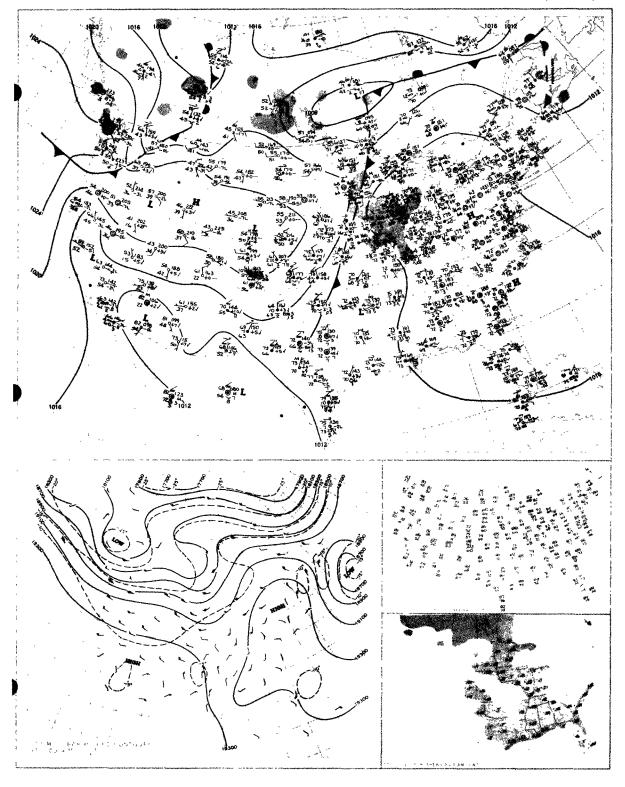


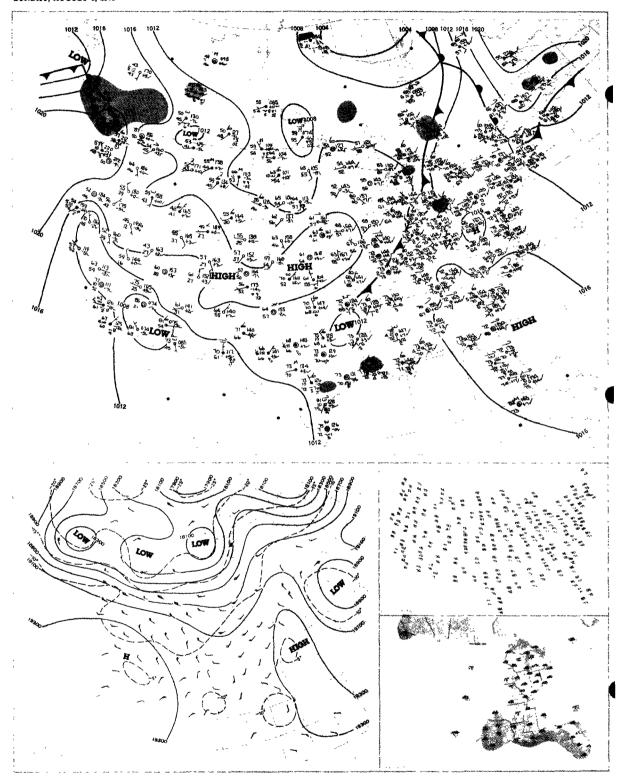


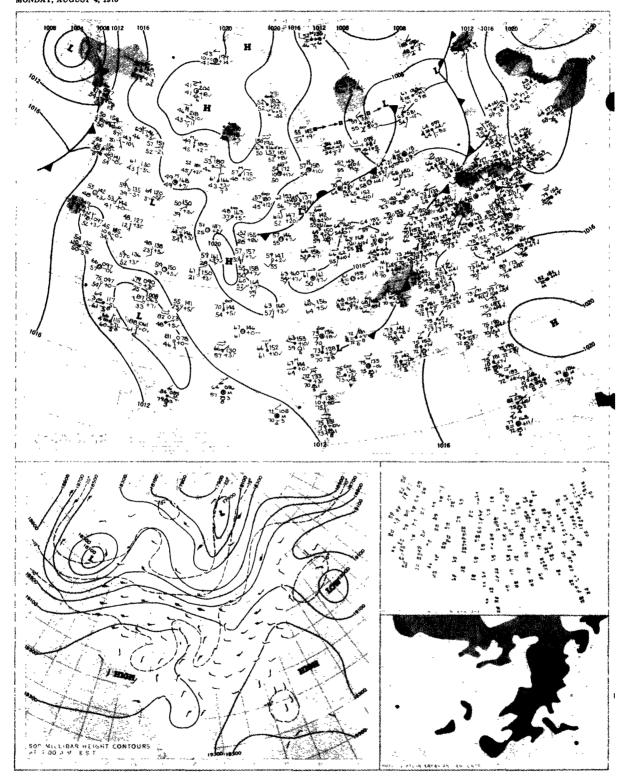


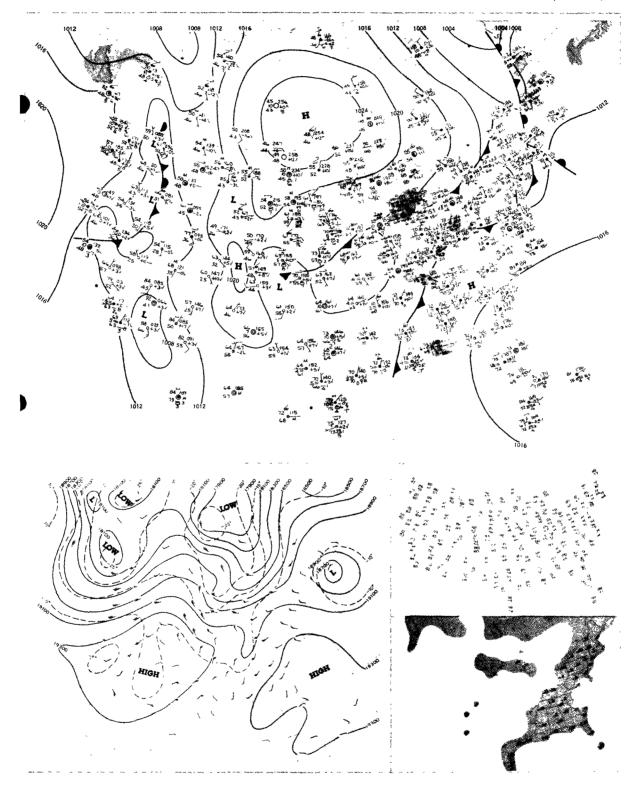


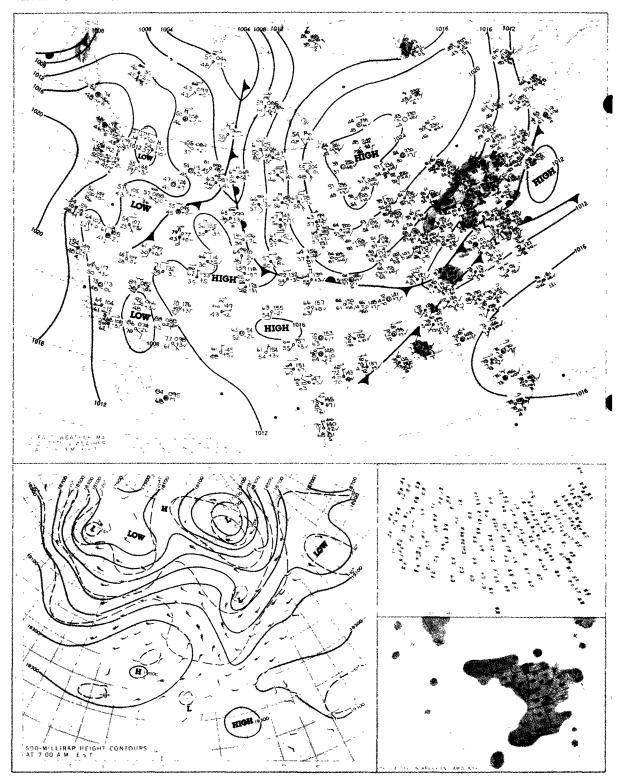


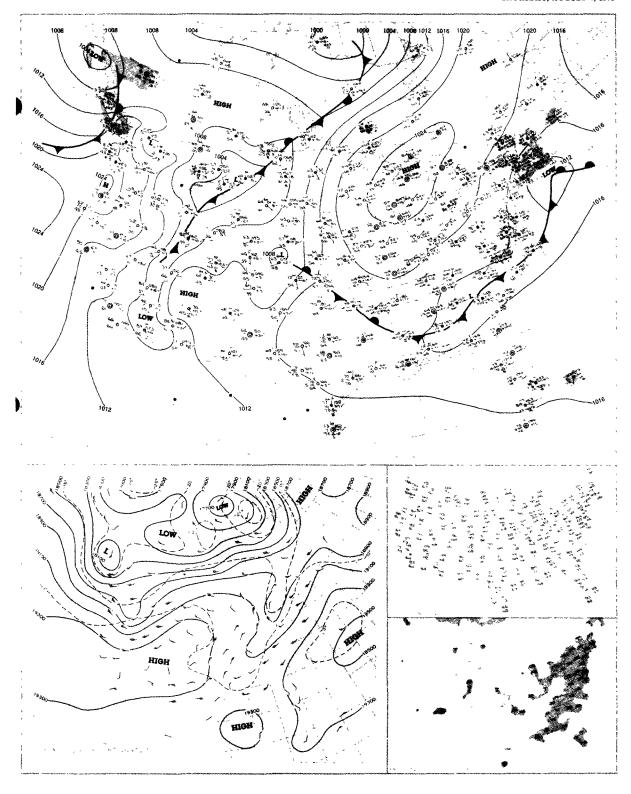


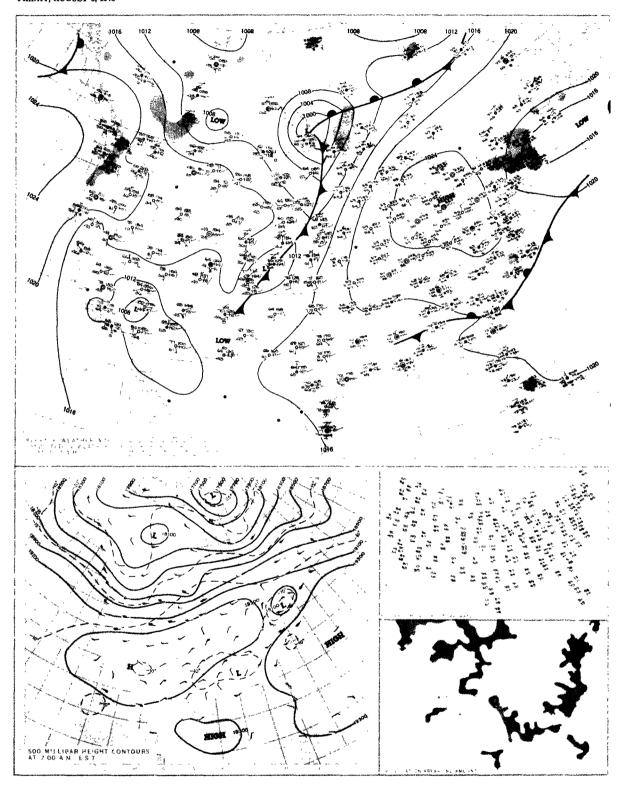


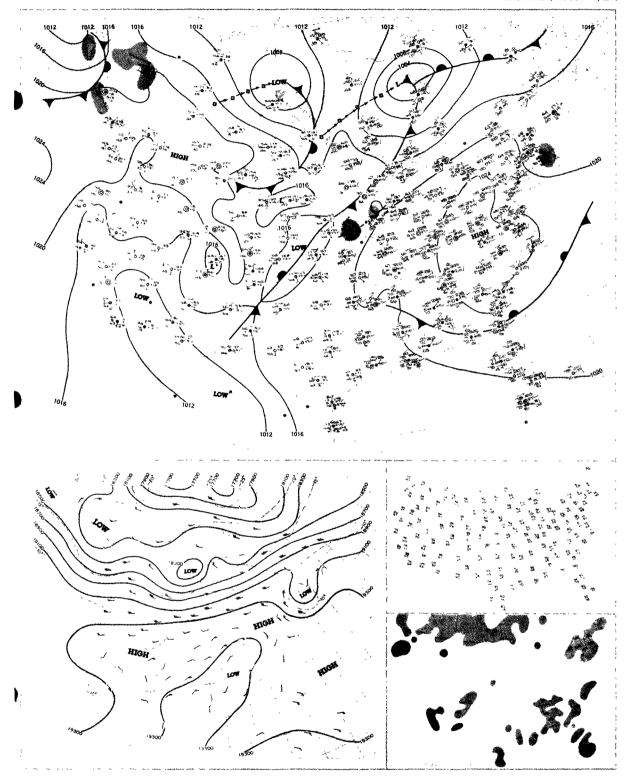


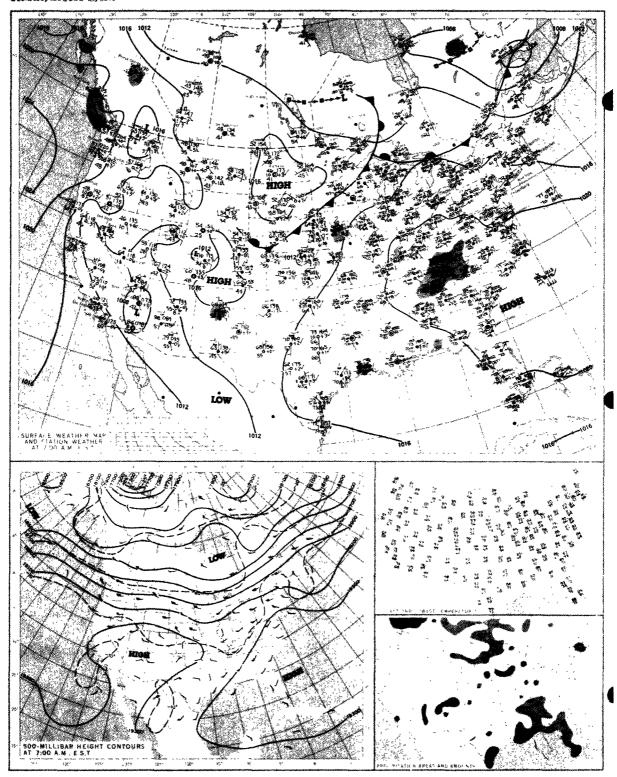


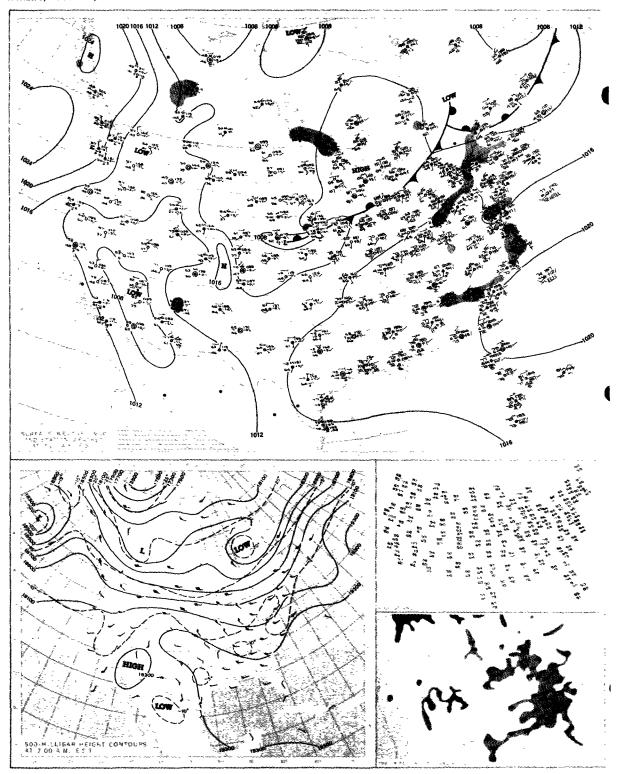


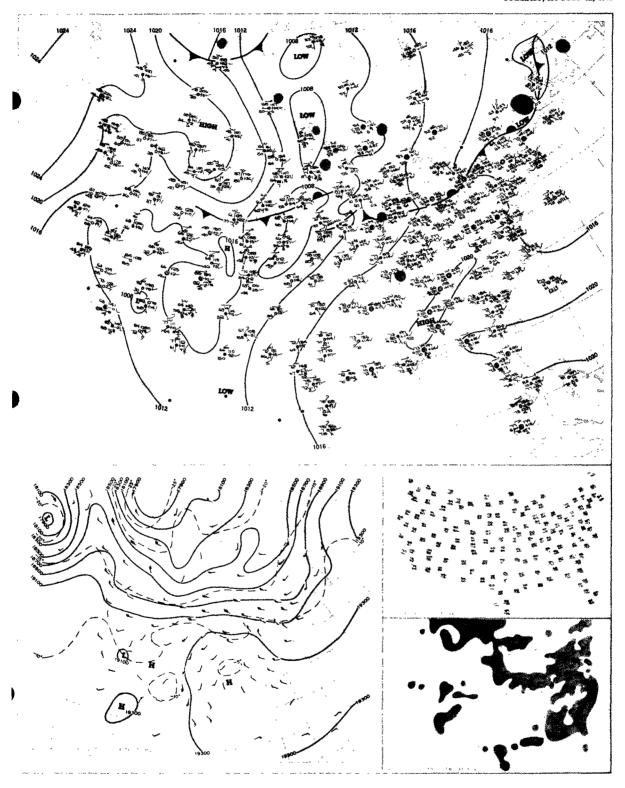


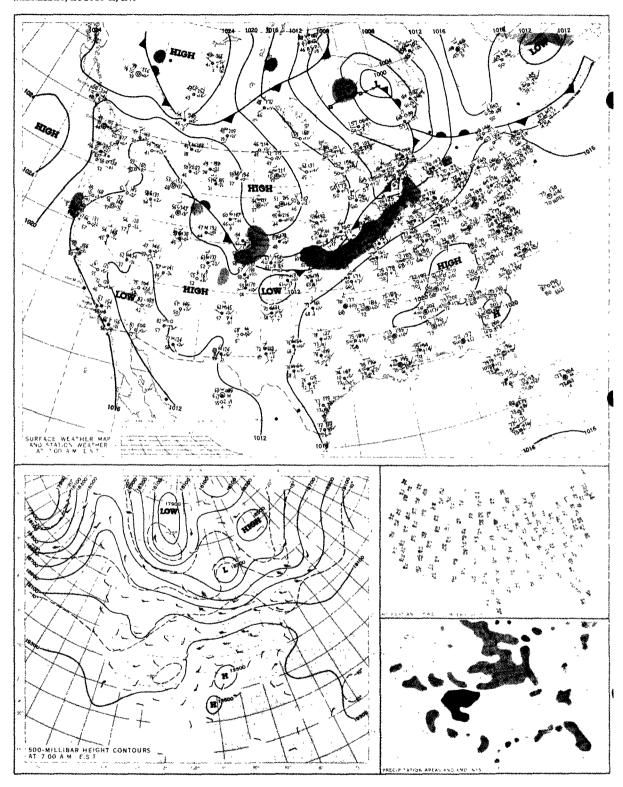


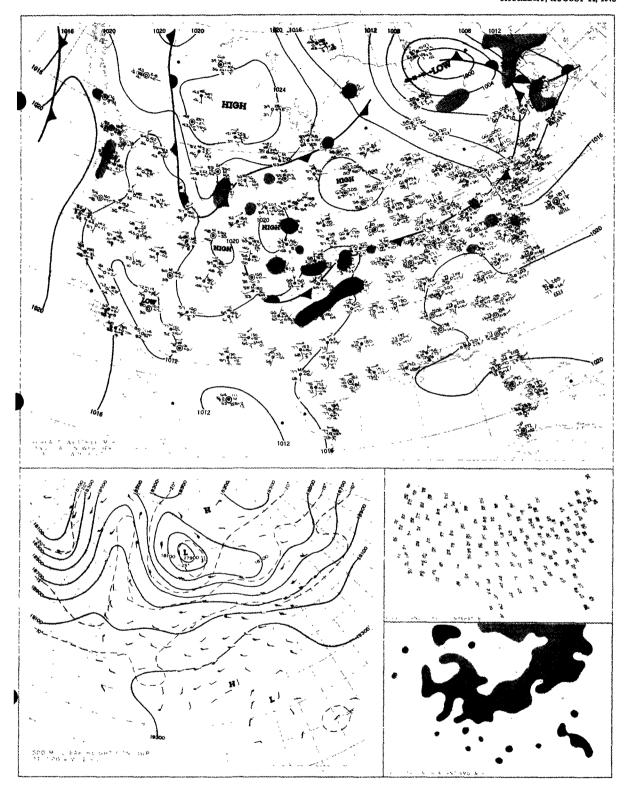


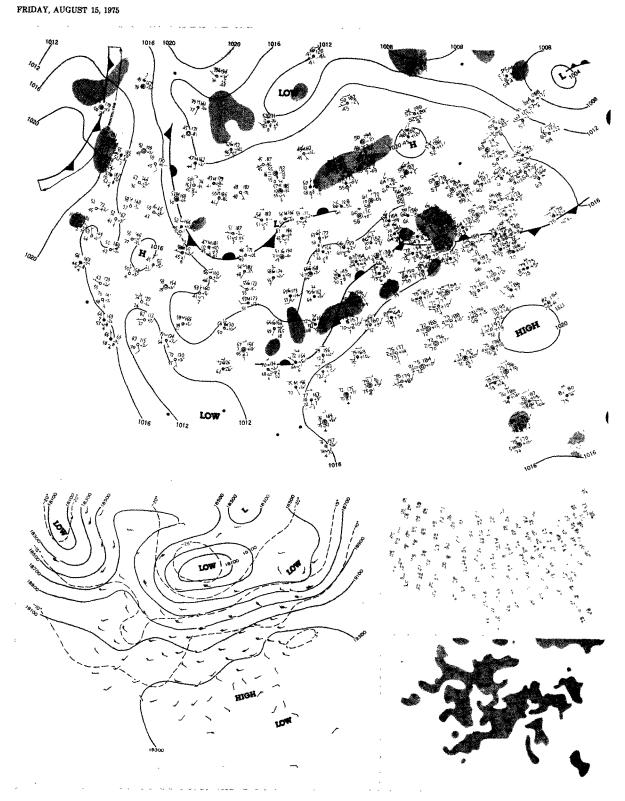


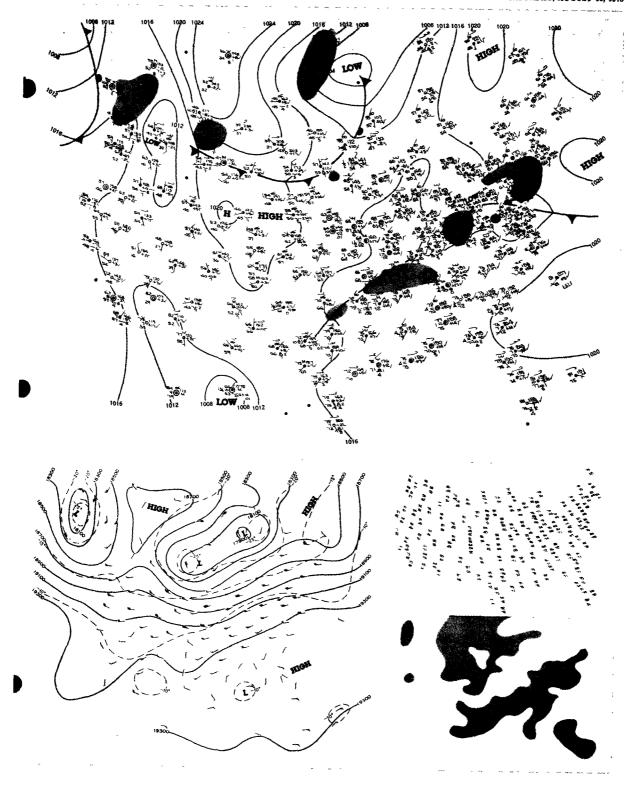


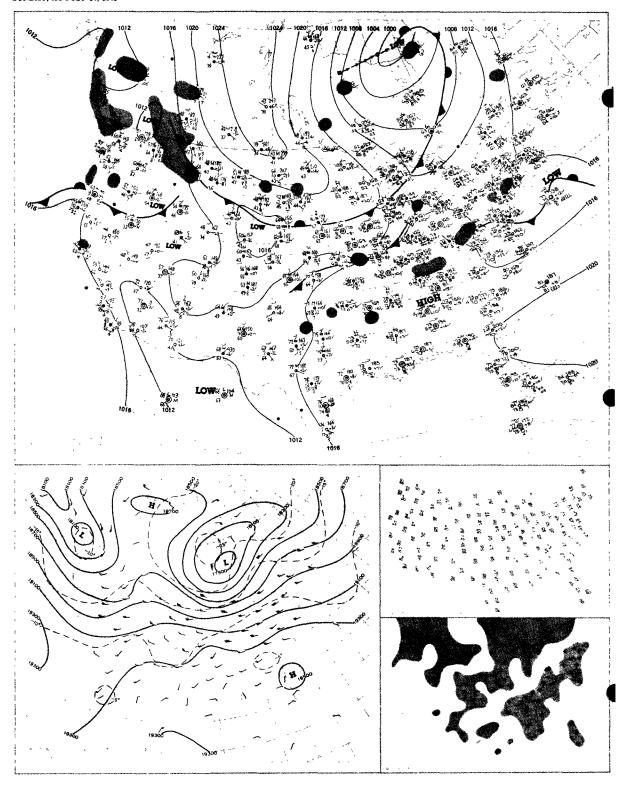


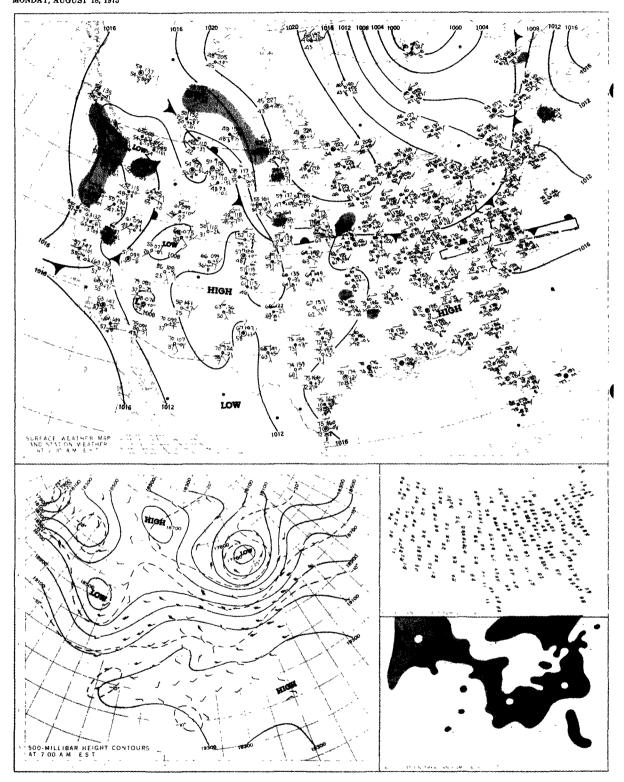


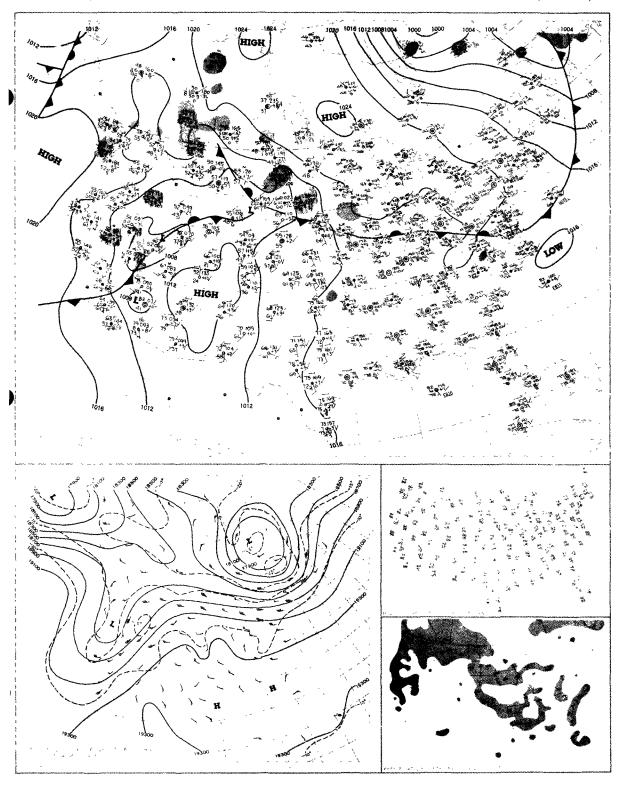


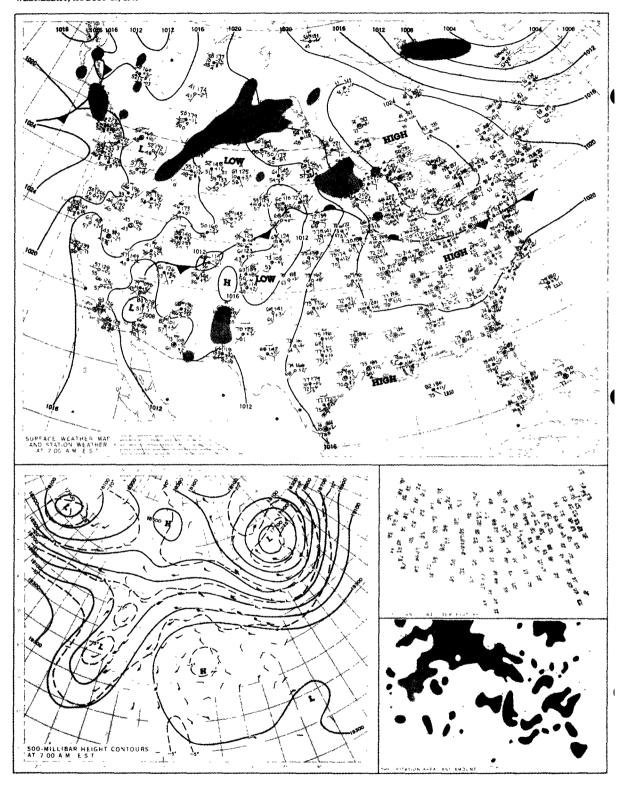


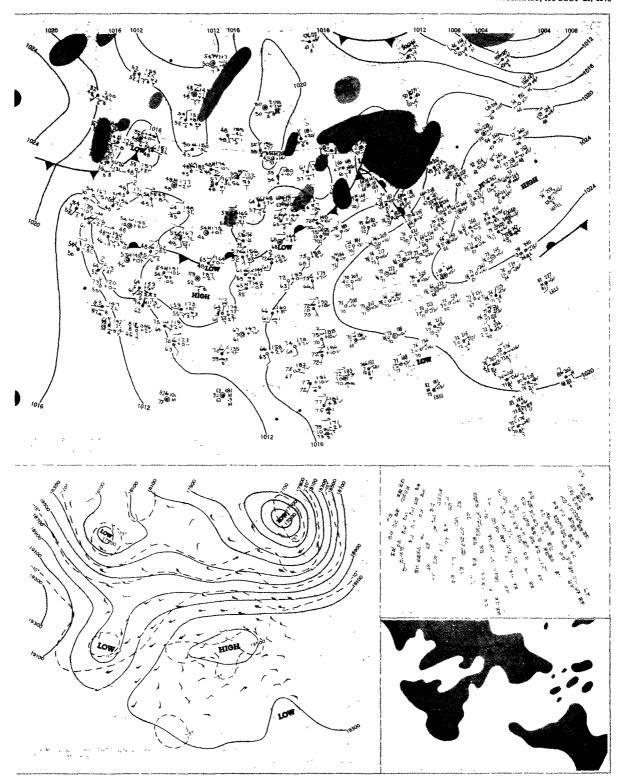


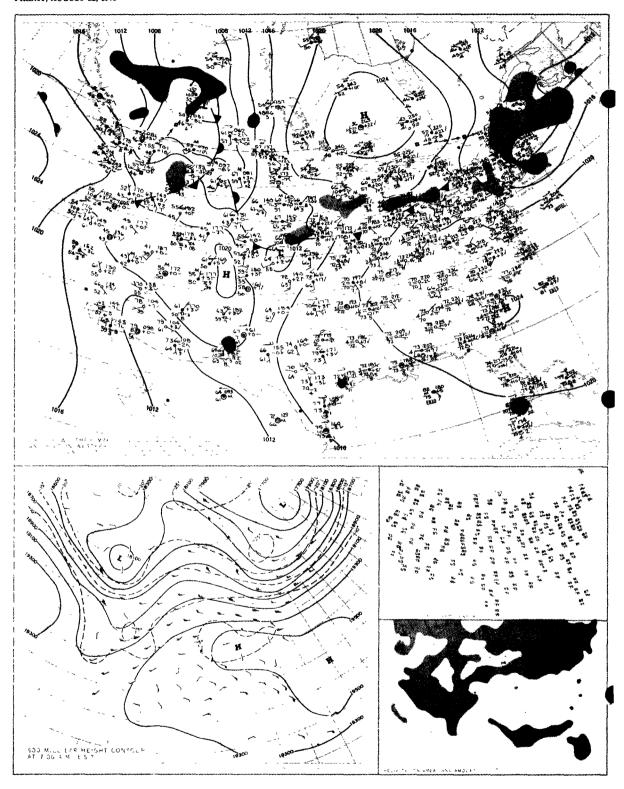


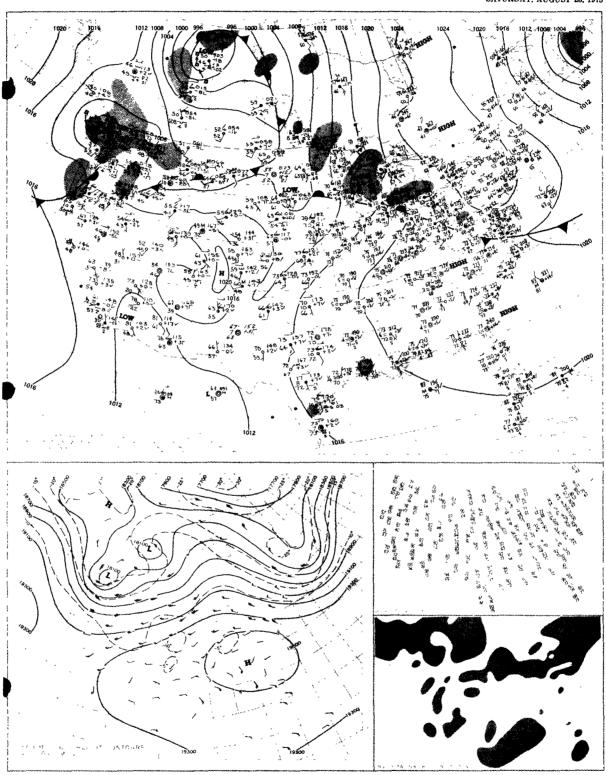


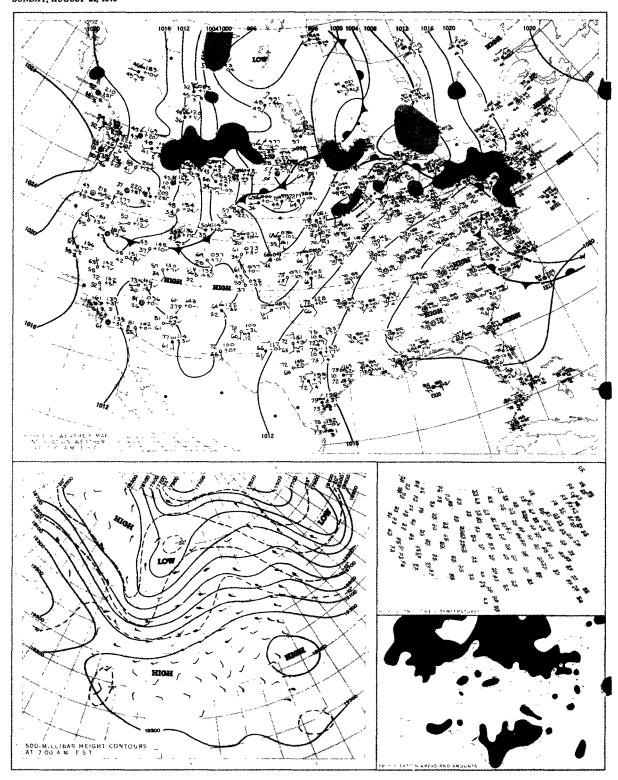


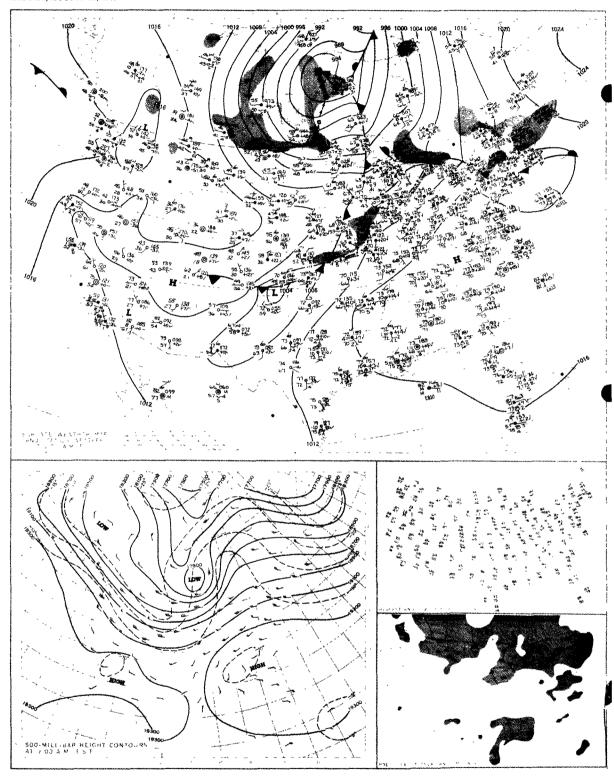


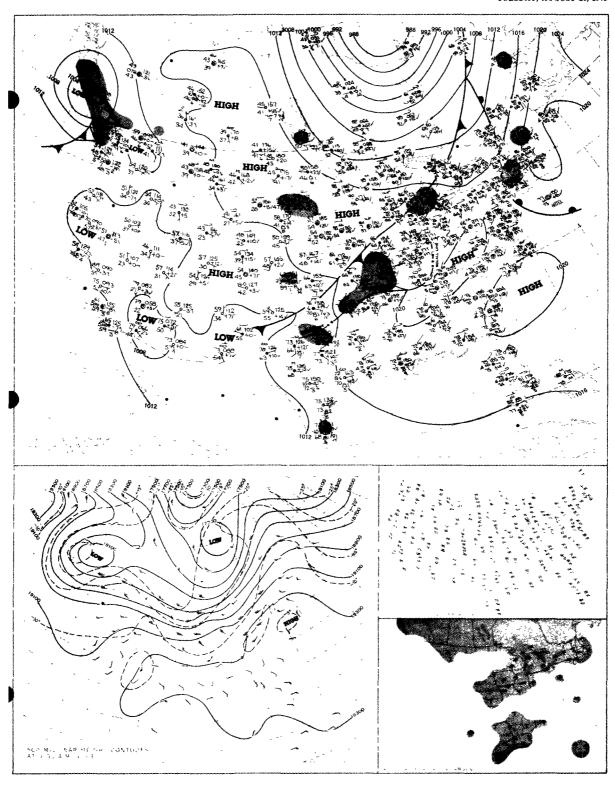


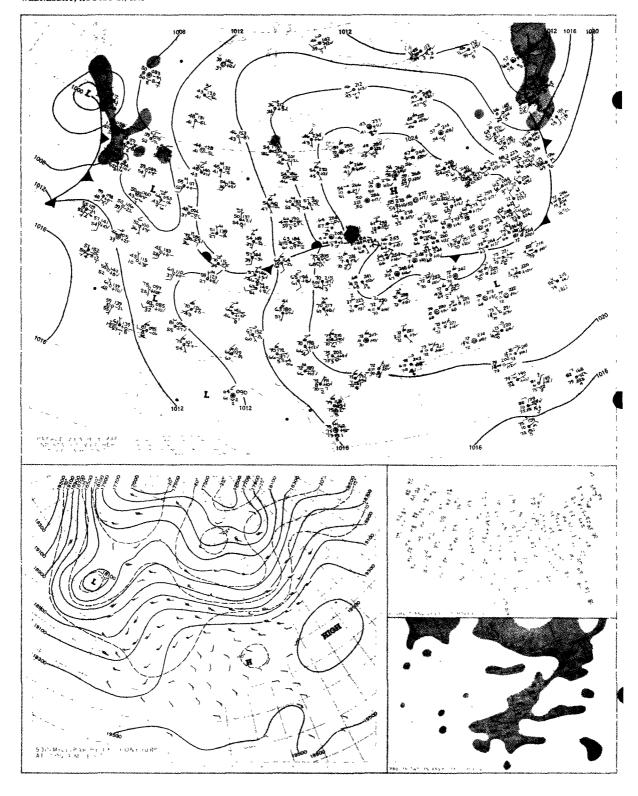


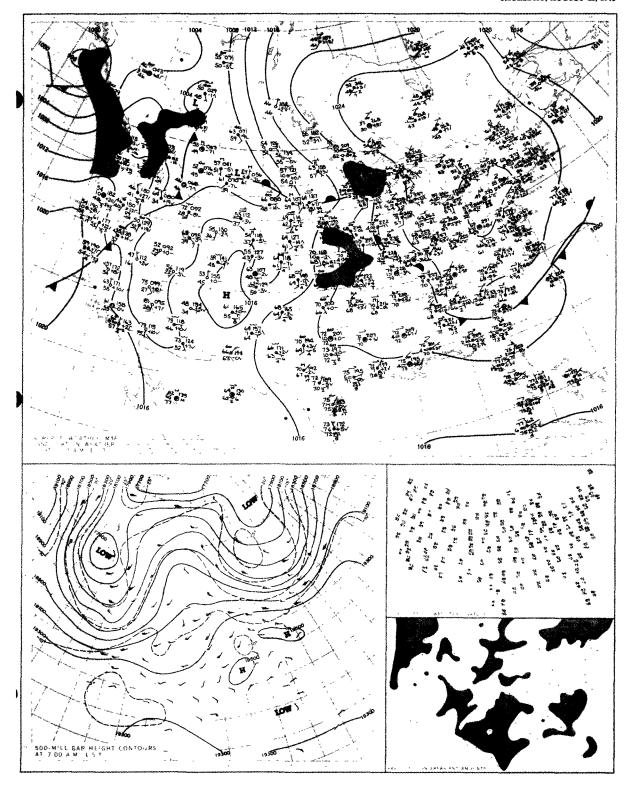


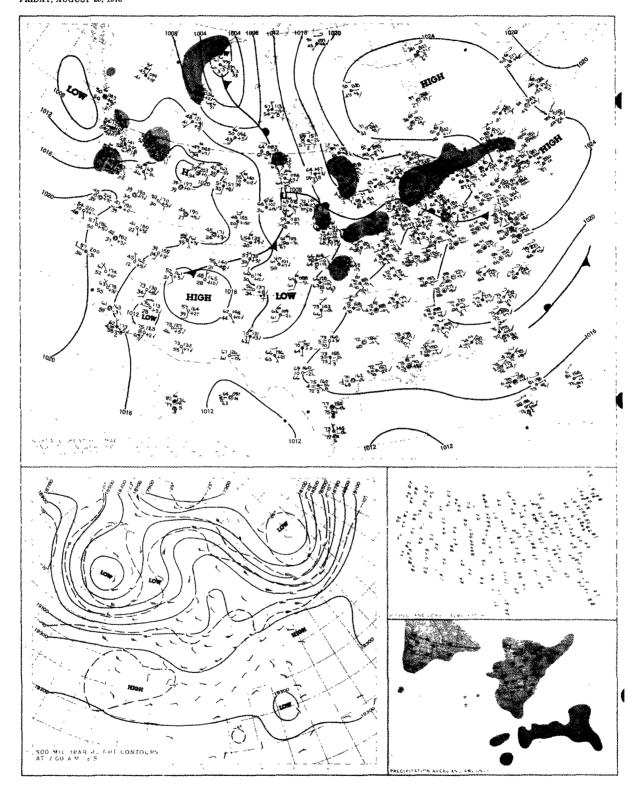


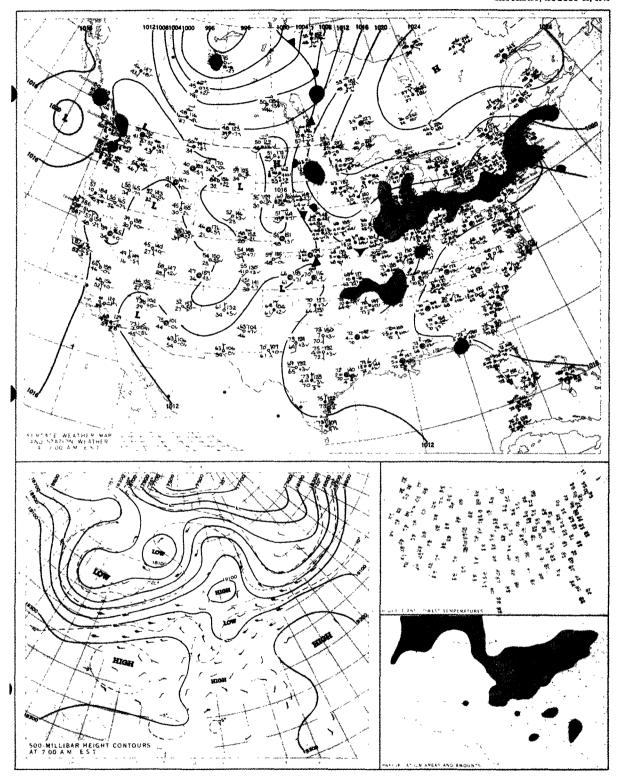


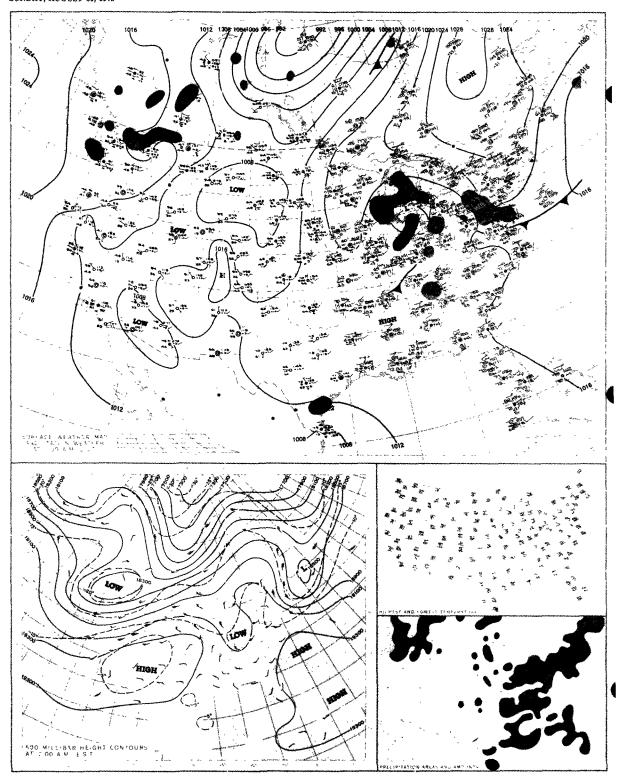










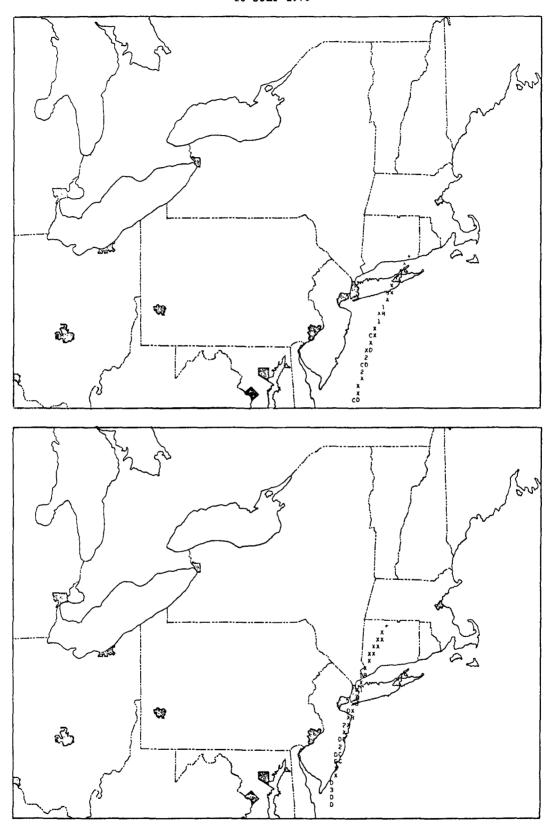


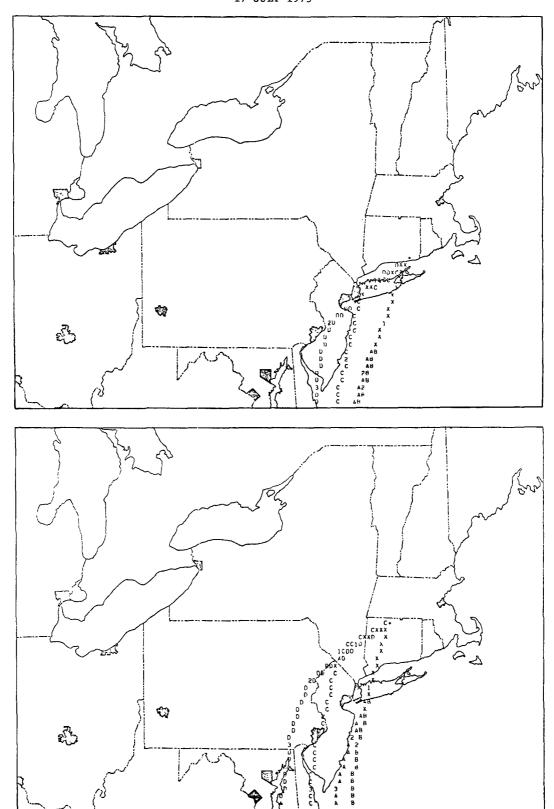
Appendix B

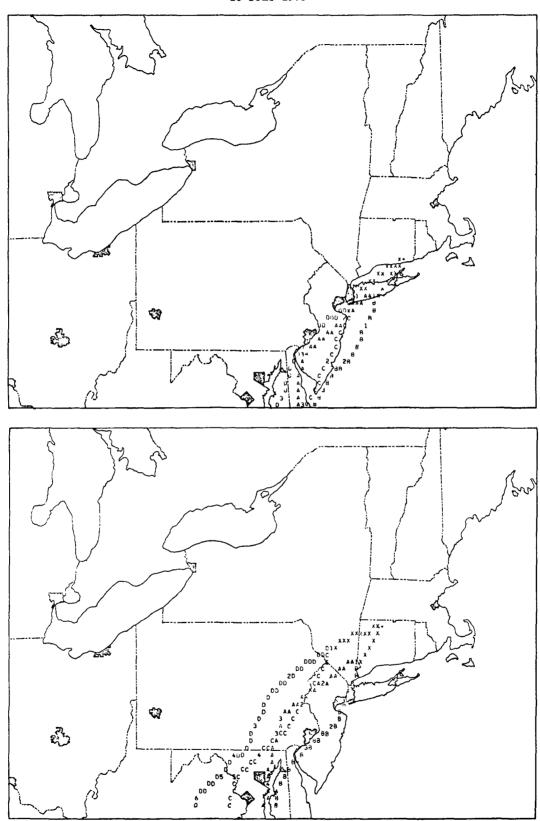
TRAJECTORIES OF AIR ARRIVING AT GROTON AND SIMSBURY

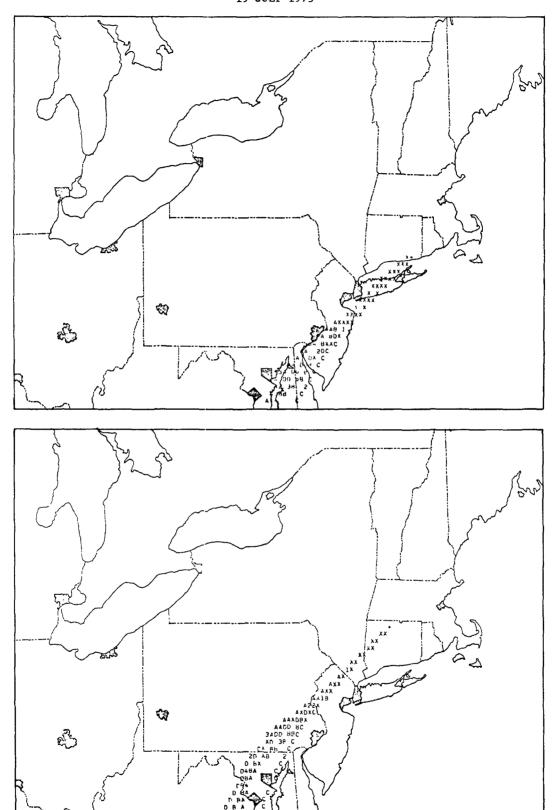
This appendix shows the calculated trajectories of air arriving at 6-hour intervals at Groton, and Simsbury, Connecticut, during the period from 16 July to 31 August 1975. The methods and data used to calculate these trajectories are described in the text of this report. Anyone who uses these trajectories should consult that discussion in the report so that they would be aware of the assumptions involved and of some of the shortcomings of the results.

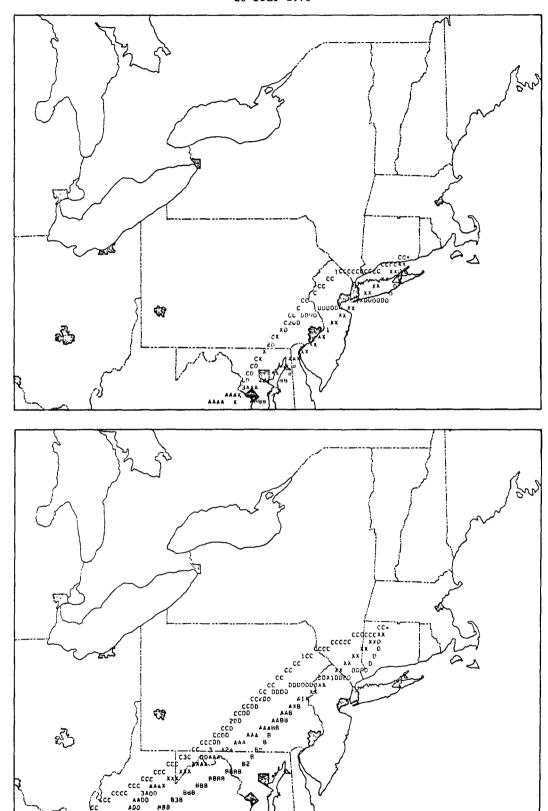
Trajectories shown on the following pages were plotted on computer line printer so that the north-south and east-west axes are of different scales. This is the reason for the distortions in the maps. Trajectories arriving at the end point at 0000 GMT (1000 EST of the preceding day) are marked by the symbol "A". Those arriving at 0600 GMT (0100 EST) are marked by "B", those arriving at 1200 GMT (0700 EST) by "C" and trajectories arriving at 1800 GMT (1300 EST) are shown by the symbol "D". When two or more trajectories passed through the same point, an "X" is shown. The positions of the air at 6-hour intervals are marked by numerals. This position 6 hours prior to arrival at the end point is shown by a "1", 12 hours prior to arrival is indicated by a "2", and so forth.

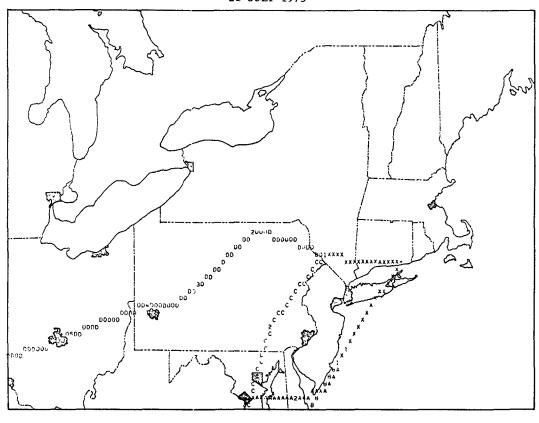


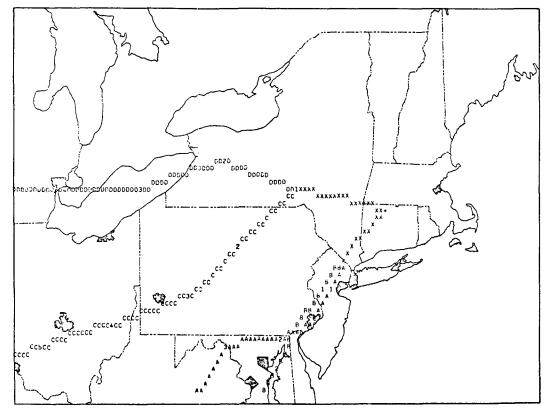


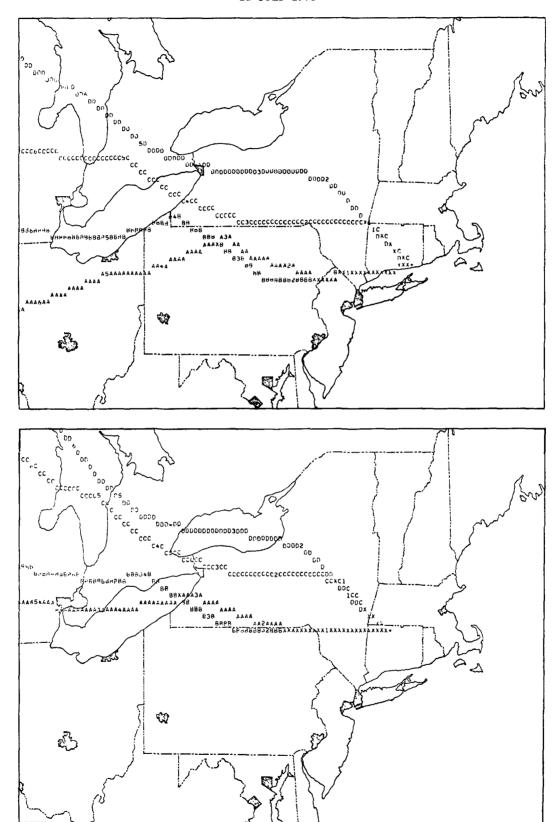


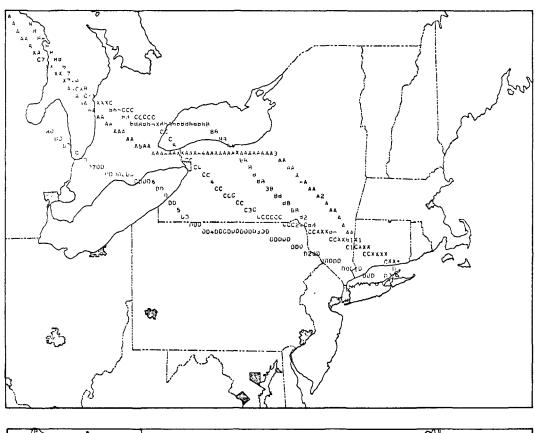


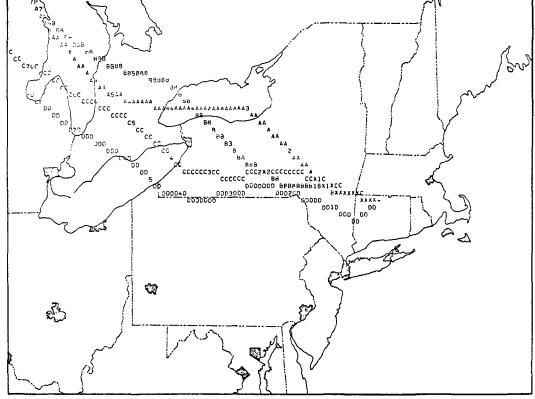


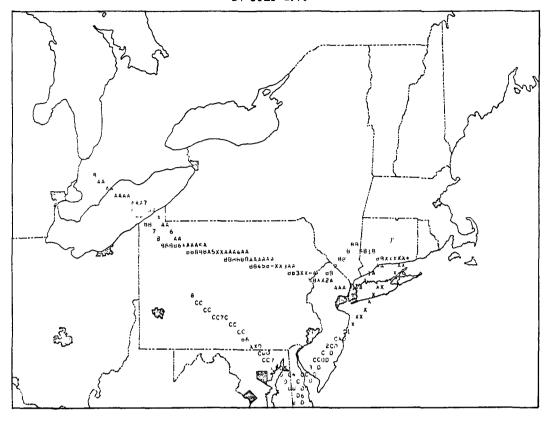


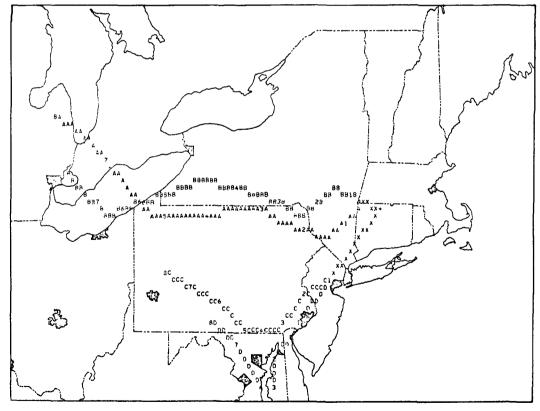


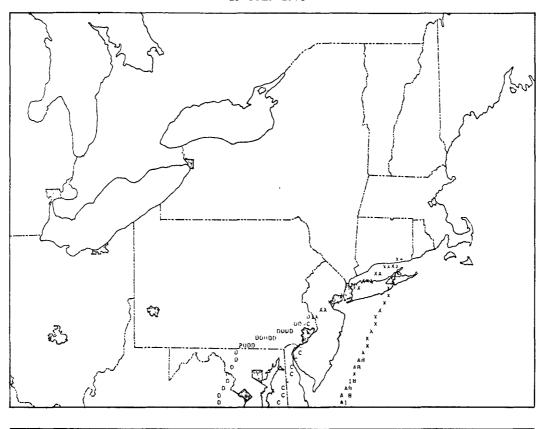


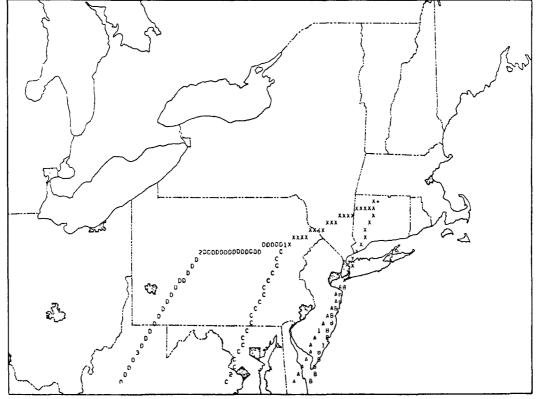


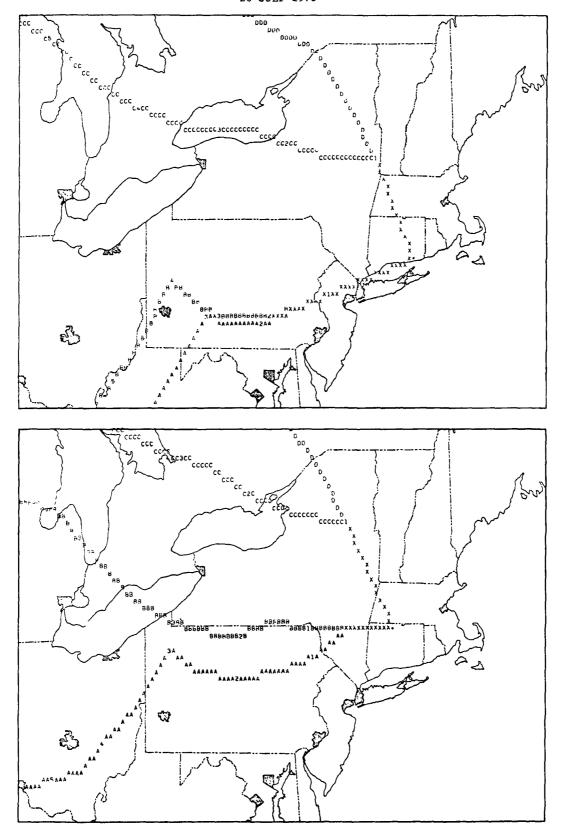


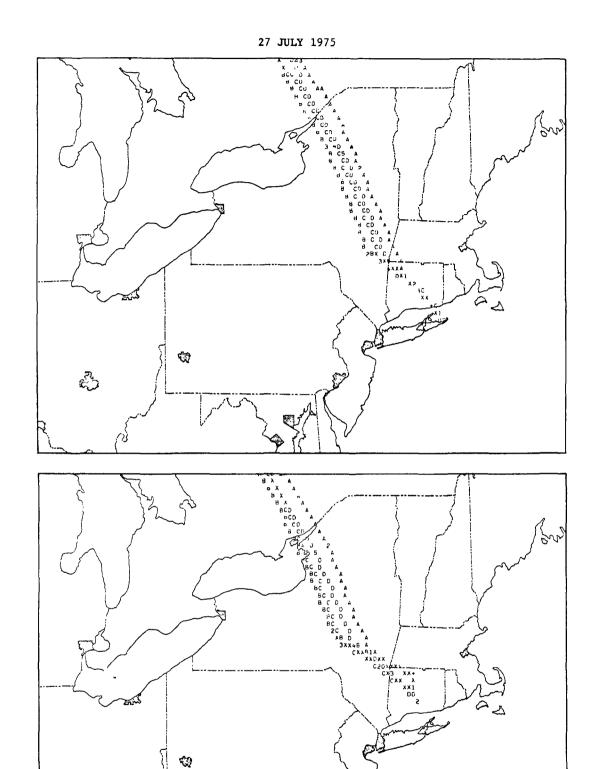


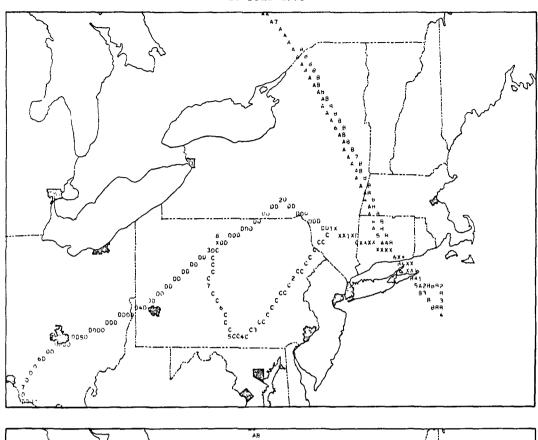


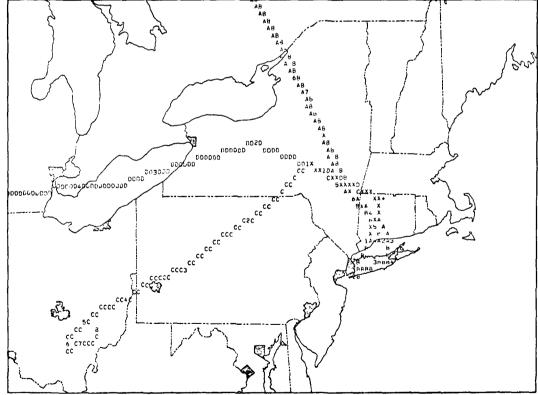


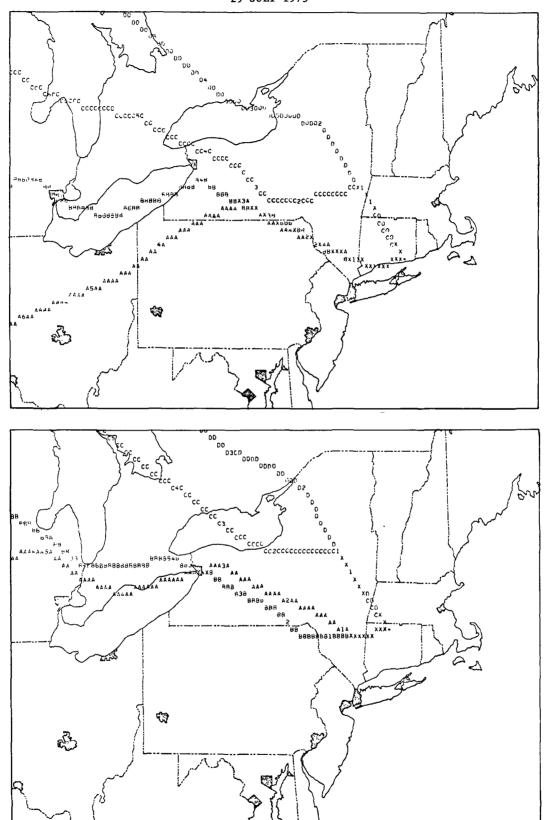




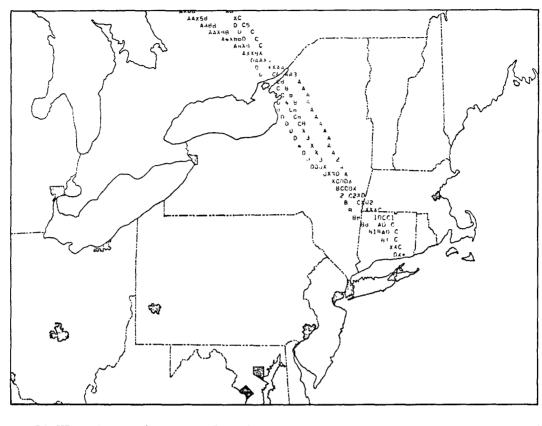


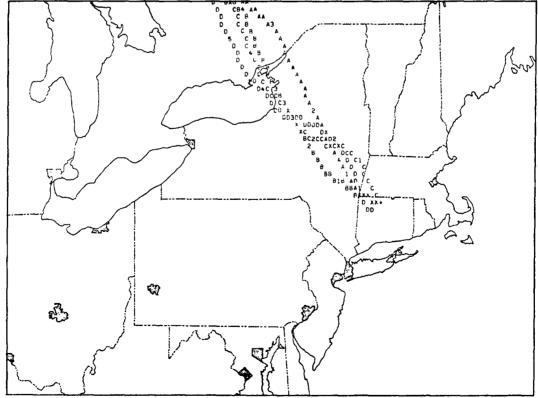


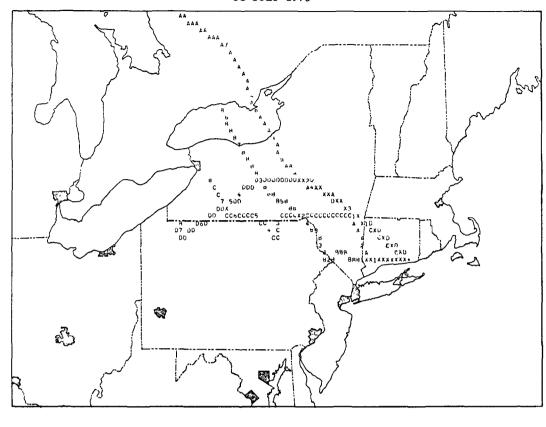


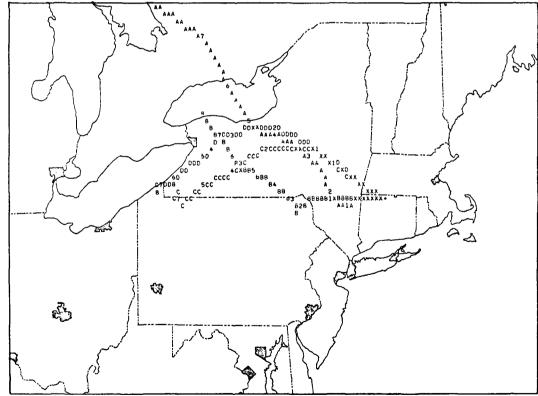


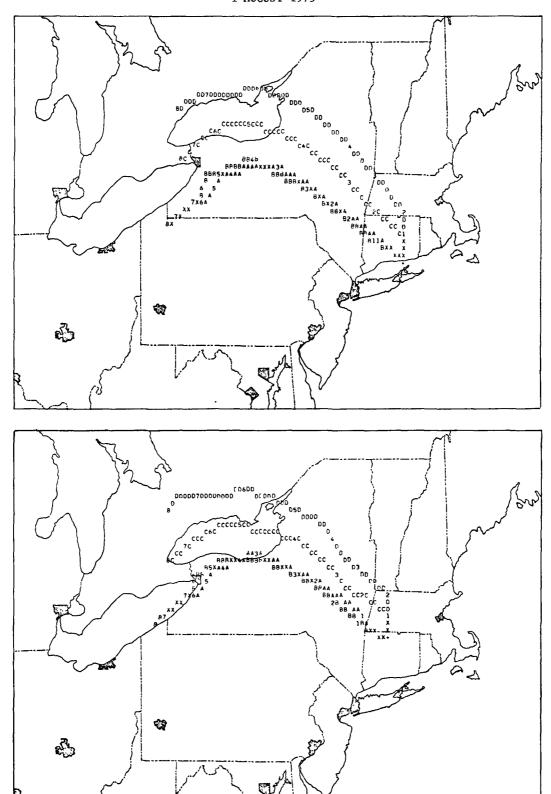
B-16

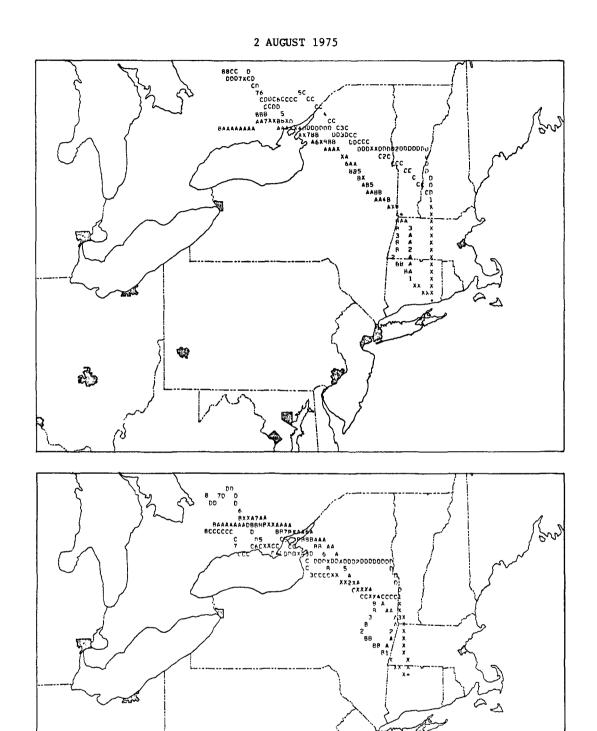


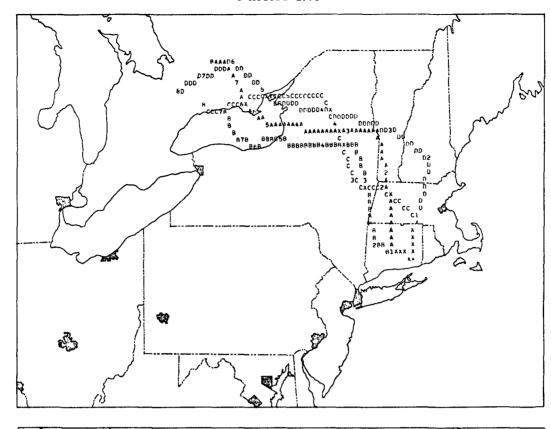


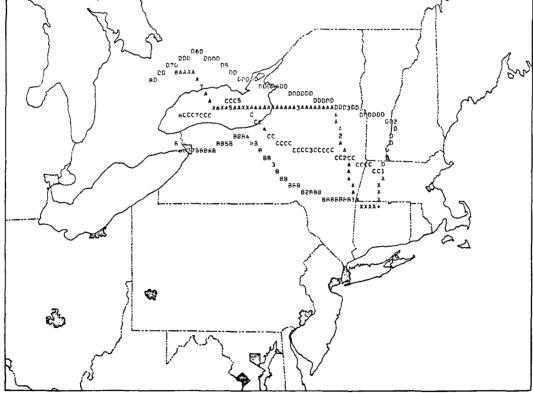


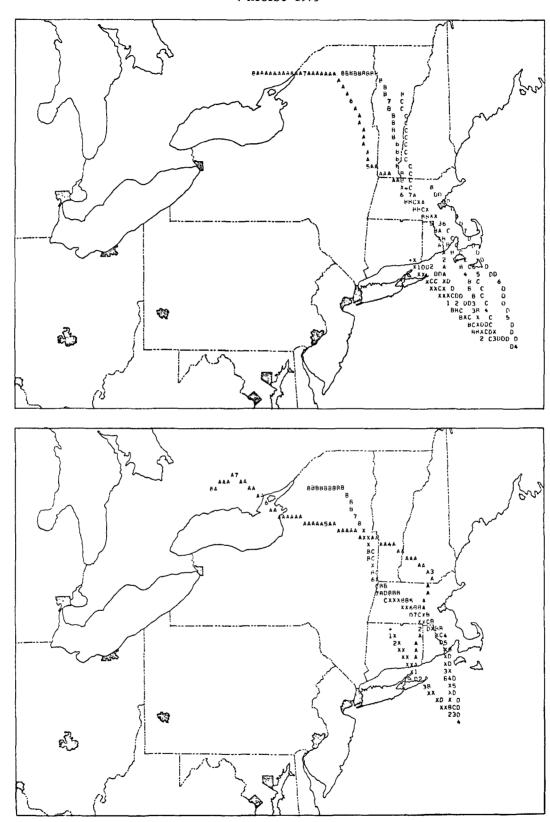


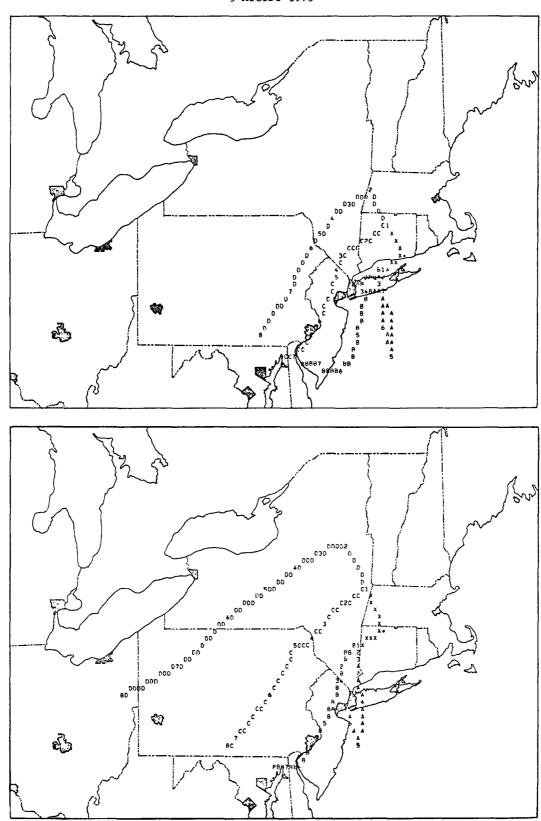


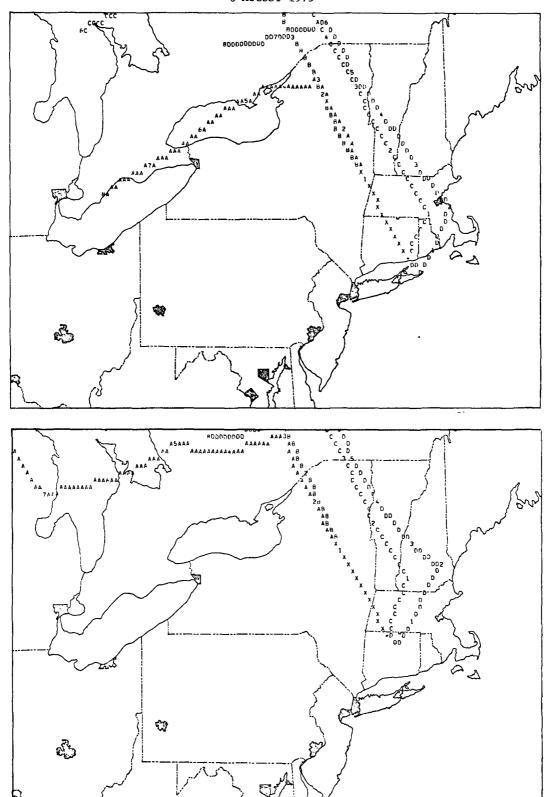


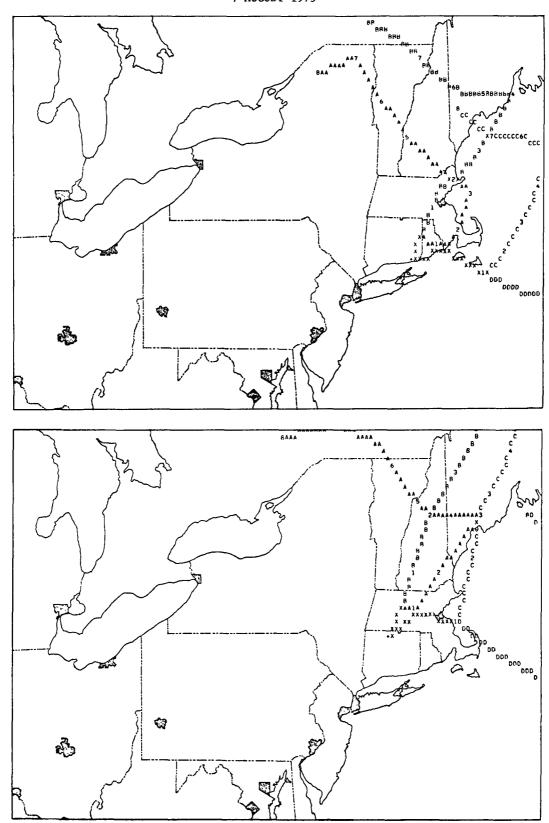


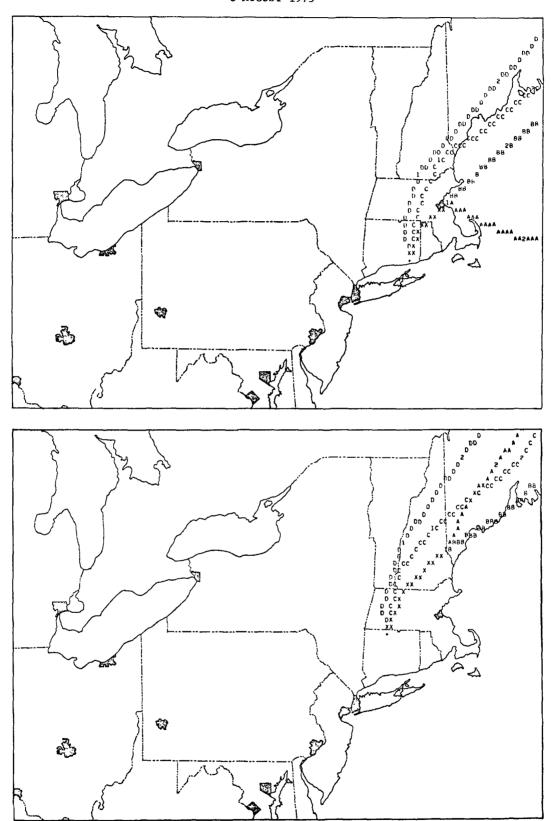


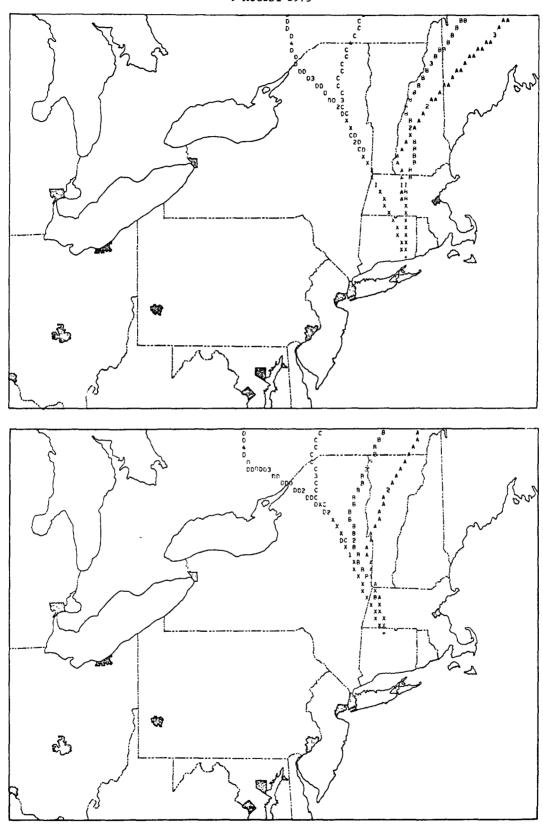


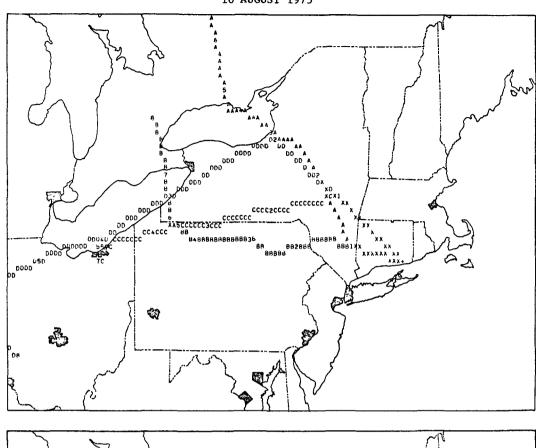


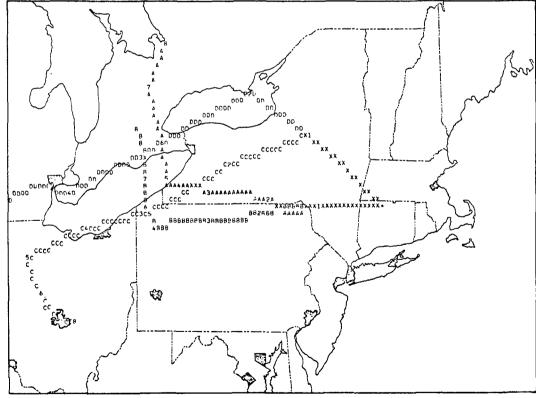


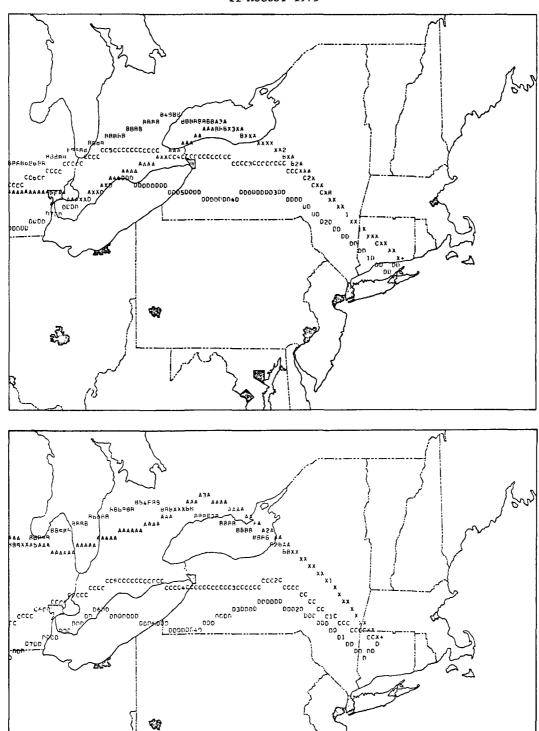


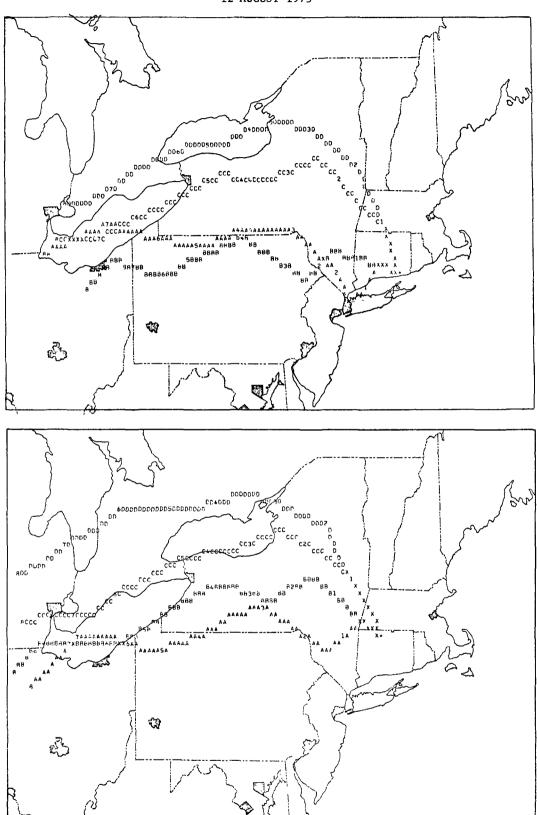


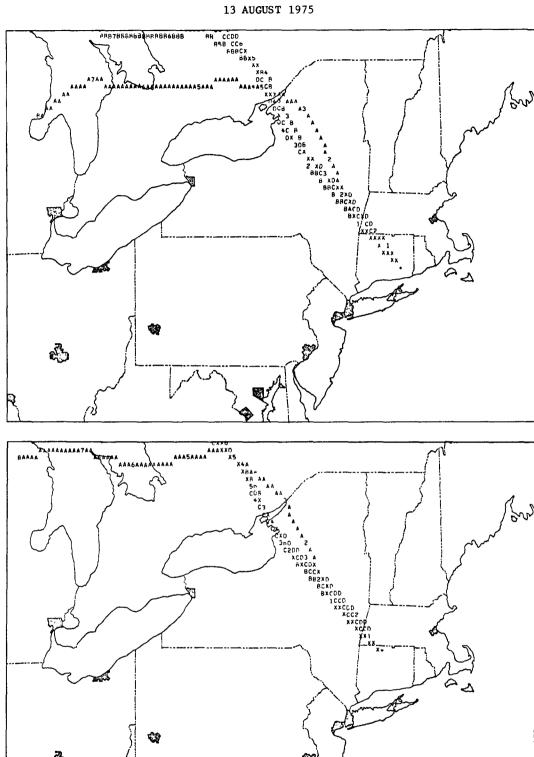


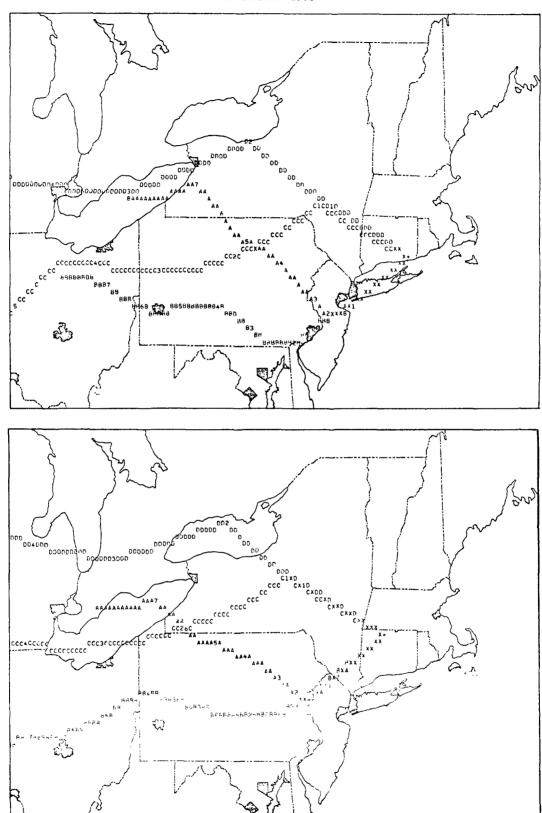


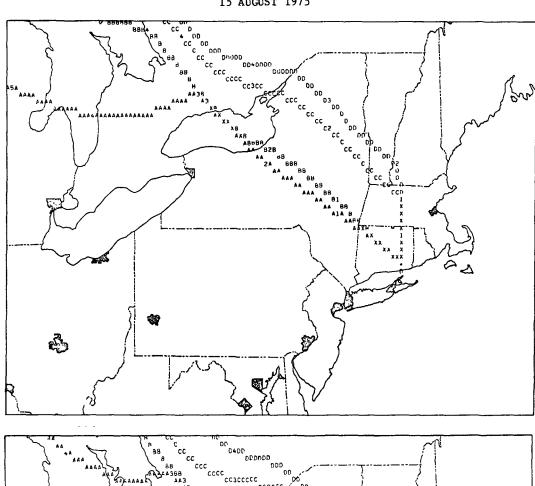


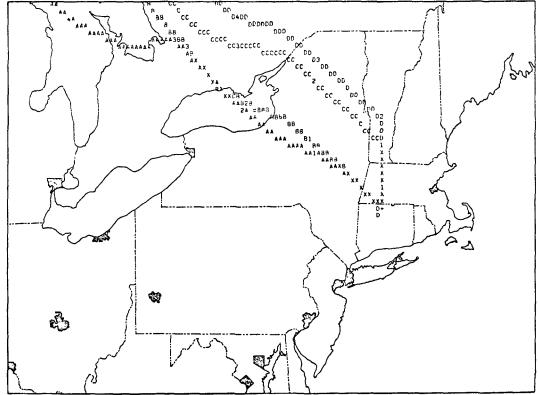


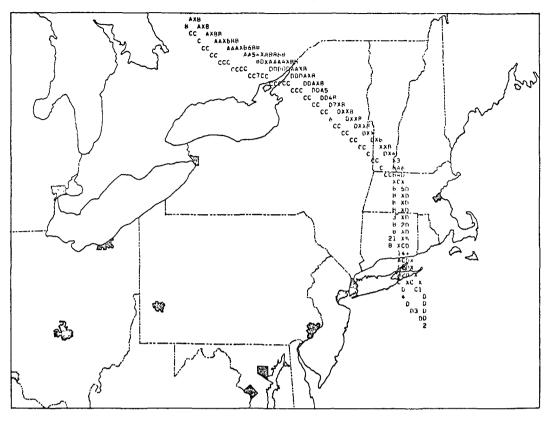


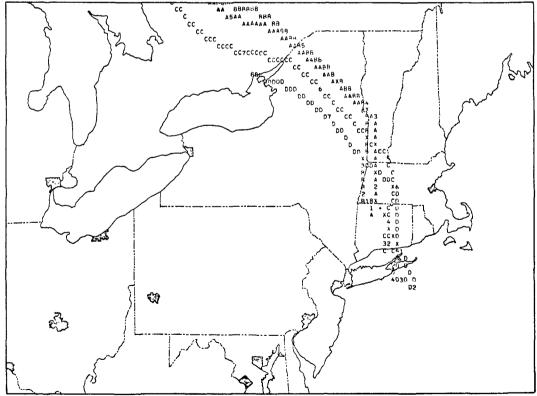


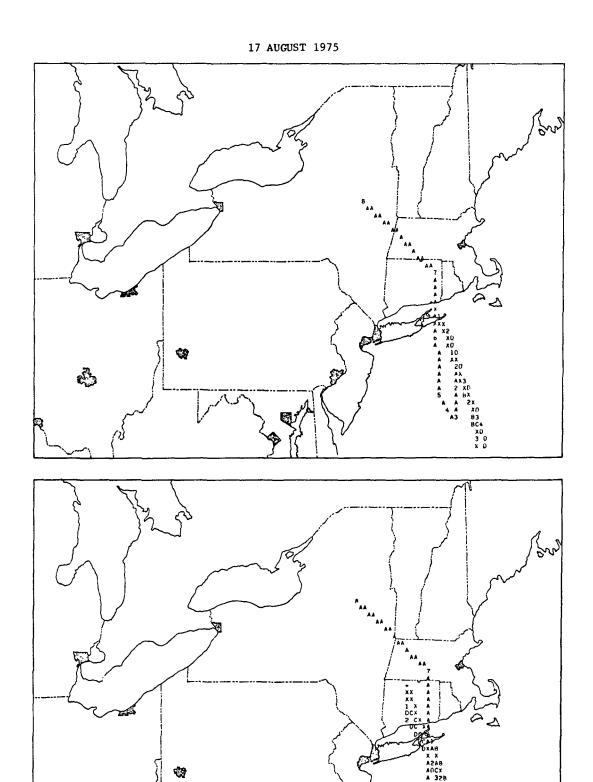


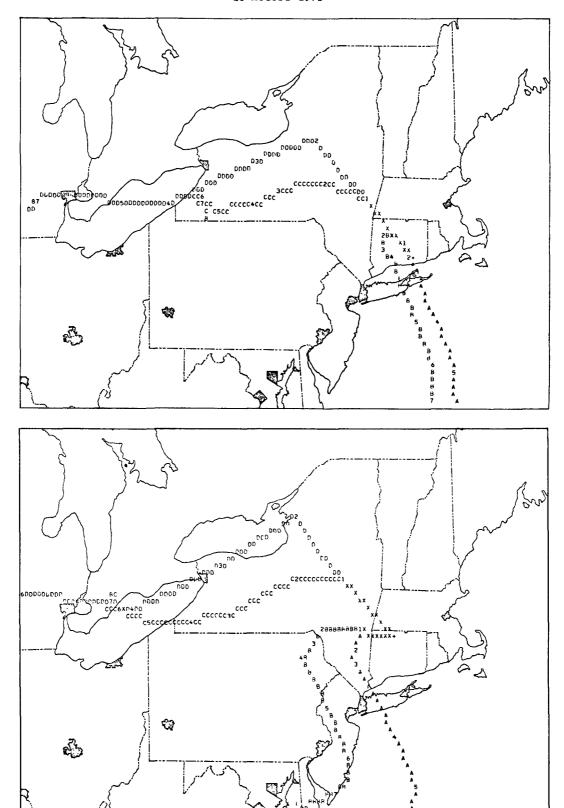


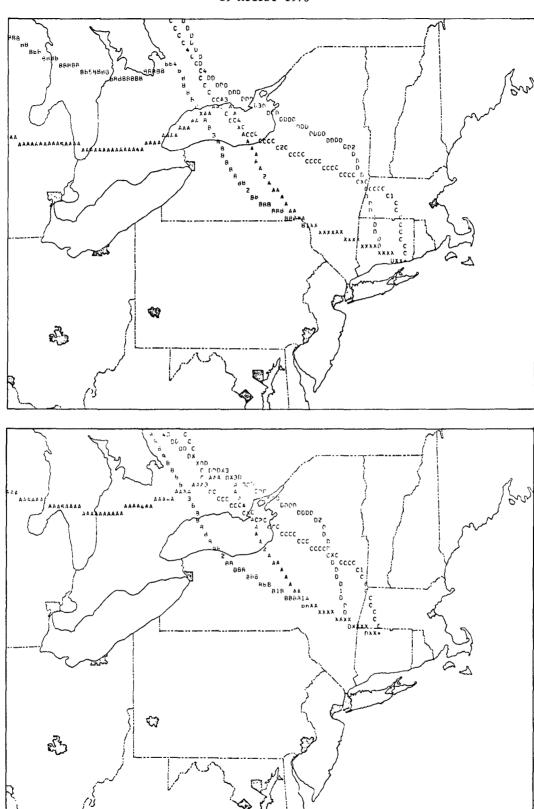


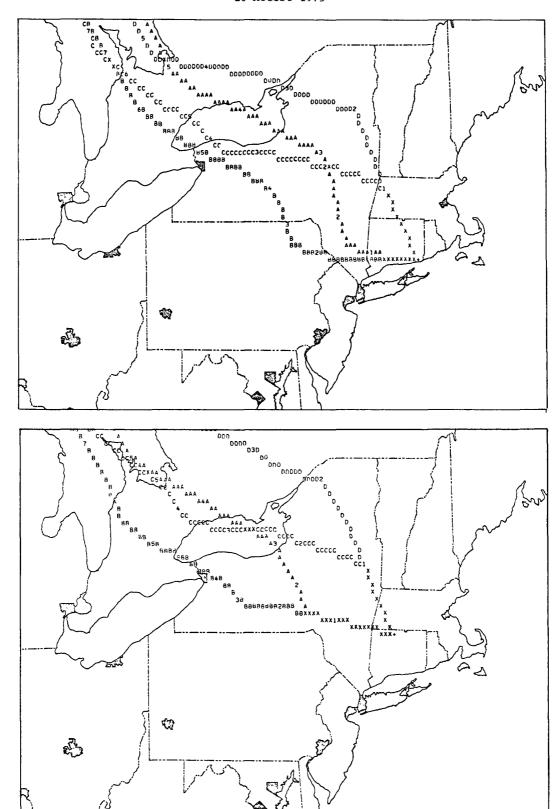


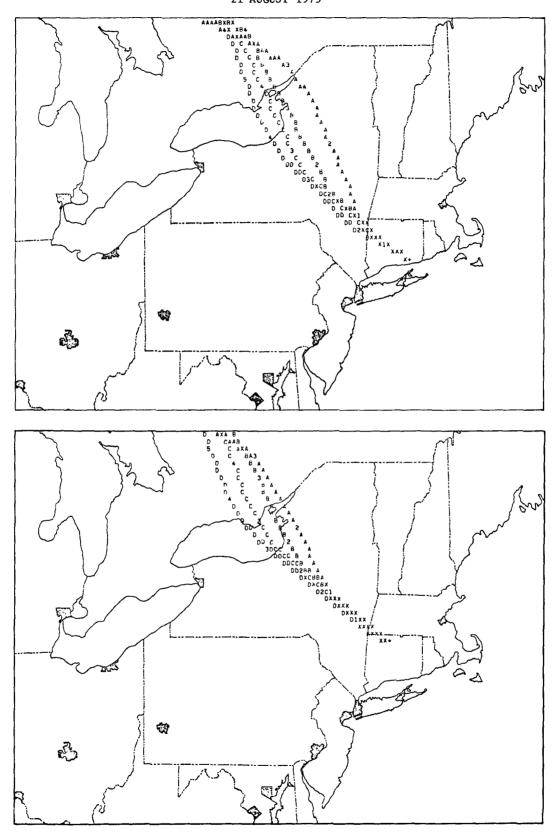


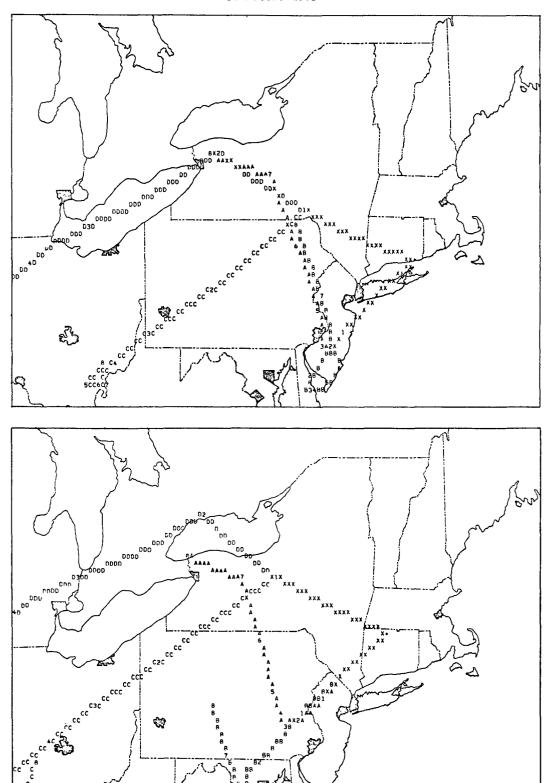


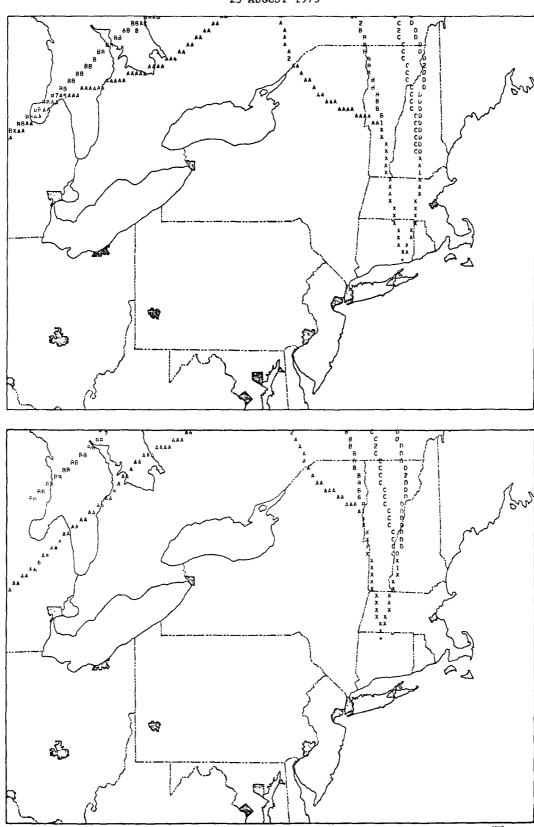


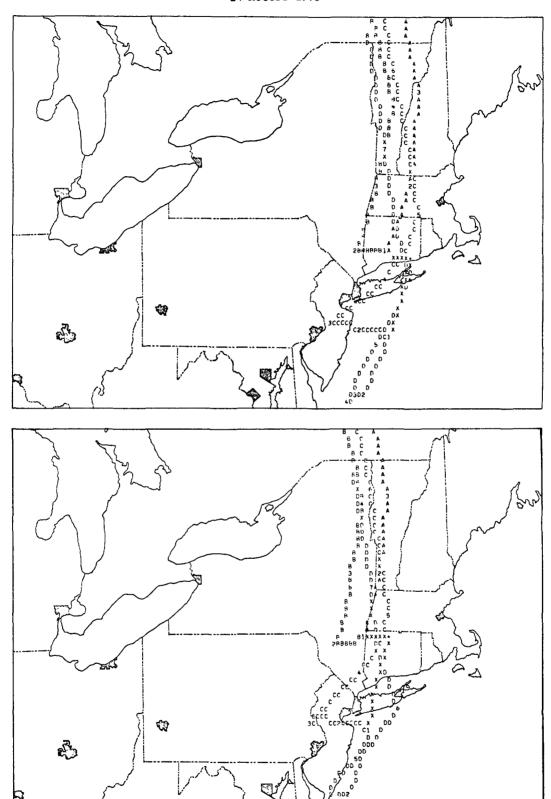


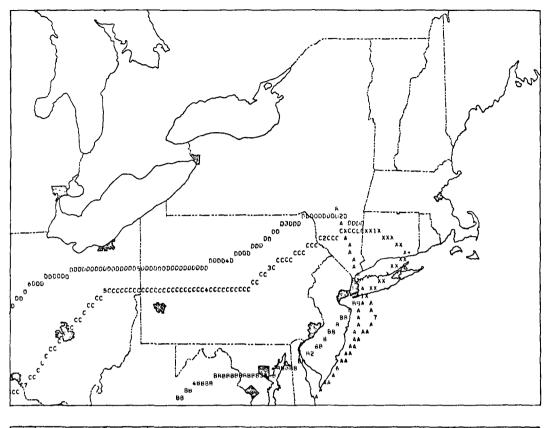


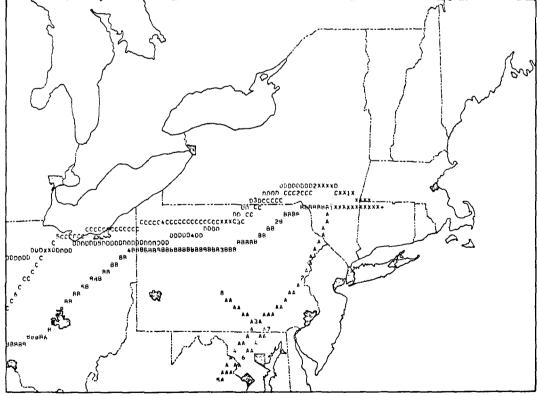


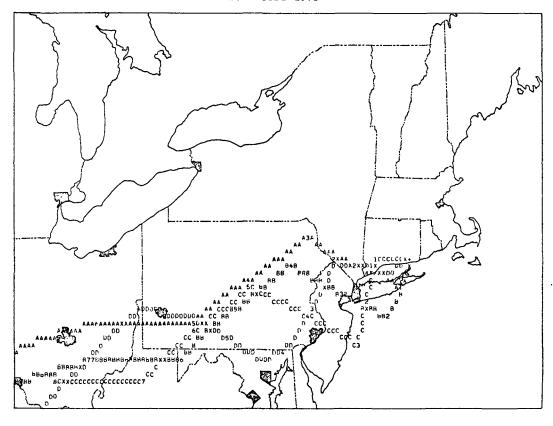


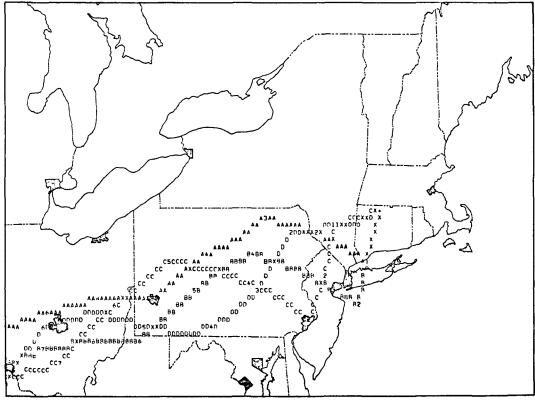


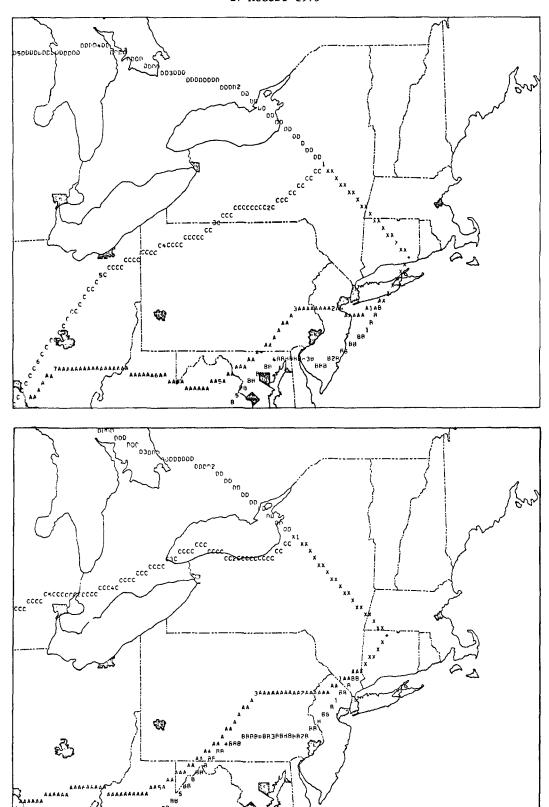


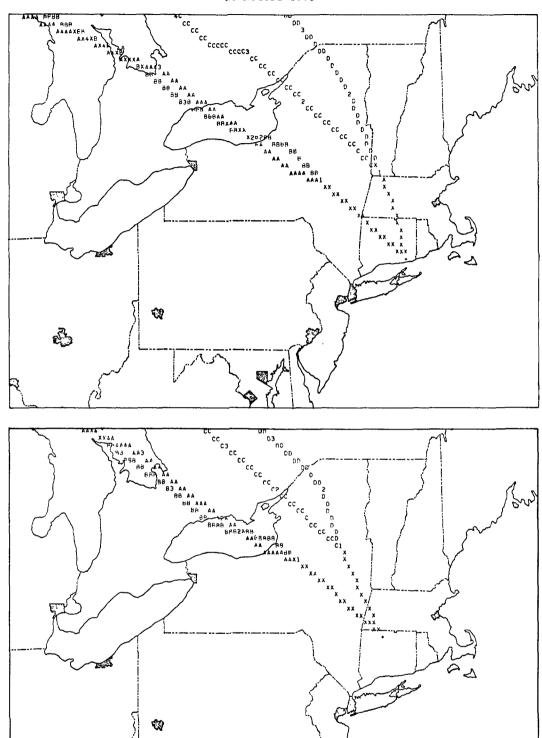


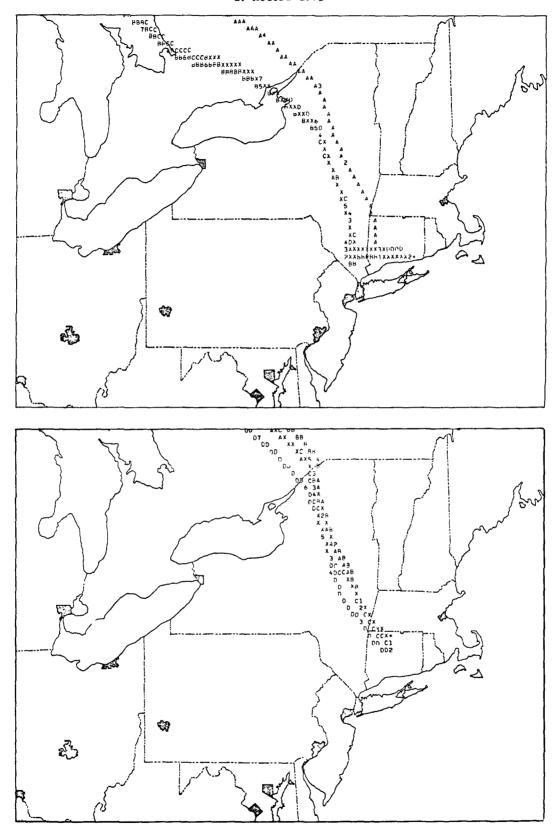


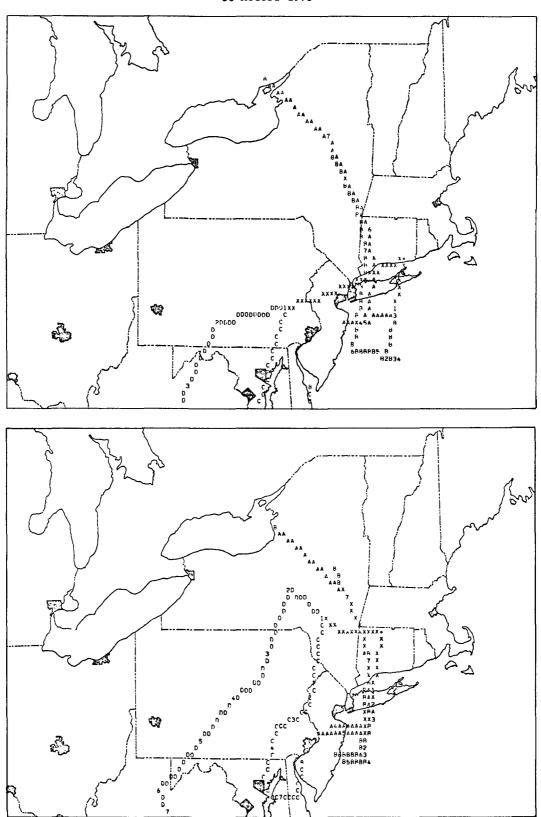


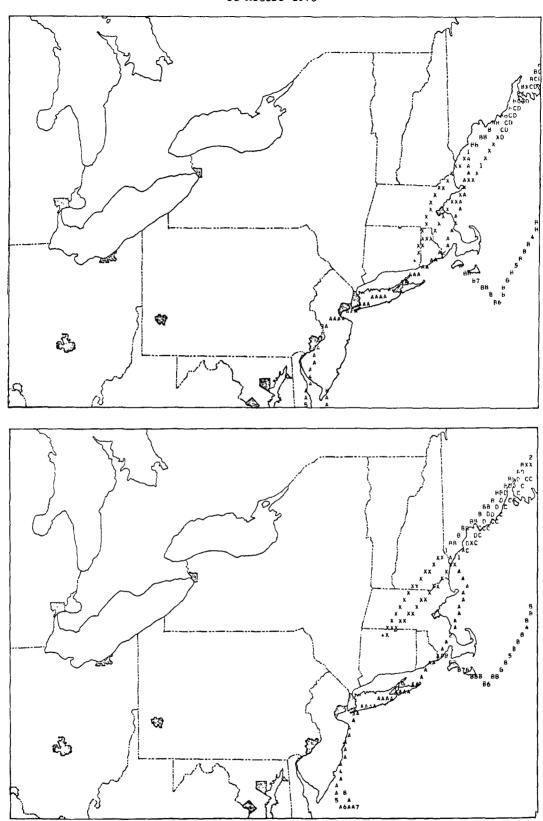








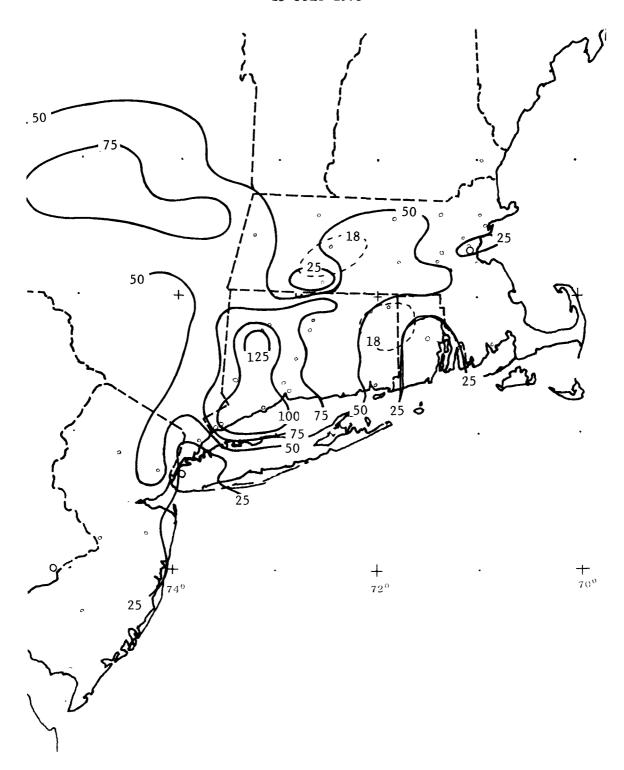


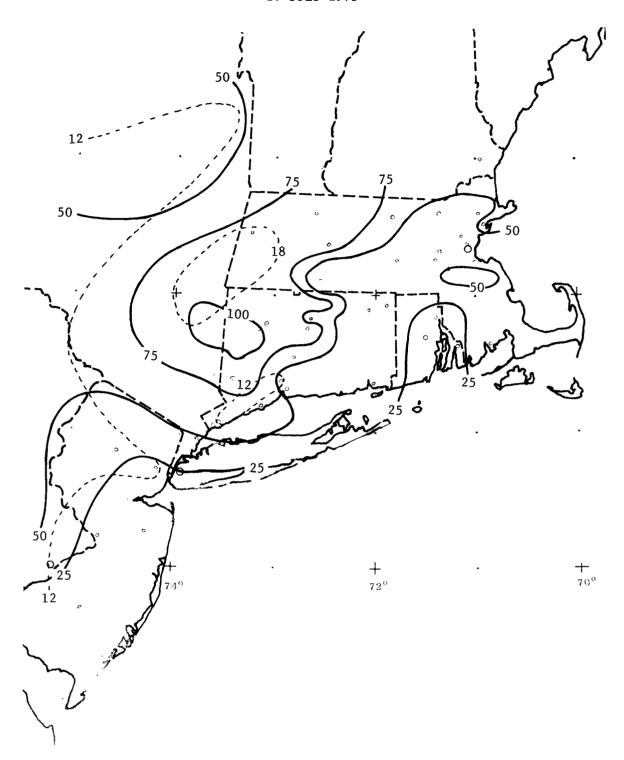


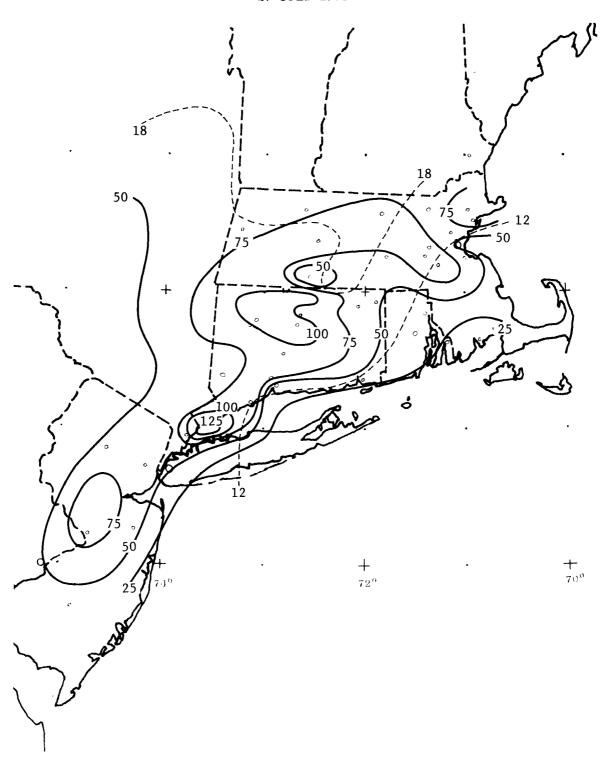
Appendix C

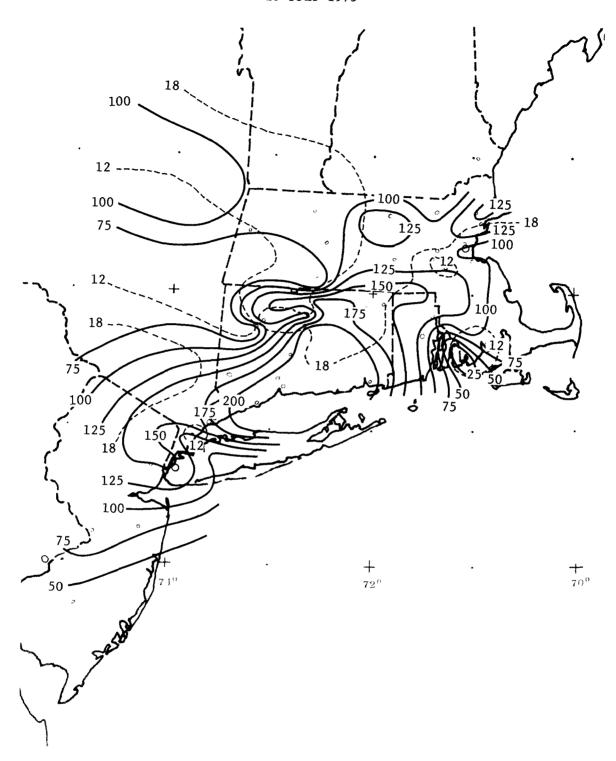
MAXIMUM-HOUR OZONE CONCENTRATIONS

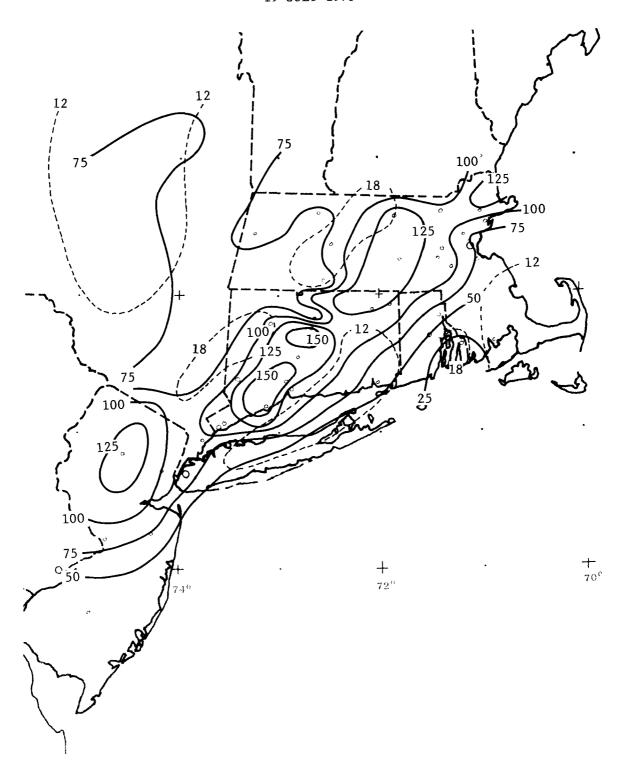
Maps of the maximum-hour ozone concentrations (ppb) in the study are shown on the following pages for the period from 15 July to 31 August 1975. Isochrones, showing the hour (EST) at which the maximum occurred are also plotted (as dashed lines) on the maps. The interpretation of these maps is discussed in more detail in the body of this report.

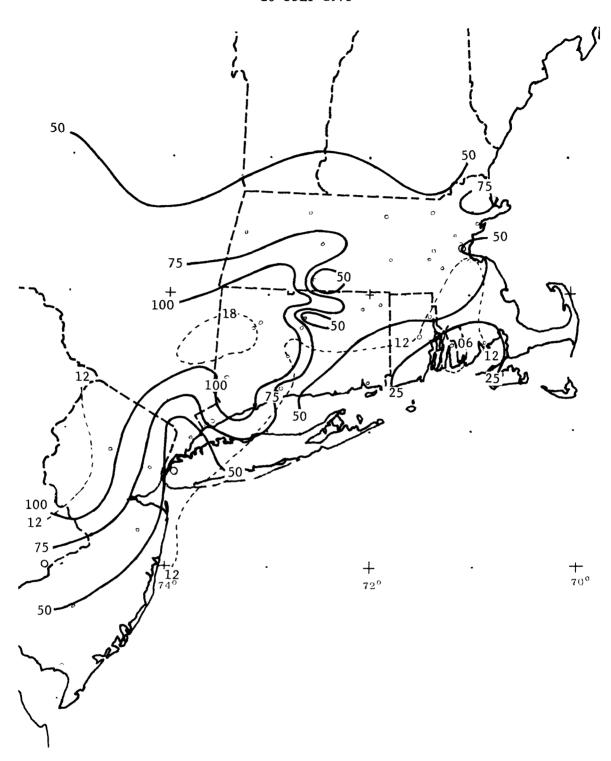


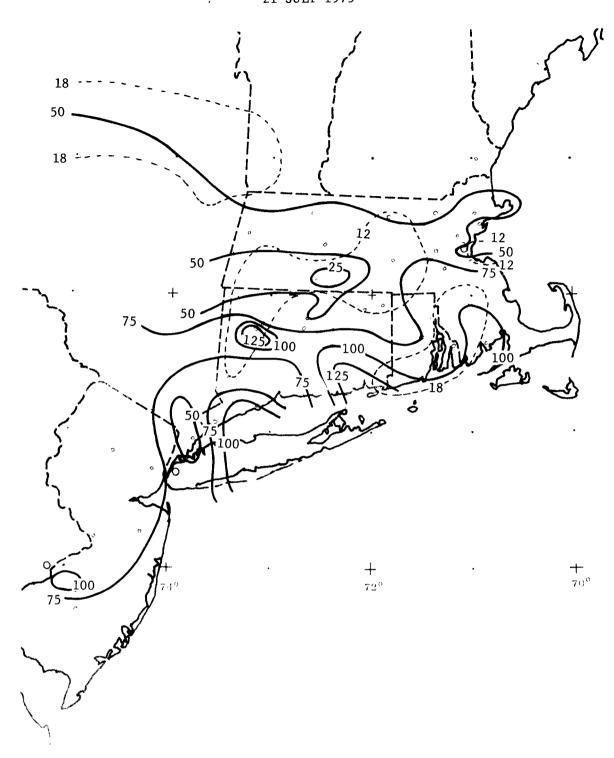


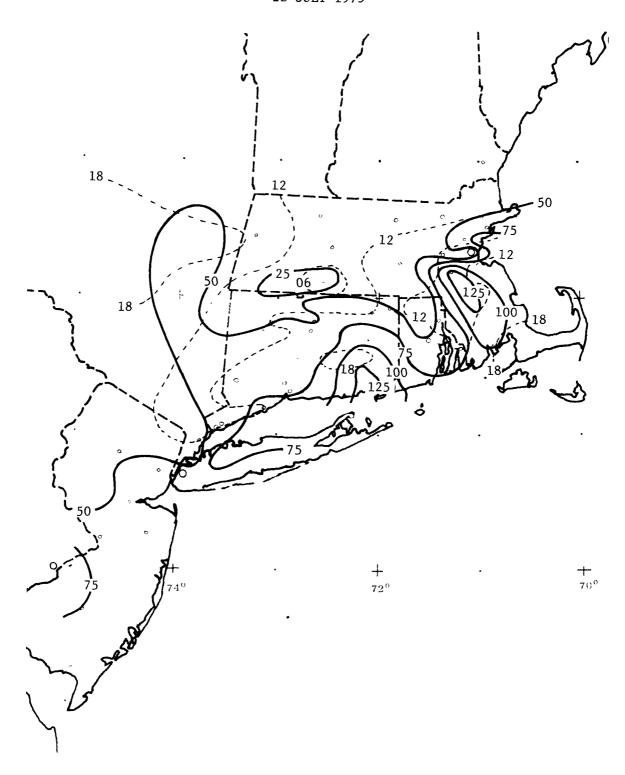


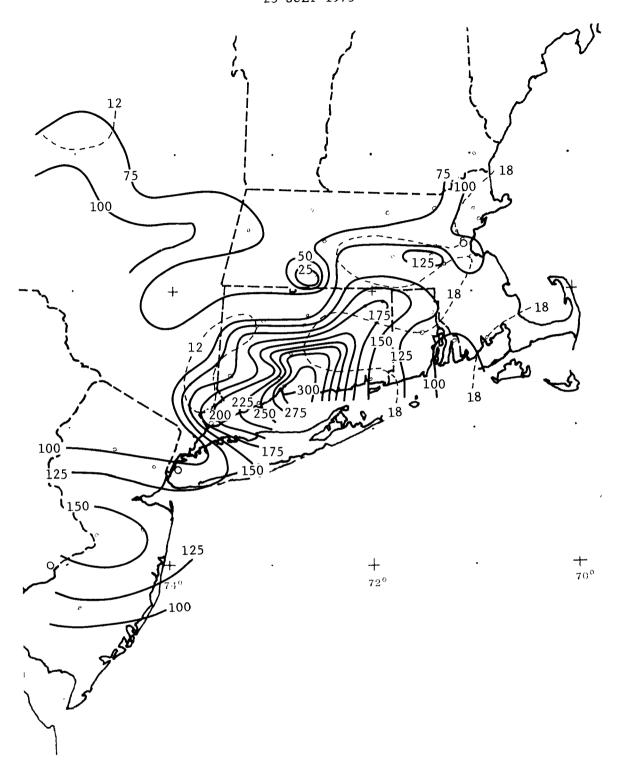


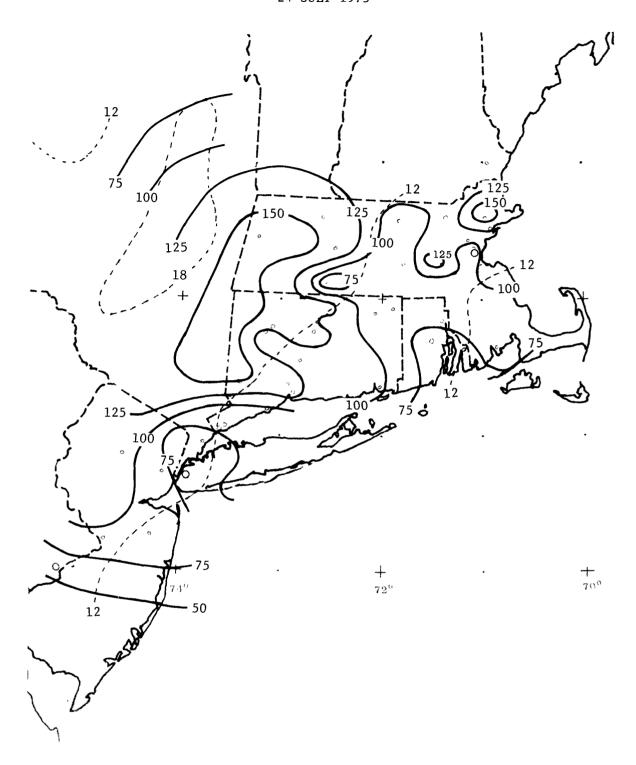


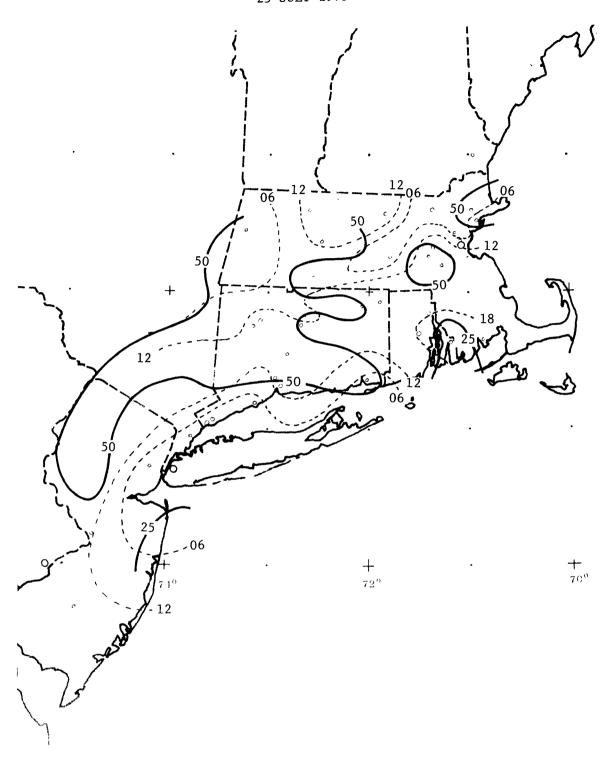


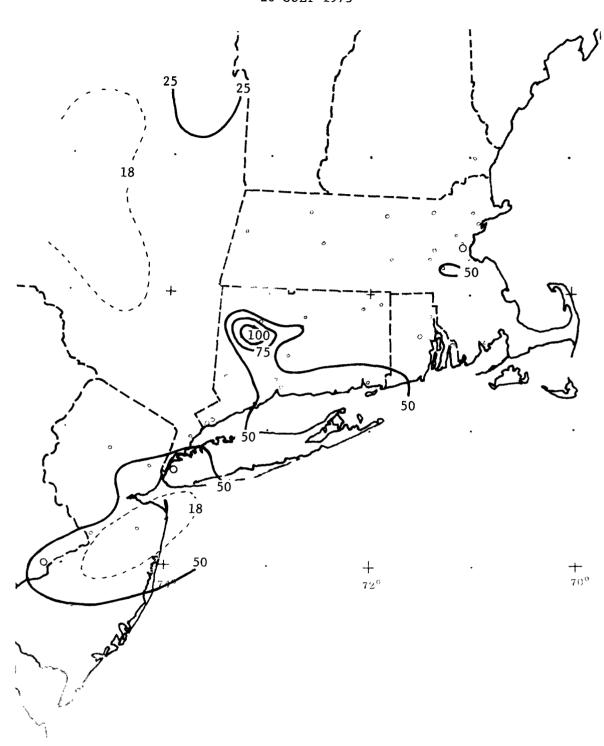


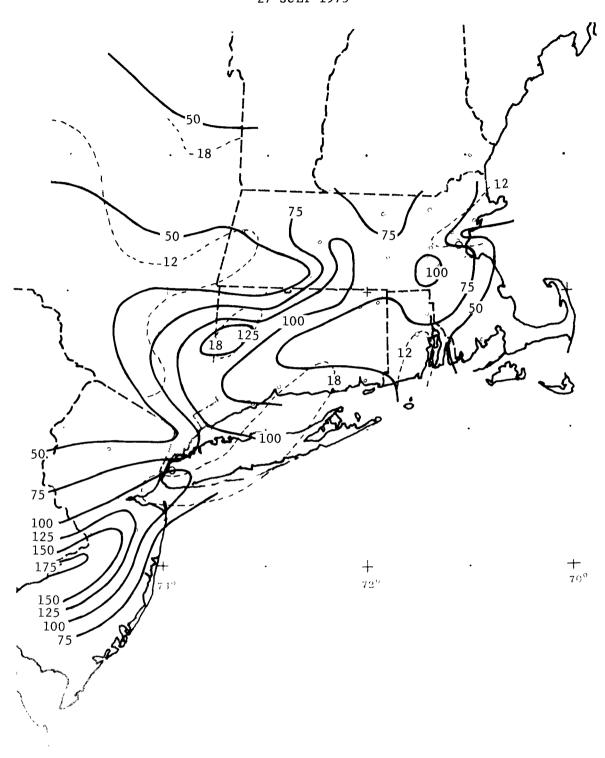


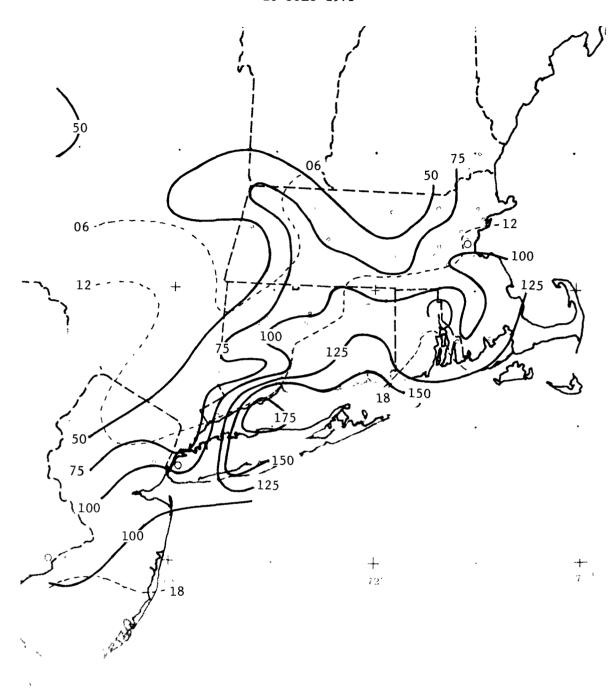


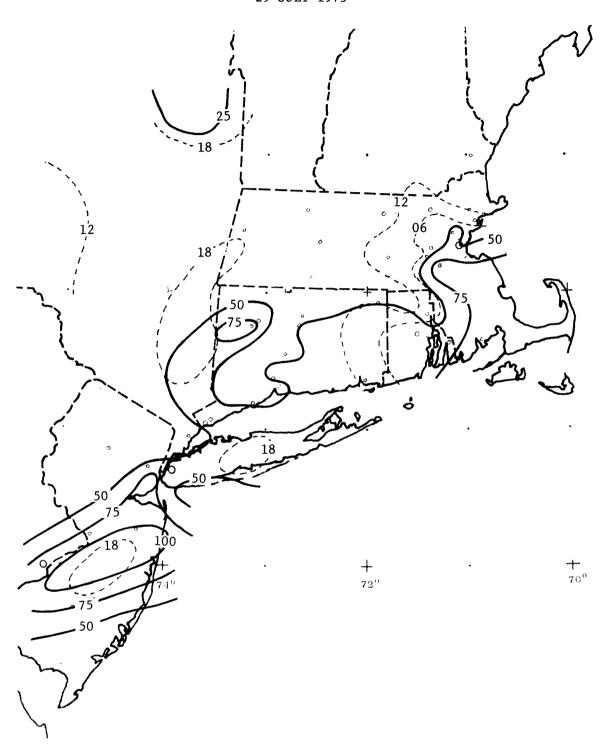


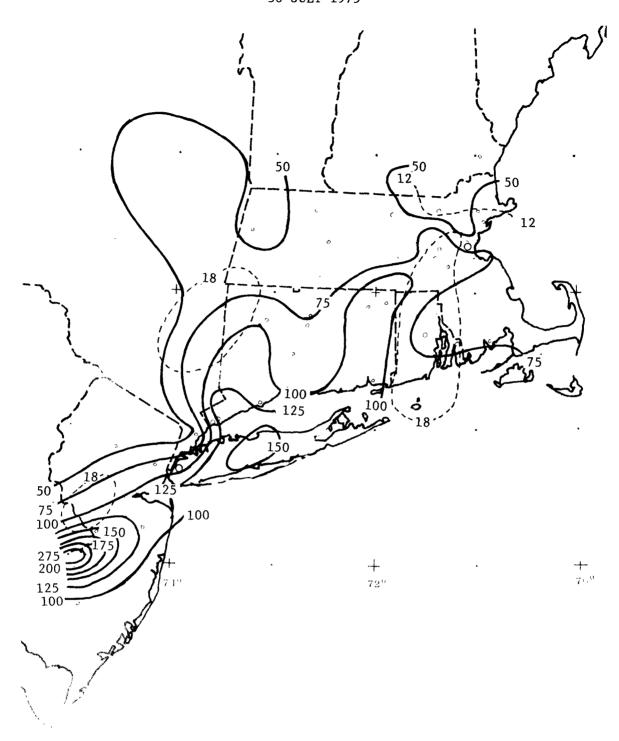


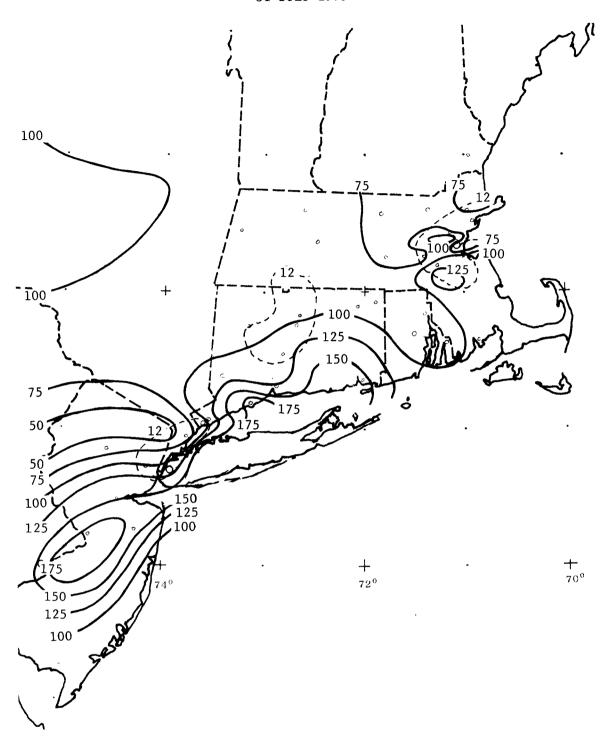


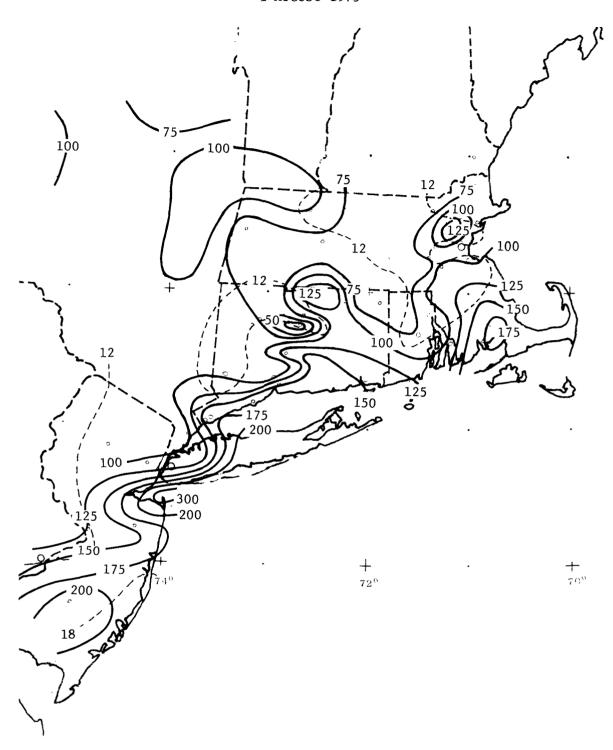


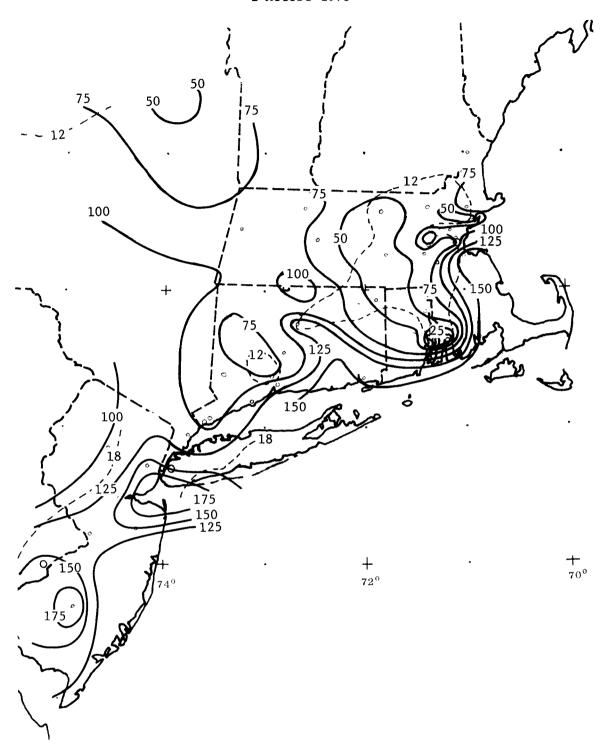


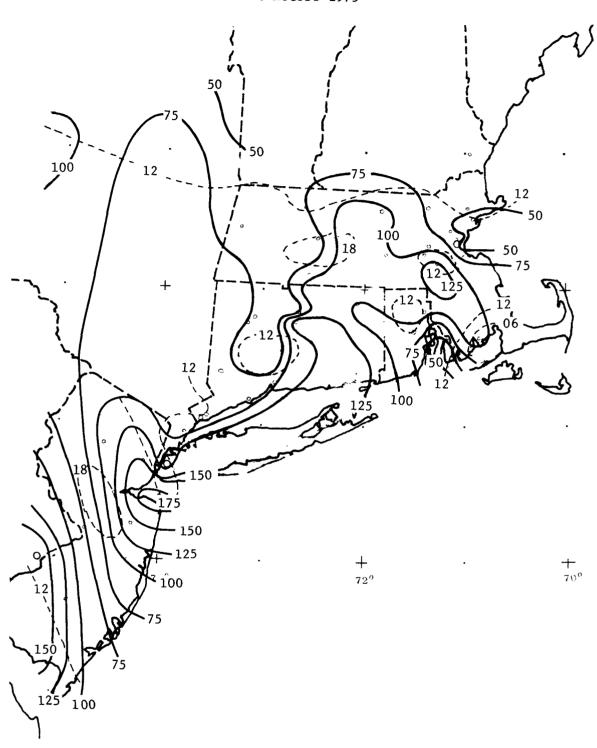


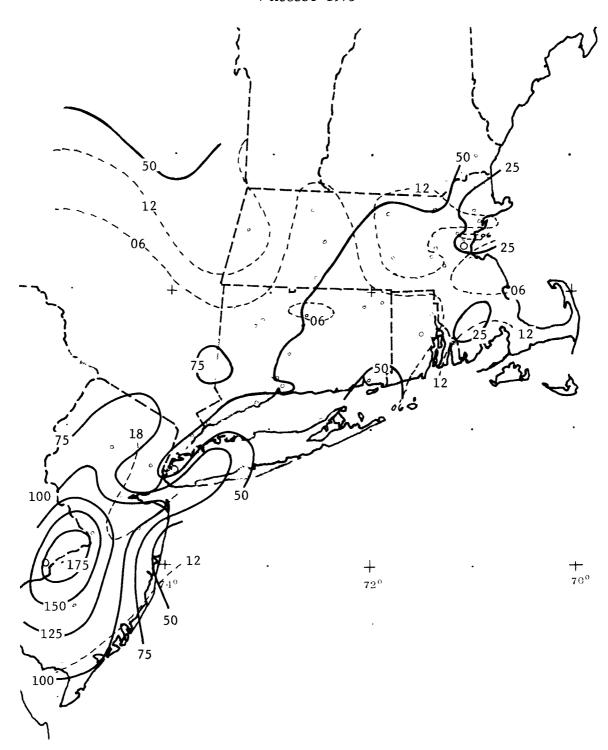


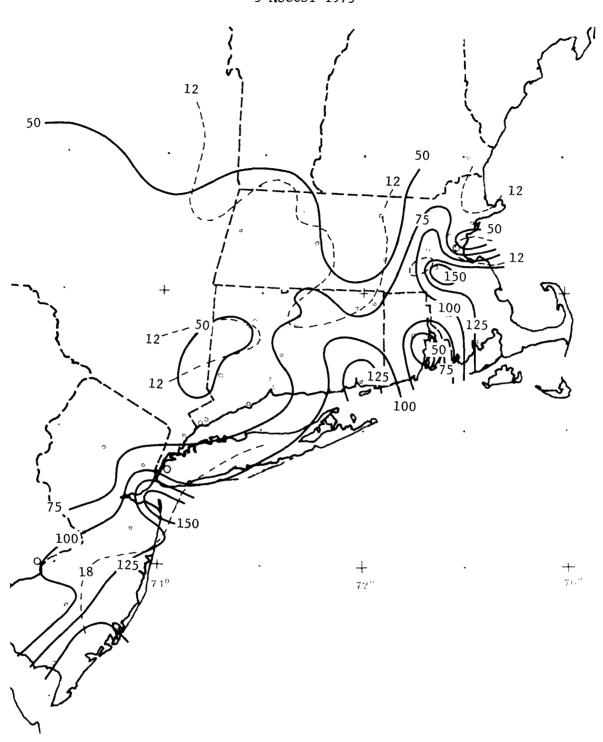


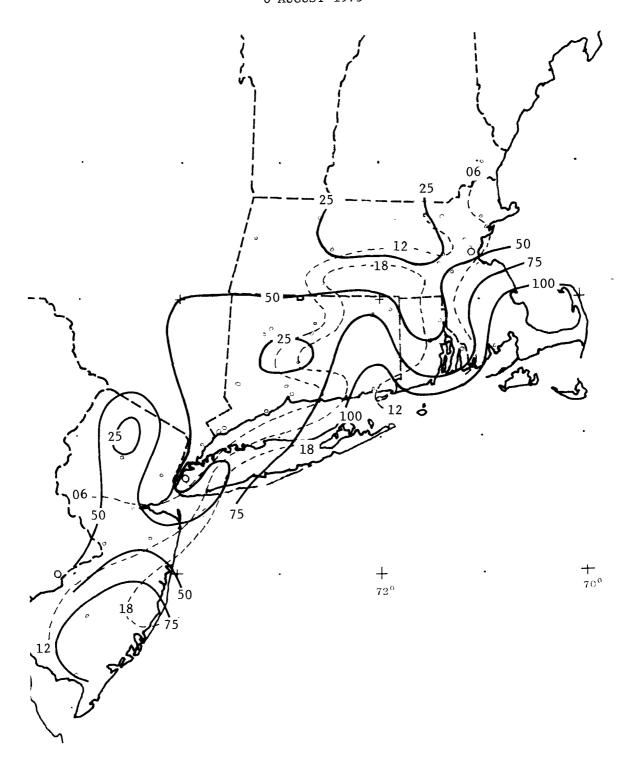


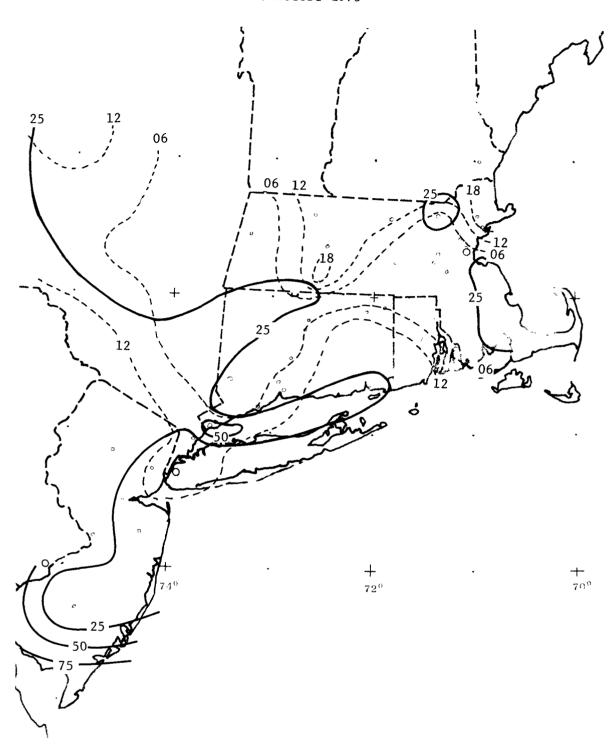


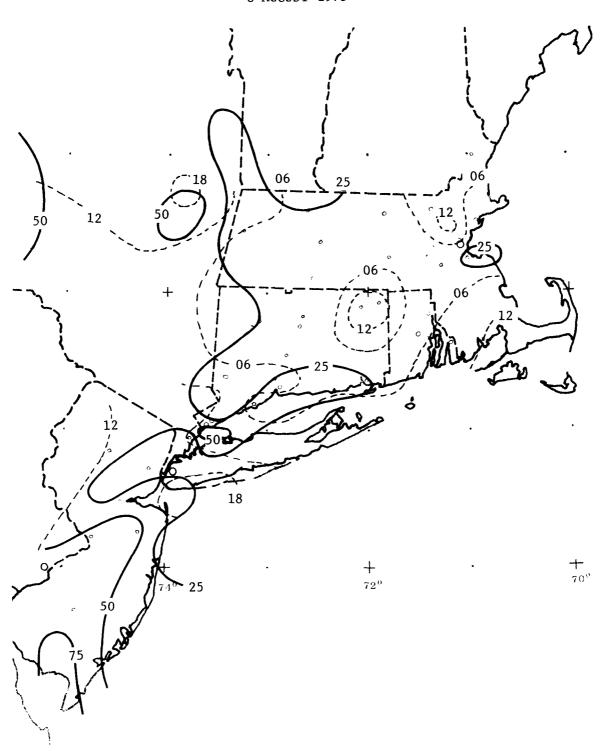


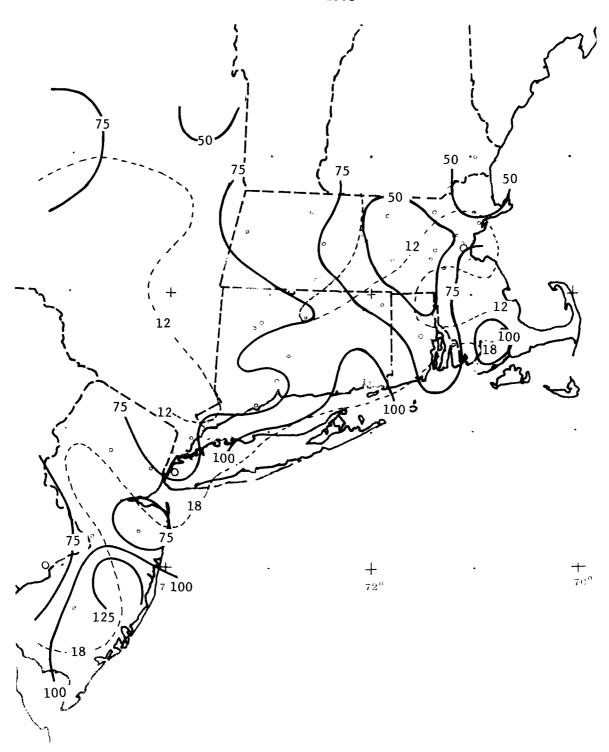


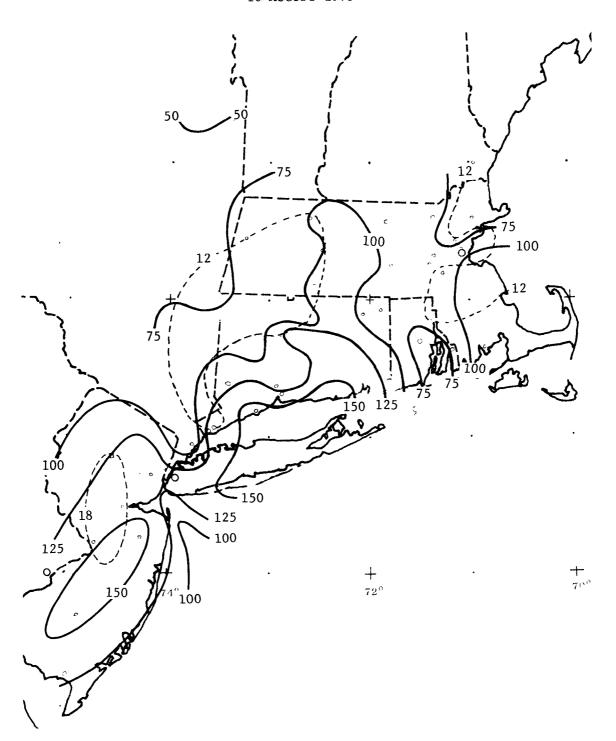


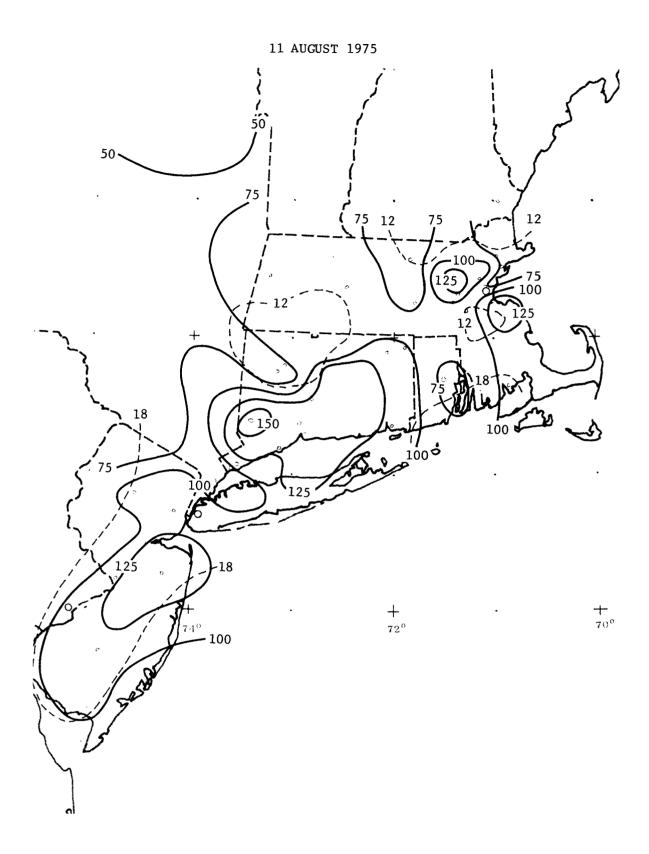


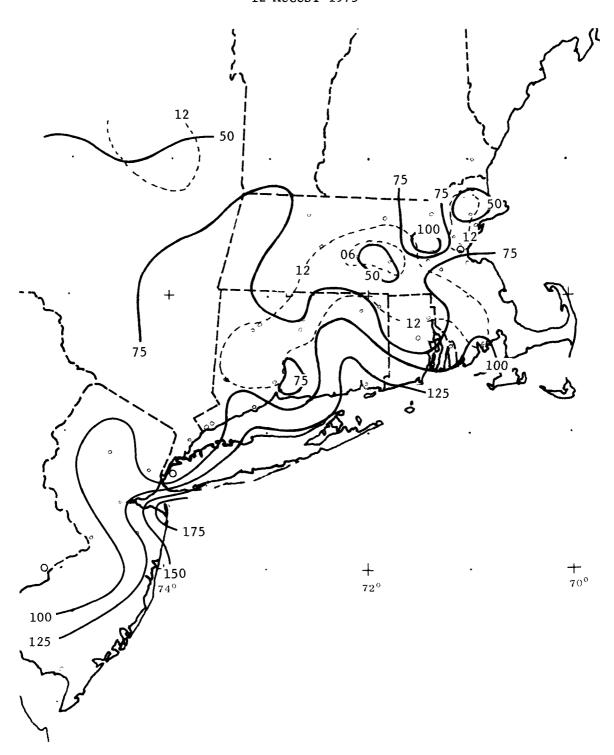


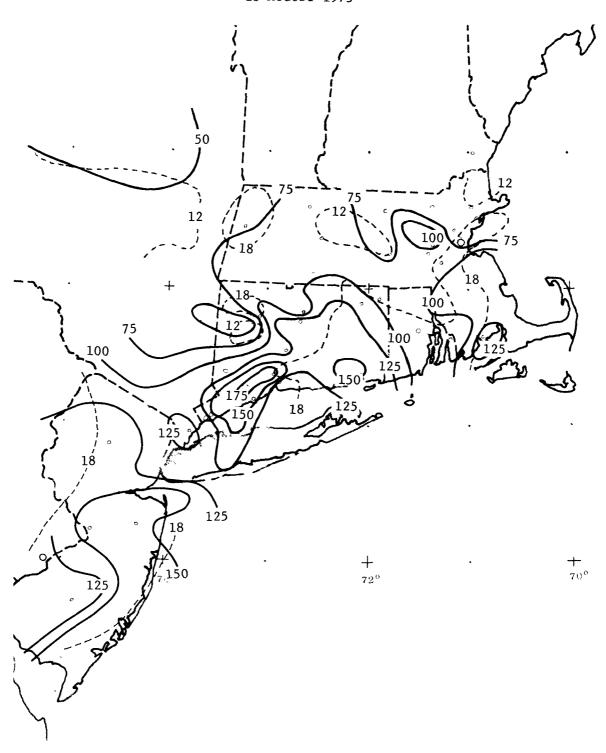


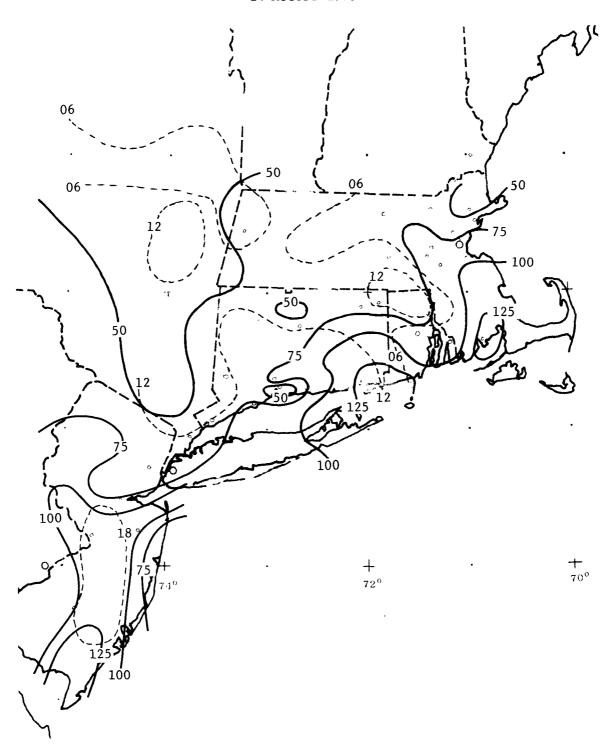


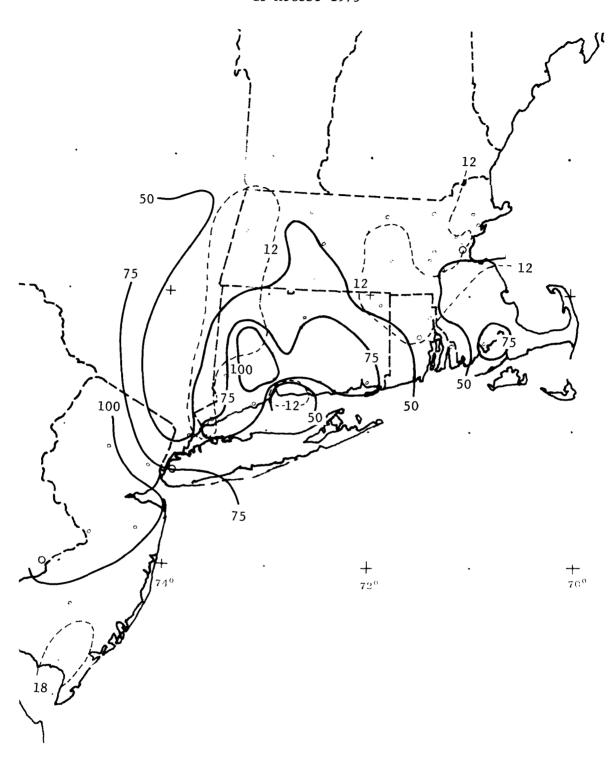


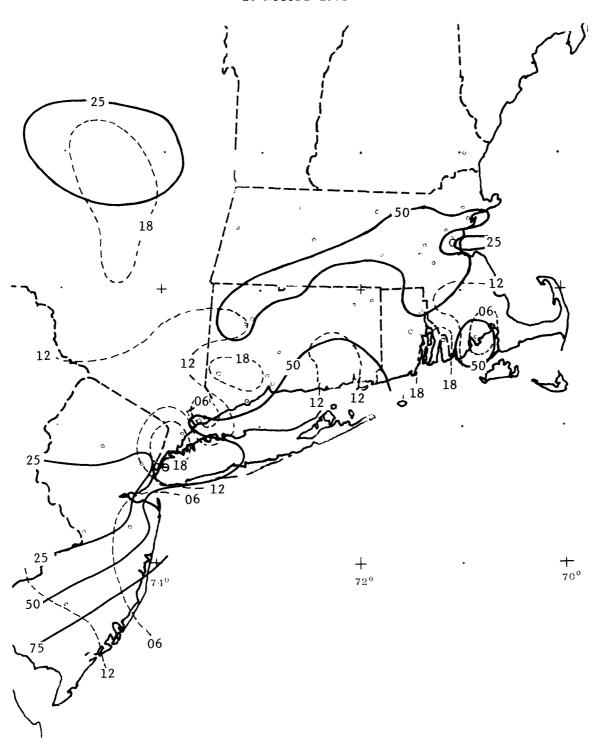


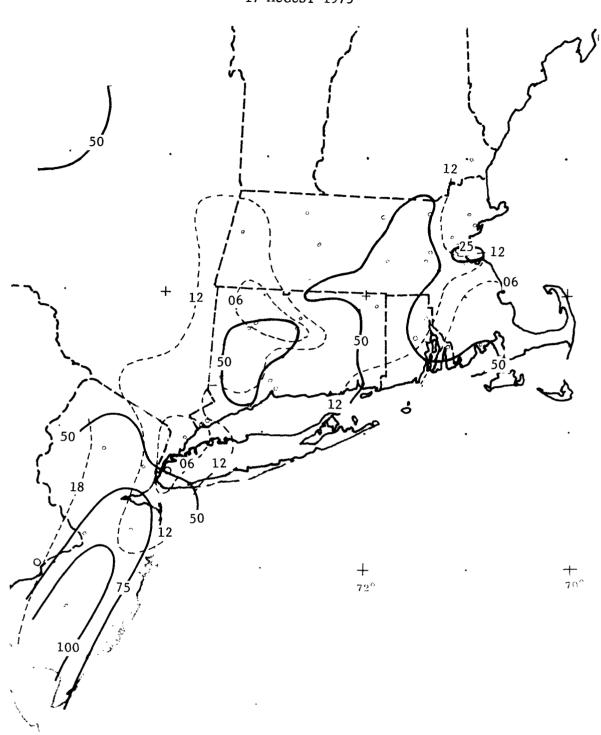


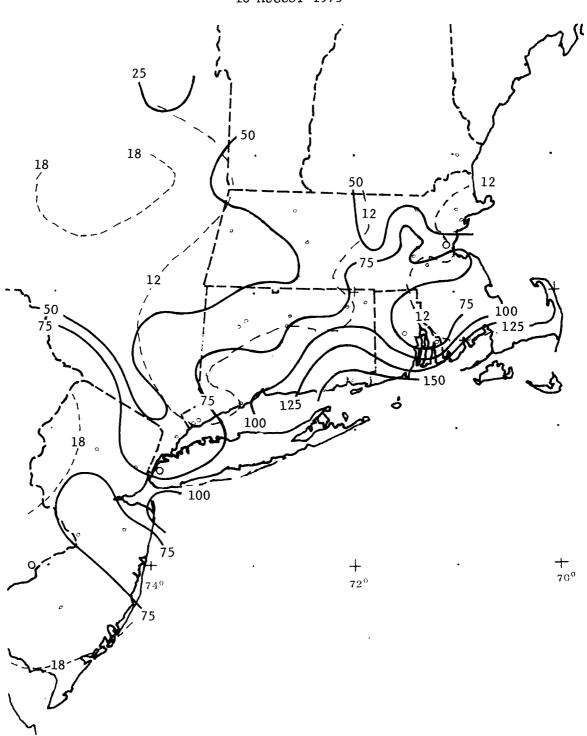


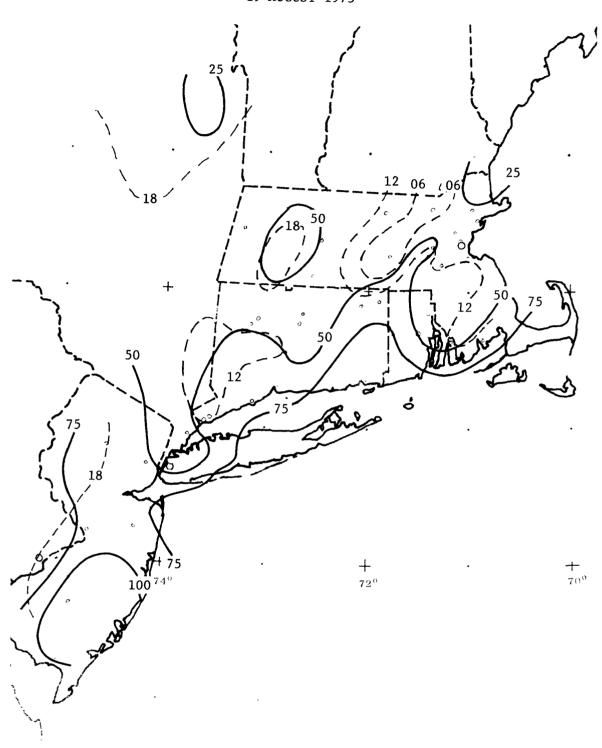


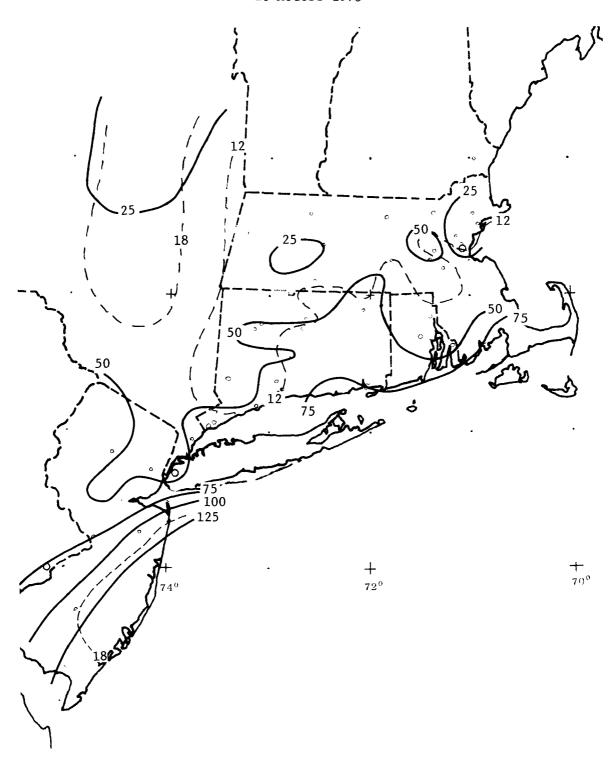


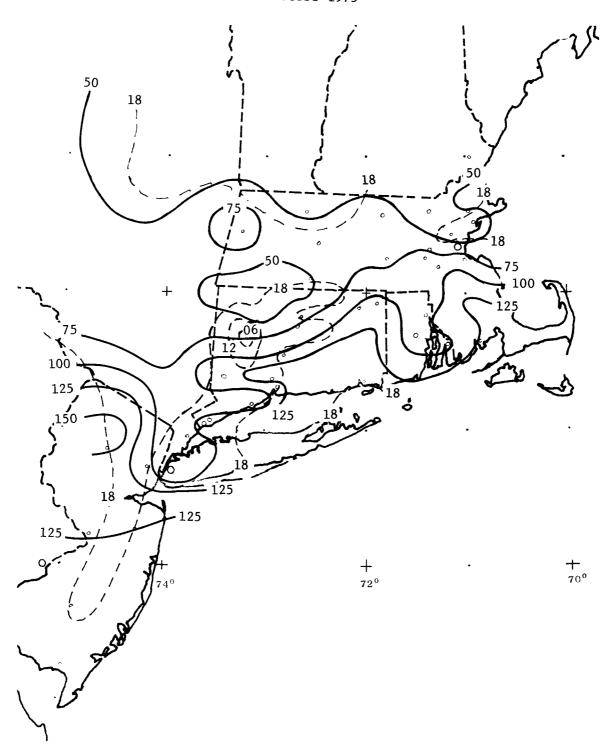


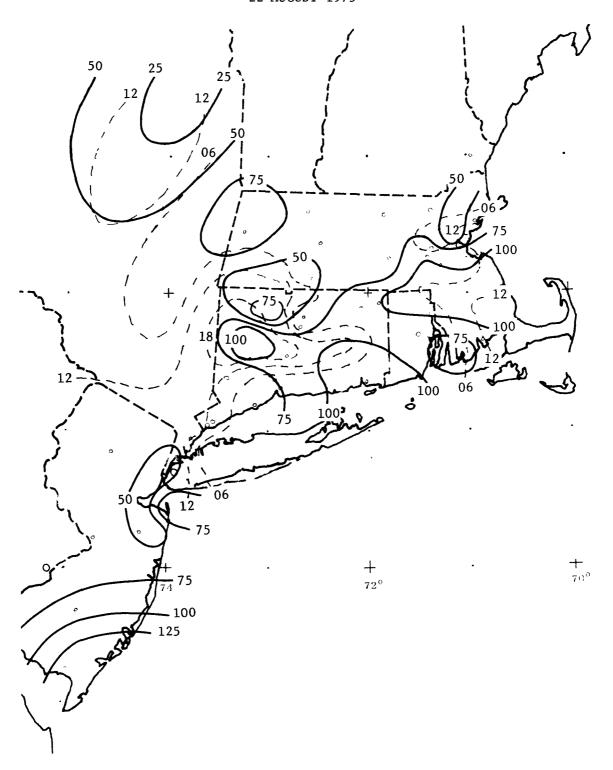


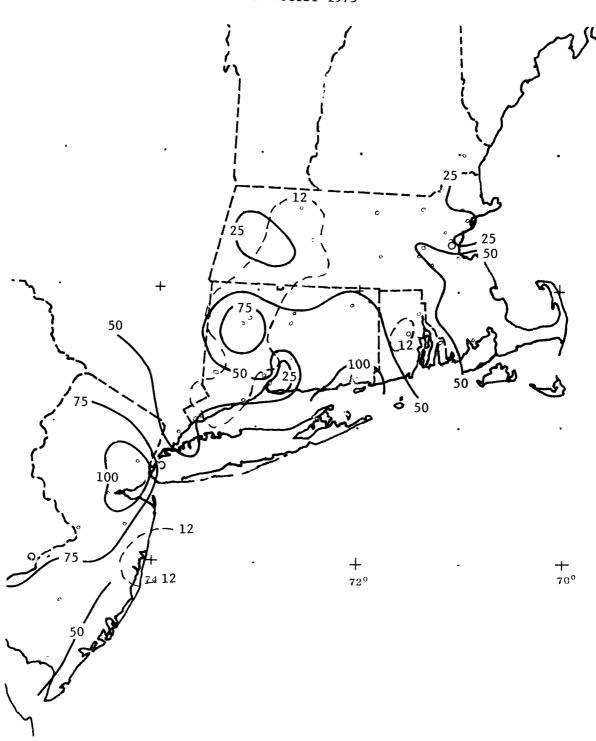


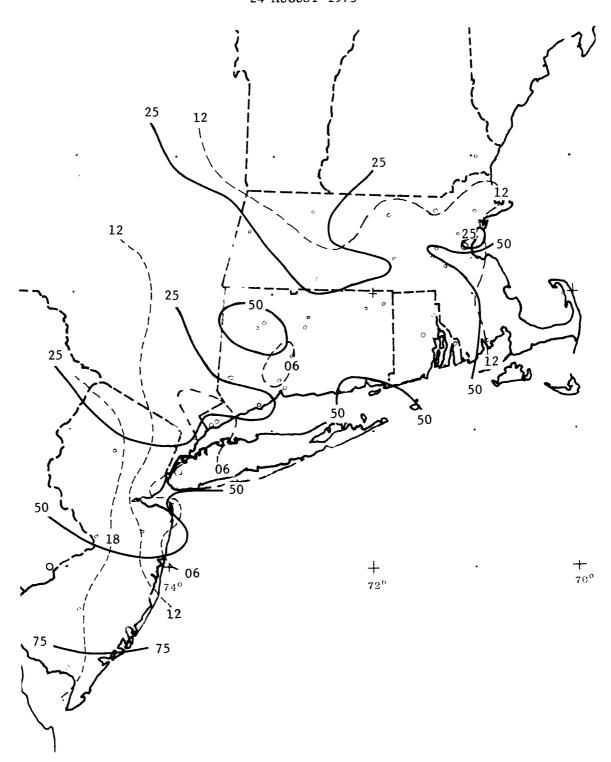


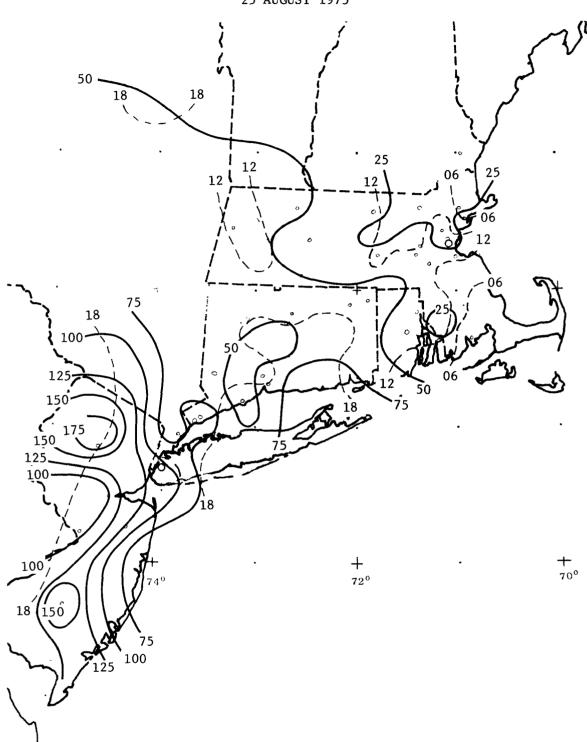


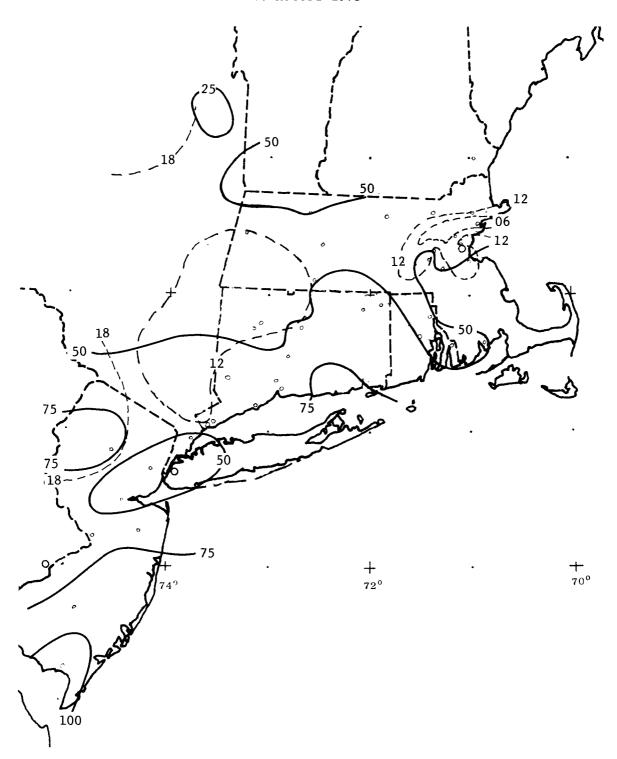


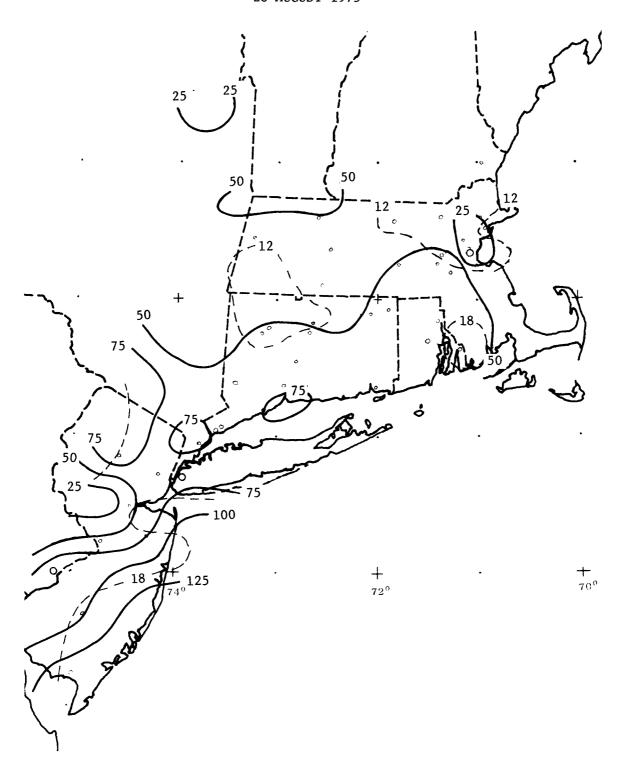


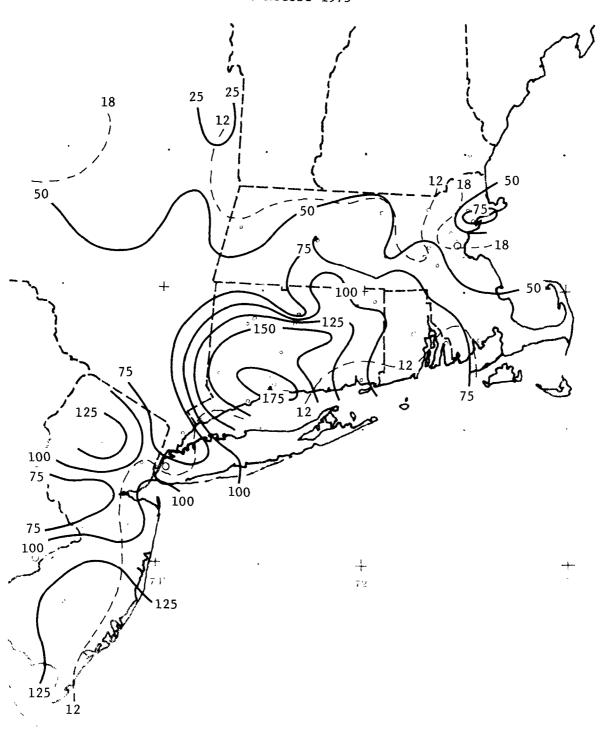


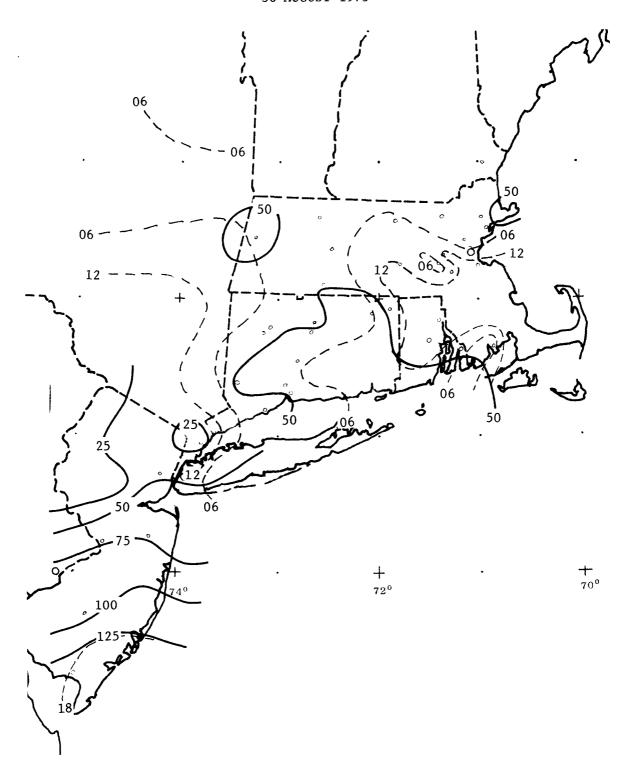


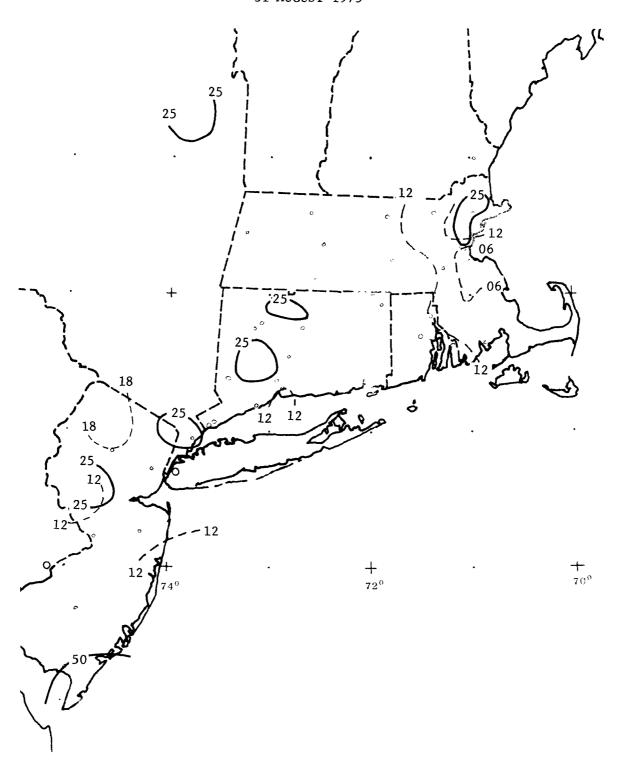








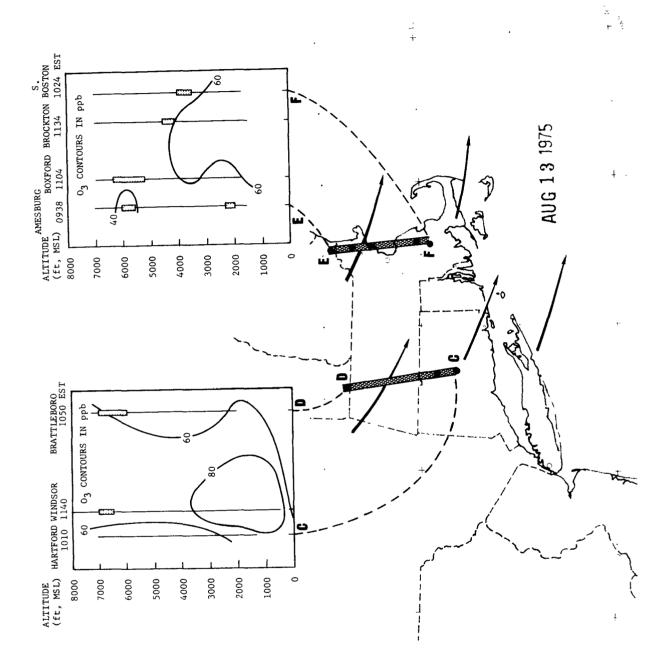


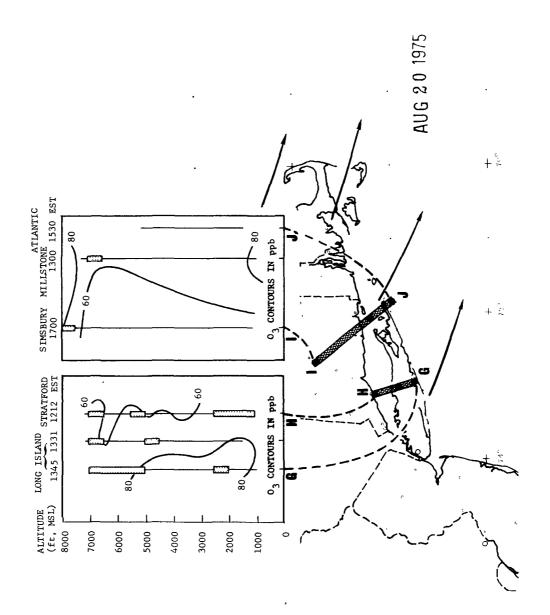


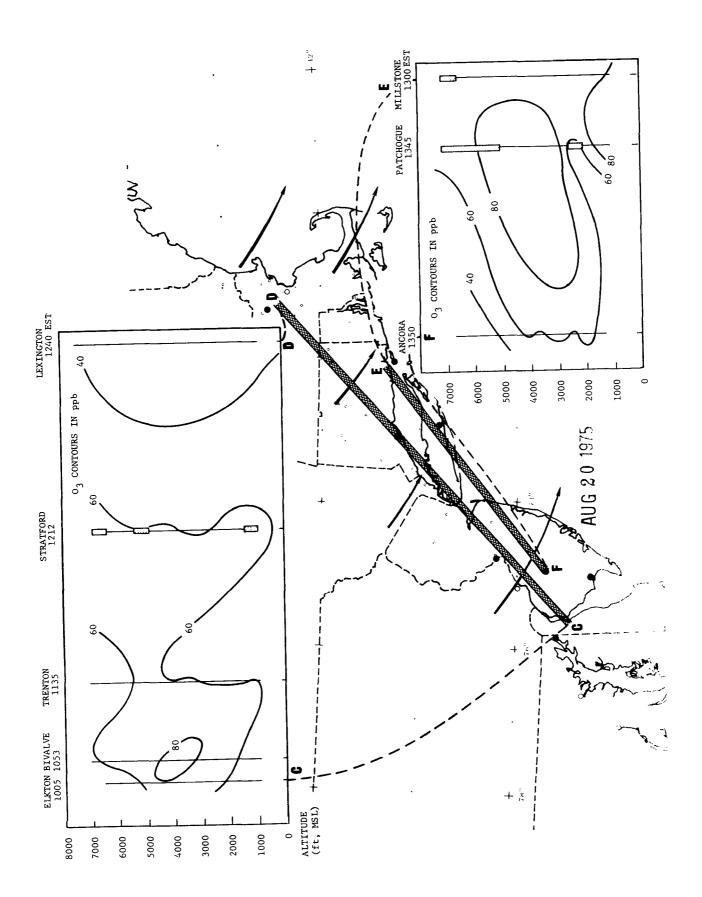
Appendix D

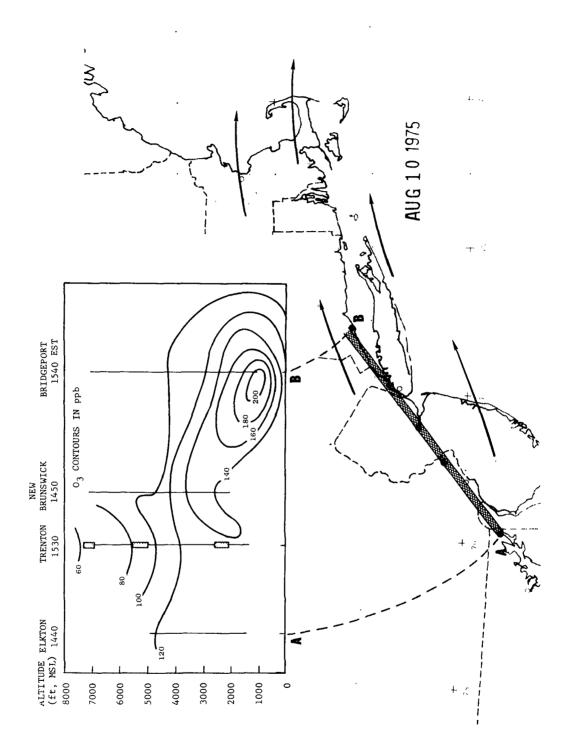
VERTICAL OZONE CROSS SECTIONS

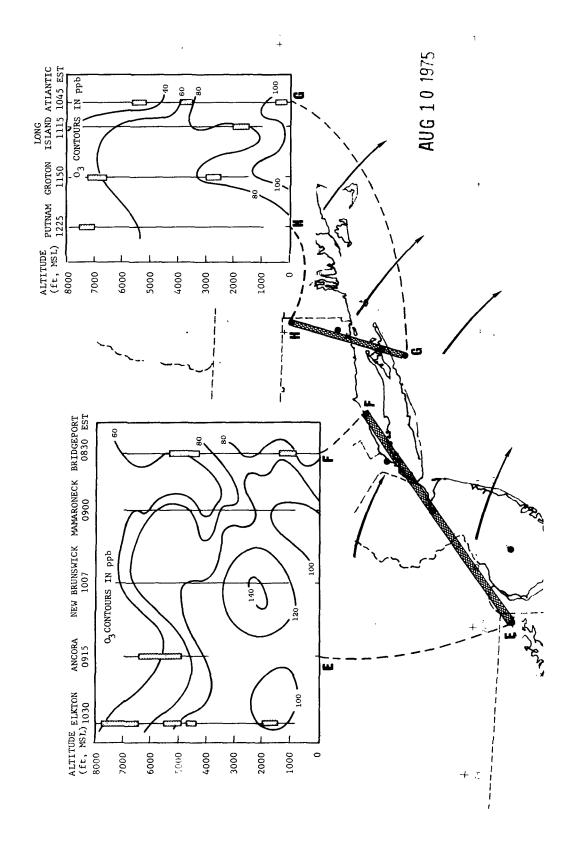
During the course of this investigation, numerous vertical cross sections of ozone concentration were prepared. Not all of these analyses were used in the discussions presented in the text of this report. This appendix reproduces those analyses not presented elsewhere. The symbols used are discussed in the text.

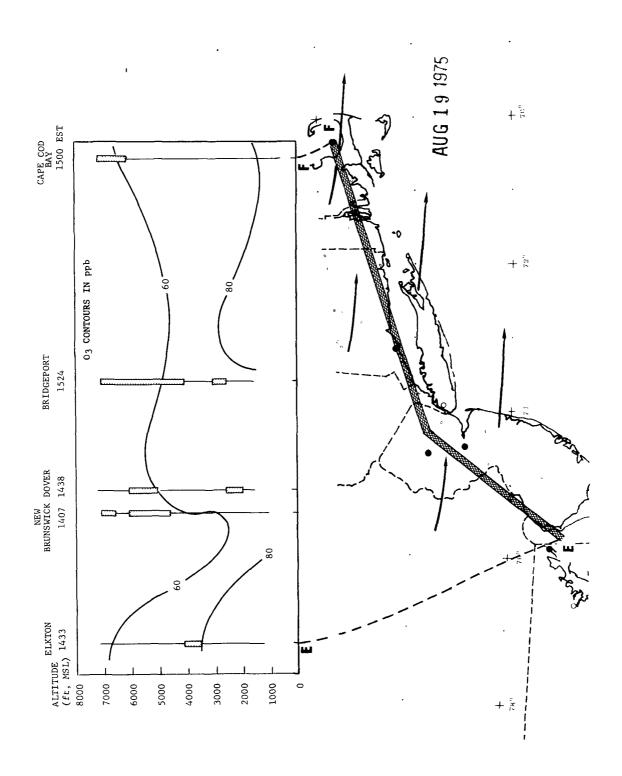


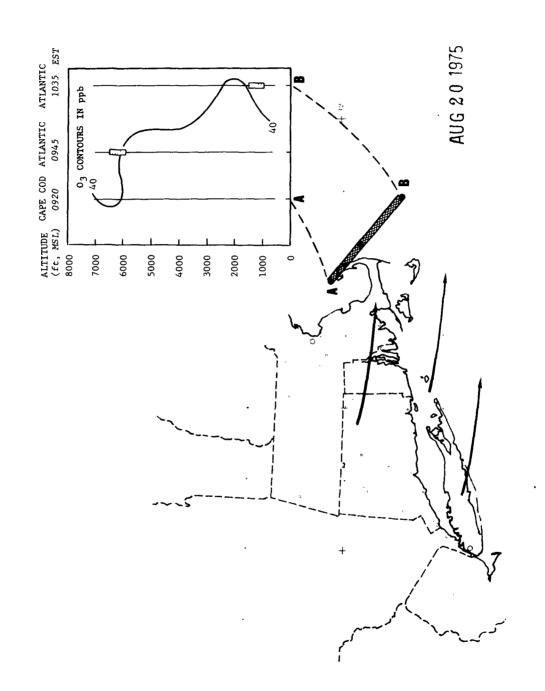


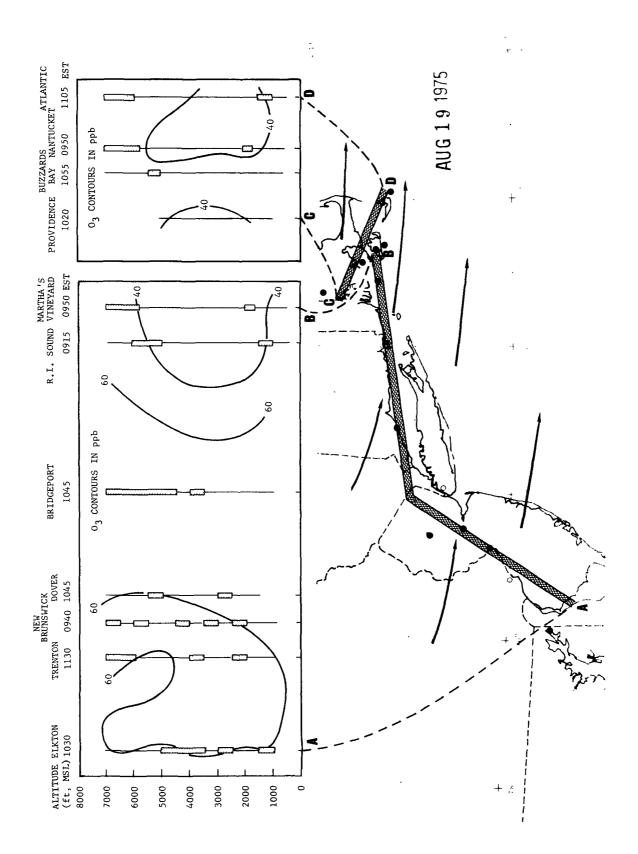


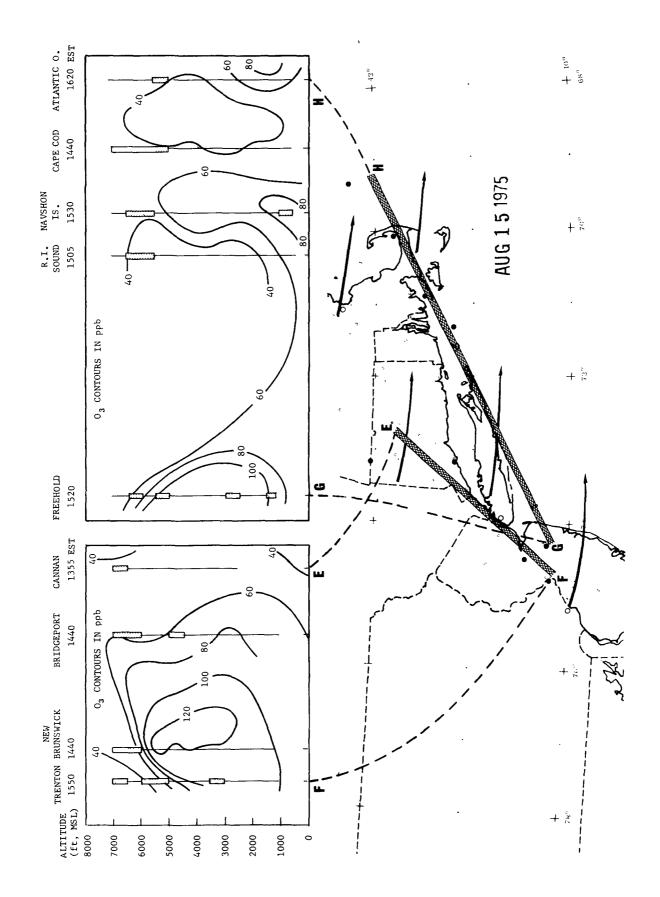


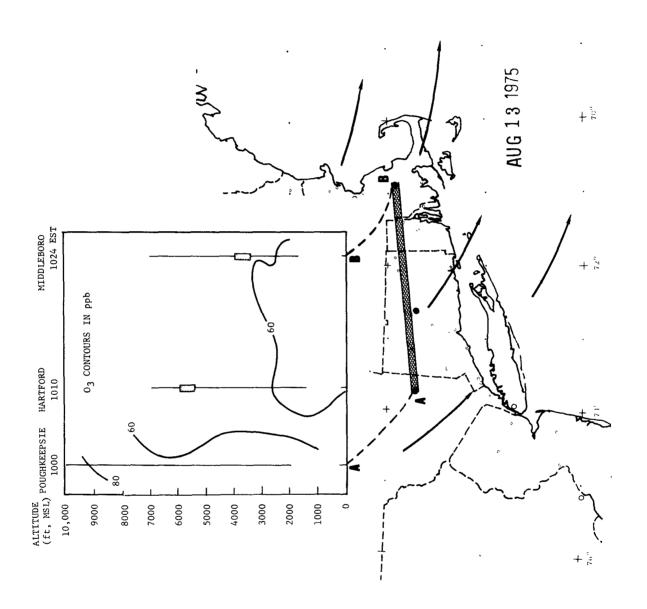


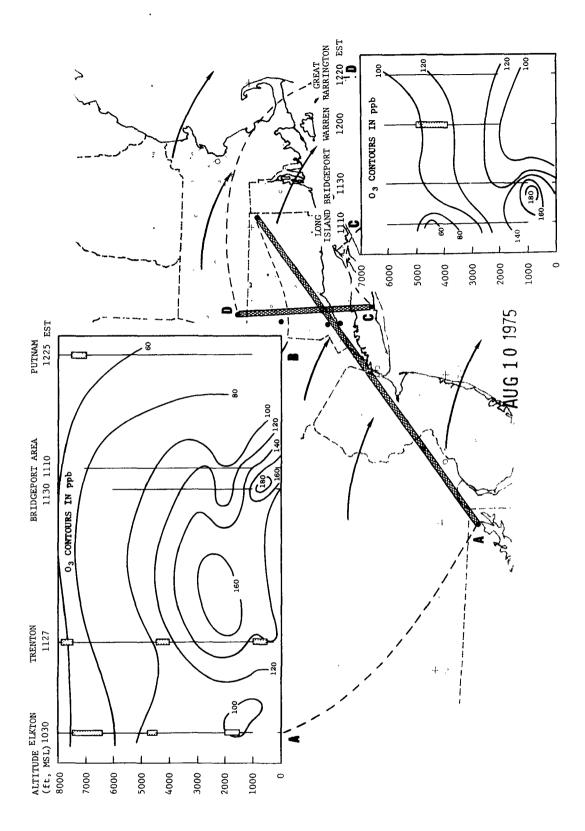


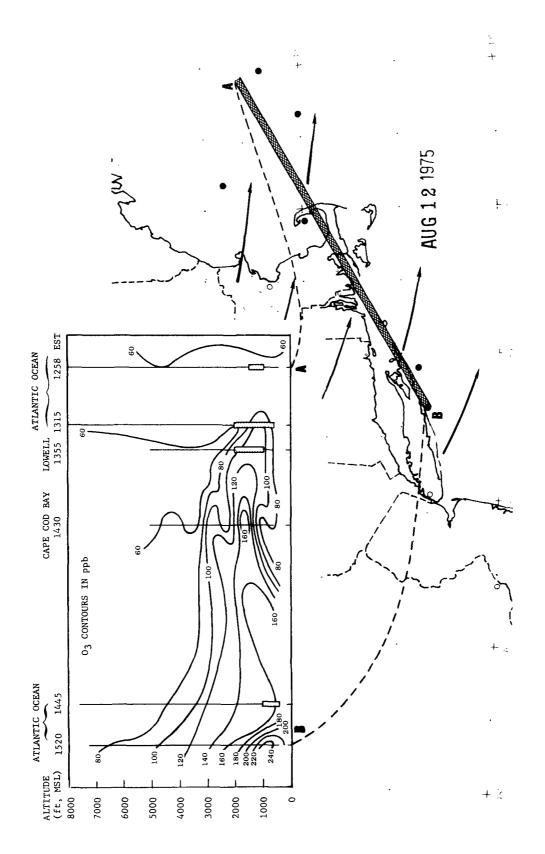


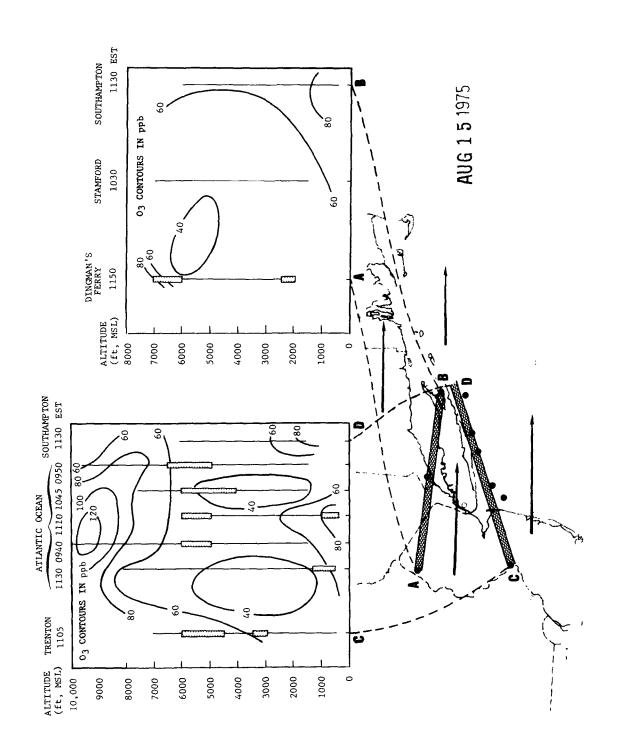


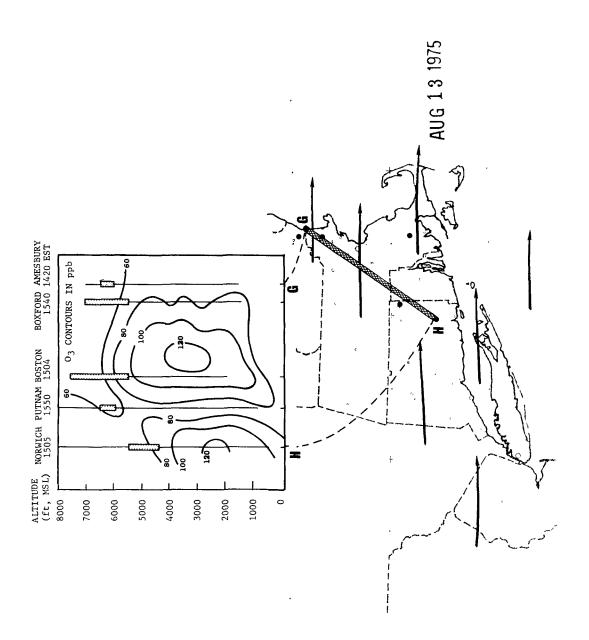


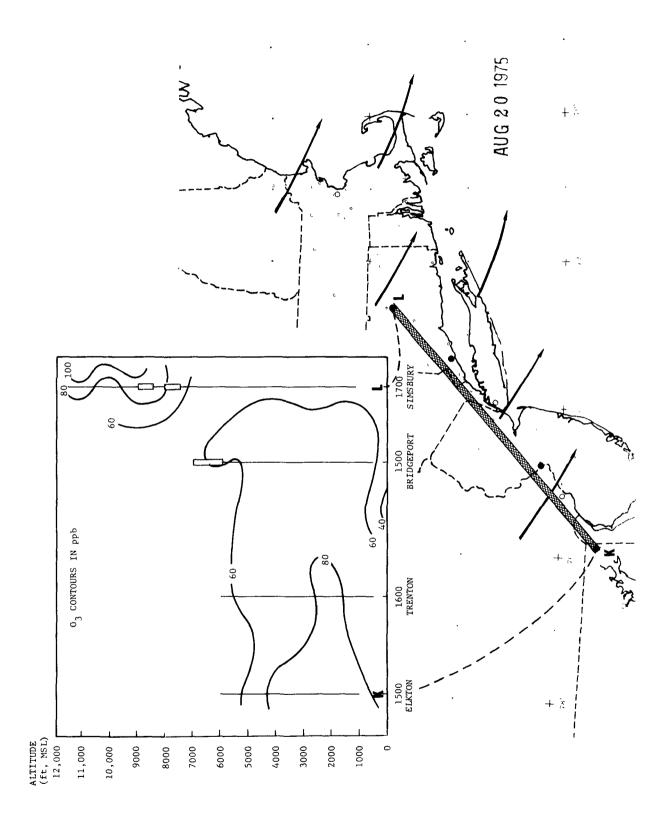


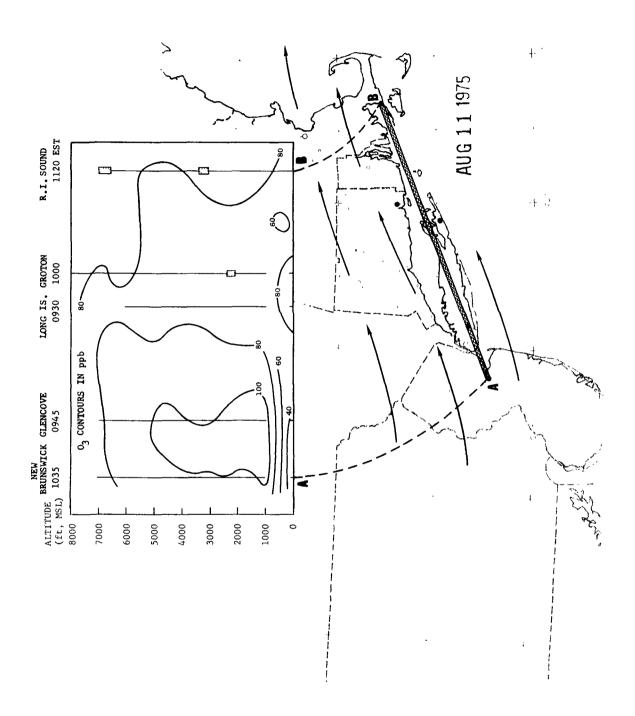


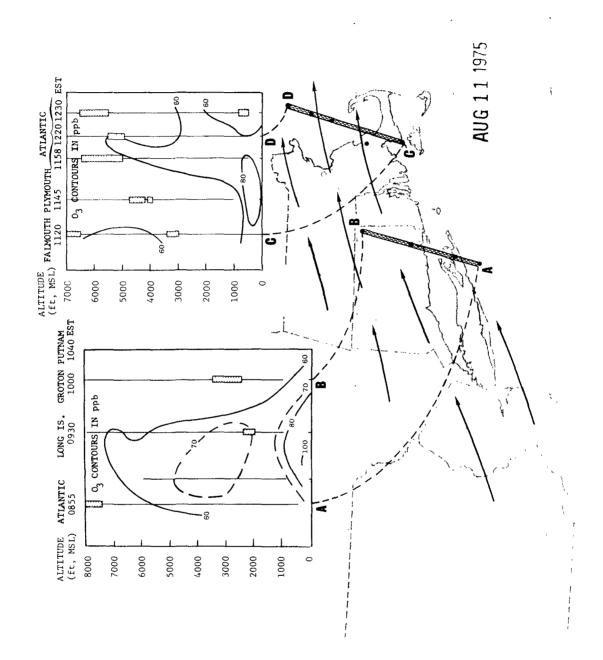


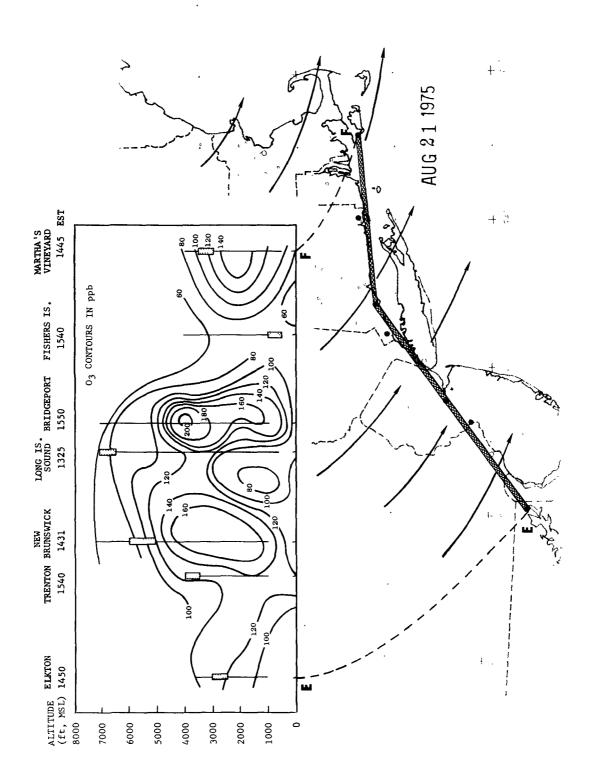


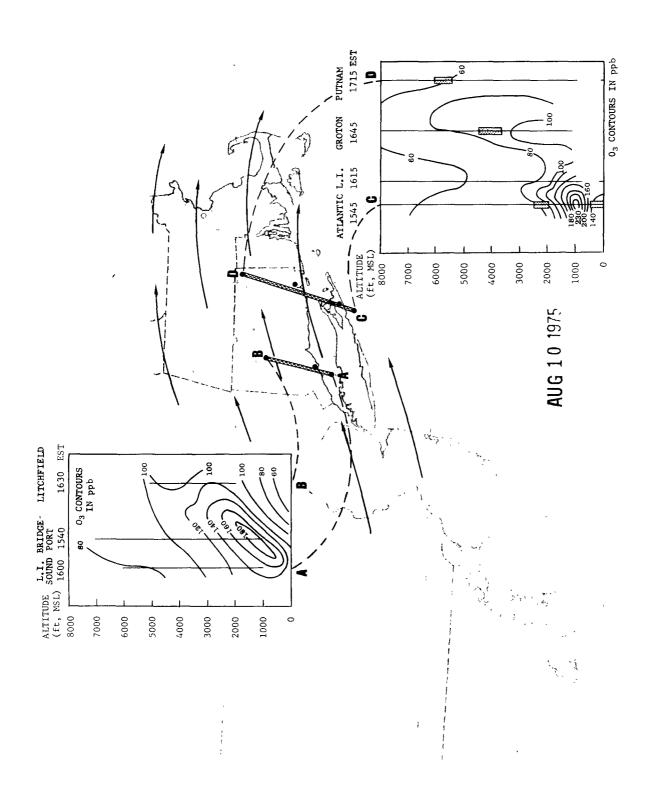


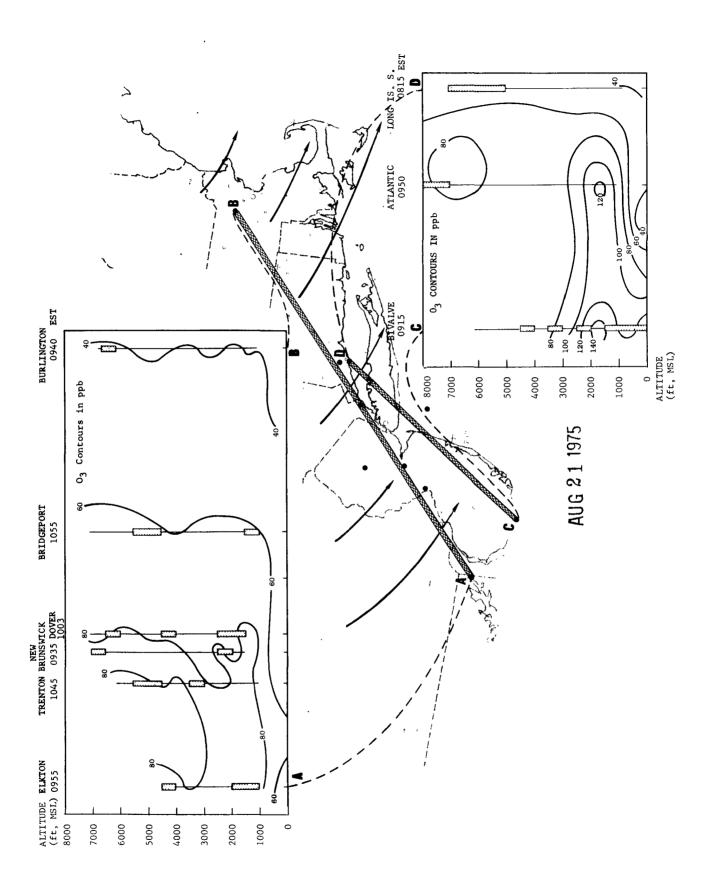












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15. SUPPLEMENTARY NOTES

16. ABSTRACT

The data from the summer 1975 Northeast Oxidant Study have been combined with routinely collected weather and pollutant data to demonstrate that oxidant and its precursors are transported for distances in excess of 100 km in the New York, New Jersey, and southern New England region. Vertical cross sections of ozone concentration clearly show urban ozone plumes. During a daytime passage of a weather front, strong ozone gradients are observed between the warm polluted air ahead of the front and the clearer, cooler air behind; at any fixed site, concentrations drop rapidly as the front passes and clean air replaces polluted. Nighttime frontal passages do not show the marked ozone gradients found during a daytime frontal passage. High nighttime ozone concentrations are associated with the simultaneous occurrence of unusual vertical mixing and an ozone layer aloft. The ozone layer aloft appears to be the remnant of daytime photochemical production in an urban plume.

17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS	b.identifiers/open ended terms	c. COSATI Field/Group	
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Atmospheric Transport			
Photochemistry			
Air Quality			
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