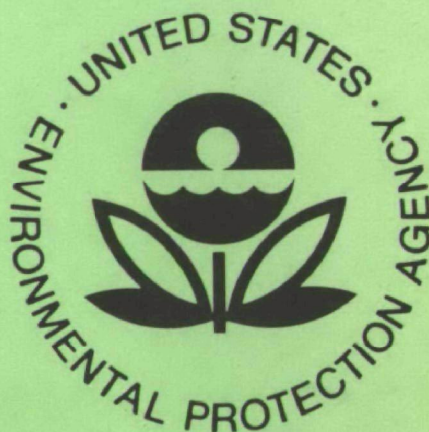


**EPA-600/3-77-041**  
**May 1977**

**Ecological Research Series**

**THE TRANSPORT OF OXIDANT BEYOND  
URBAN AREAS**  
**Data Analyses and Predictive  
Models for the Southern  
New England Study, 1975**



**Environmental Sciences Research Laboratory  
Office of Research and Development  
U.S. Environmental Protection Agency  
Research Triangle Park, North Carolina 27711**

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EPA-600/3-77-041  
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THE TRANSPORT OF OXIDANT BEYOND URBAN AREAS  
Data Analyses and Predictive Models for the Southern New England Study, 1975

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## ABSTRACT

The objective of this study has been to use data collected during the 1975 Northeast Oxidant Study to determine the cause of high ozone concentrations in the Connecticut River Valley and to develop a method for predicting ozone levels that can be expected in southern New England under various meteorological conditions.

During the summer months, the prevailing southwesterly winds place the valley directly downwind of the New York/New Jersey/southwestern Connecticut urban complex (and on some days the Philadelphia and Washington/Baltimore areas). The ozone formed from the urban emissions (i.e., the urban plume) was observed on many case study days to move into Connecticut from the southwest in early afternoon, cross the Connecticut River Valley, and continue into Massachusetts during the evening. In one case an  $O_3$ -rich air mass was tracked as far north as the coast of Maine. The dimensions of the urban plumes on several days were found to vary from 30-80 miles in width and 100-175 miles in length, seemingly depending on wind speed.

Several methods of predicting ozone in southern New England were investigated including regression integrals, simple regression and multiple regressions.

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## SECTION 1

### INTRODUCTION

In recent years elevated ozone concentrations have been observed in many rural areas which were previously thought to be relatively immune from the symptoms of photochemical smog. The finding of ozone in rural atmospheres, far from the generally accepted sources of photochemical smog precursors (i.e., urban areas), has very important implications in terms of the strategies devised to control smog formation. Since various strategies for the control of ozone may differ in efficiency, with some having important social and economic consequences, it is important that the strategies be conceived with a thorough understanding of the origins of both rural and urban ozone. A number of recent field investigations have dealt with the sources of ozone and the impact of ozone transport in the midwest<sup>(1-6)</sup>, and far west<sup>(7-9)</sup>. Results of these and other studies indicate transport of ozone and its precursors across regional boundaries is an important source of ozone in downwind rural and even urban areas. Analysis of data collected in the northeastern United States<sup>(10-13)</sup> suggested that transport of ozone into and within the northeast is a significant factor in determining peak oxidant concentrations in this area also.

To study these phenomena in the northeast, and continue its long-term investigations of ozone formation and movement, the EPA organized and funded the 1975 Northeast Oxidant Transport Study. The study involved the coordination and participation of a number of research groups including EPA-RTP (Research Triangle Park), EPA-LV (Las Vegas), EPA-Region I, Washington State University, Battelle-Columbus Laboratories, and the Interstate Sanitation Commission. A number of state and local air pollution agencies also provided invaluable data and assistance during the field study.

Descriptions of the study and preliminary data reports were published early in 1976 by the major study participants<sup>(14-20)</sup>. In addition, the proceedings of a symposium held in January, 1976, dealing with the preliminary results of the 1975 study will soon be published<sup>(21)</sup>. These reports should

be consulted for a detailed description of the study design and tabulations of the data.

Subsequent to the 1975 field investigation, contracts were awarded to Battelle-Columbus, Stanford Research Institute, and Washington State University to analyze selected portions of 1975 Northeast Oxidant Study data in an attempt to answer some of the important questions relating to ozone formation and transport.

The two topics to be addressed by Battelle-Columbus, and the subjects of this report, concern

- (1) The source of high ozone concentrations observed in the Connecticut River Valley, and
- (2) The development of a predictive model for ozone in southern New England.

The specific objectives of this study are defined below.

## OBJECTIVES

The investigation described in this report had two main objectives. The first objective was to determine the cause of the high ozone concentrations observed in the Connecticut River Valley. The second objective was to develop a method for predicting the ozone levels that can be expected in southern New England under various meteorological conditions. Some additional topics are discussed in this report since they are pertinent to the overall question of oxidant transport.

The question of high ozone levels in the Connecticut River Valley will be discussed first, followed by a description of the predictive model developed for the southern New England area.

## SECTION 2

### OZONE IN THE CONNECTICUT RIVER VALLEY

In recent years, high concentrations of ozone have been observed in the Connecticut River Valley<sup>(10,11)</sup>. The high ozone levels have frequently been found to occur at progressively later times from south to north up the valley, thus leading to speculation that polluted air masses might be channeled up the valley<sup>(22)</sup>. This and other possible explanations of Connecticut River Valley ozone will be discussed in this section of the report.

The effect of New York metropolitan area emissions on Connecticut ozone levels has been discussed by Cleveland, et al.<sup>(10)</sup> and Rubino, et al.<sup>(11)</sup>. Cleveland and coworkers compared maximum daily ozone concentrations measured during the summer of 1974 with wind directions on the same day. They report that the highest ozone levels at sites throughout Connecticut and Massachusetts occurred with wind directions from the New York metropolitan area. Sites as far away as Boston showed this effect. They also found that air entering the New York area frequently exceeded the federal oxidant standard, but that the New York area added substantially to the ozone/precursor burden of the air entering southern New England.

Rubino, et al.<sup>(11)</sup> describe a Connecticut ozone episode which occurred on June 10, 1974. They suggest "...the advective transport of  $O_3$  and  $O_3$  precursors into Connecticut from New York are probably responsible for a significant portion (approximately two-thirds) of the elevated  $O_3$  concentrations measured throughout Connecticut on days when winds are from the south-southwest direction".

It is evident from these two reports that polluted air moving into Connecticut from the southwest has a definite impact on Connecticut ozone levels. In the remainder of this section we will use data collected during the 1975 Northeast Oxidant Study to investigate the extent to which transport affects ozone levels in the Connecticut River Valley. Other possible causes of high ozone in the valley, such as channeling of polluted air up the valley and local generation of ozone within the valley will also be discussed. Our investigations have focused on seven specific days out of the approximately 38 days of data



collected during the main portion of the 1975 study. Preliminary screening of the chemical and meteorological data indicated that these seven days would be the most interesting and elucidating in terms of ozone in the Connecticut River Valley. The days selected for study include July 18, 19, 23, 24, and August 10, 13, and 21. These days include all of the important O<sub>3</sub> episode periods during the 1975 Northeast Oxidant Study; the air flow during some portion of each of these days was southwesterly to westerly.

A description of the Connecticut River Valley and its potential effect on local meteorology is instructive and is presented next. The remainder of this section is dedicated to a discussion of the individual study days.

#### AIRFLOW IN THE CONNECTICUT RIVER VALLEY

Terrain heights in Connecticut range from zero along the southern coastline adjoining Long Island to around 2000 feet in the northwest part of the state. The southwest quarter and most of the eastern half of the state have elevations between 300 and 1000 feet. The Connecticut River, which forms the border between New Hampshire and Vermont in northern New England flows south through Massachusetts and bisects the state of Connecticut. The Connecticut River Valley is the broad shallow depression formed by the flowing river over many thousands of years. The valley is narrower and deeper in northern Massachusetts and further north. From central Massachusetts south, however, the valley is broad and shallow to Long Island Sound. South of Hartford the river no longer flows within its historical valley, but has formed a new channel to the southeast. The original valley, which is the subject of this report, continues south-southeast from Hartford to New Haven.

On either side of the Connecticut portion of the river the hilltops are between 500 and 800 feet above the river. The difference in height between these hills and the base of the valley causes the hilltop areas to receive about four more inches of rain a year than the valley<sup>(23)</sup>. These higher rainfalls are due to increased convective activity and uplifting of moist air when easterly winds from the Atlantic Ocean blow against the hills on the west side of the valley. Terrain is also responsible for the lower rainfall received in the area northeast of Hartford<sup>(24)</sup>. This area is sheltered from the easterly winds by an intermediate range of hills and as a result experiences subsiding motion and lower rainfall. Thus the terrain along the Connecticut River Valley can cause local variations in vertical motion when winds blow across the valley.

A narrow and deep river valley can steer wind flows so that the upvalley and downvalley directions are clearly predominant. For example, winds at Albany, New York, during the Northeast Oxidant Study showed a high frequency of south directions paralleling the direction of flow up the Hudson River between the Taconic Range and the Catskill Mountains. Wind observations from East Hartford and from Bradley International Airport, which lie in the broad shallow northern Connecticut portion of the Connecticut River Valley, show only a slight increase in the frequency of winds from the south as opposed to other directions. Thus the effect of the Connecticut River Valley on wind direction was minimal. Any channeling was markedly less than at Albany during the same period. The possibility that a polluted air mass residing over Long Island Sound could be transported up the Connecticut River Valley to Hartford and further north by the afternoon sea breeze off the Sound can be discounted. While the sea breeze is an important feature of Connecticut's climate in the late spring and summer, it penetrates inland only 5 to 10 miles.

Two effects on wind are caused by friction with the surface. The wind speed at the ground is less than the speed above the surface where the retarding frictional force is smaller. Secondly the wind at the ground blows in a direction toward the left (in the Northern Hemisphere) of the direction of the upper wind. The gradient wind level, at which the ground's frictional effects become insignificant, will depend upon the roughness of the underlying surface, but will be on the order of 2000 feet. Comparison of the surface winds recorded by the National Weather Service and FAA observers at Bradley International Airport and at East Hartford with the pilot balloon soundings made at West Springfield, Mass., shows the effects of the Connecticut hills on the wind flow. Well-developed wind flows (wind speeds of 15 knots equal to 17 miles per hour) at 2000 feet above West Springfield were accompanied by winds of about one-third to two-thirds of this speed at the surface of the valley. Directions at the surface were about 20° to the left of those at 2000 feet.

Pilot balloon soundings routinely measure the wind at 325-meter (1000 feet) intervals. Above 1000 feet the wind should be capable of transporting pollution across southwest Connecticut with only limited blocking by the hills. The 1000-foot wind apparently provides a key for explaining pollutant transport into the northern Connecticut portion of the Connecticut River Valley. Table 1 lists surface wind observations made at Bradley International Airport

TABLE 1. COMPARISON OF SURFACE AND UPPER AIR WINDS IN THE CONNECTICUT RIVER VALLEY FOR SELECTED DAYS

Date	Time (EDT)	Upper Air				Surface			
		West Springfield, Mass -- 0900, 1200 and 1500 EDT Ft. Jolien, N.Y. -- 2000 EDT				Windsor Locks, Conn. -- Bradley Int'l Airport			
		1000 Feet		2000 Feet		Direction		Speed	
		Direction (degrees)	Speed (knots)	Direction (degrees)	Speed (knots)	Direction (degrees)	Speed (knots)	Direction (degrees)	Speed (knots)
July 18, 1975	1200	180	2	280	5	120	9	200	10
	1400								
	1500	180	13	190	11	190	12	190	7
	1700								
	2000	—*	—	—	—	170	9	190	6
July 23, 1975	0900	250	7	260	15	200	9	190	7
	1100								
	1500	210	13	220	17	220	11	220	10
	1700								
	2000	—	—	—	—	230	7	180	5
July 24, 1975	0900	230	13	240	22	210	10	220	9
	1100								
	1500	180	22	190	23	190	15	190	10
	1700								
	2000	200	32	200	30	190	13	180	14
Aug. 10, 1975	0900	290	9	320	18	200	5	210	8
	1100								
	1500	290	14	290	18	260	7	290	7
	1700								
	2000	—	—	—	—	240	6	230	5
Aug. 11, 1975	0900	310	9	310	17	200	5	210	5
	1100								
	1500	260	9	270	8	220	7	180	5
	1700								
	2000	210	12	270	11	210	7	160	5
Aug. 12, 1975	0900	340	5	340	17	310	7	350	10
	1100								
	1500	300	7	310	4	310	6	360	10
	1700								
	2000	000	0	330	12	300	5	320	8
Aug. 13, 1975	0900	240	4	80	6	70	3	000	0
	1100								
	1500	220	9	200	10	230	9	200	10
	1700								
	2000	MSG <sup>§</sup>	MSG	260	26	160	5	190	8
Aug. 21, 1975	0900	310	1	320	11	200	5	NA <sup>†</sup>	NA
	1100								
	1500	220	14	220	15	200	9	NA	NA
	1700								
	2000	230	23	230	26	200	8	NA	NA

\* — = No sounding made.

<sup>§</sup>MSG = Data missing.

<sup>†</sup>NA = Data not available for this report.

and at East Hartford at times within 2 hours of the launch times of pilot balloons at West Springfield, Massachusetts, and at Fort Totten, New York. West Springfield balloons were generally launched at 0900 and 1500 EDT. Fort Totten generally also made a wind sounding at 2000 EDT, so its sounding is included in Table 1 to augment the evening data at West Springfield. From this table several observations can be made about wind flow during the Northeast Oxidant Study.

(1) When the 1000-foot wind at Springfield is 10 knots (11.5 mph) or more, the surface winds in Hartford will reflect the direction of the upper winds, although the surface wind direction may be as much as 30° to the left of the direction at 1000 feet. The surface winds will also be somewhat slower than the upper winds. Such a coupling of surface and upper winds is an important consideration in pollutant transport.

(2) If the Springfield wind at 1000 feet is less than 10 knots, the winds in the Hartford area may show little resemblance to the upper air winds. Even the wind directions at Bradley Airport and at East Hartford may disagree. When the 1000 foot wind speed exceeded 10 knots, the wind direction at Bradley Airport and at East Hartford was always similar.

(3) Generally the afternoon (1500 EDT) winds in the valley and at 1000 feet were organized (i.e., the speed at 1000 feet was greater than 10 knots). This results from the establishment of momentum exchange between the upper air and the surface. This exchange is missing during the more stable atmospheric conditions in early morning and night. When the surface and upper winds are organized, general air movement across the state results. This condition is well suited to pollutant transport.

In terms of pollutant transport across Connecticut, the foregoing discussion leads to several general conclusions:

The topography and the wind data suggest that channeling of polluted air up the Connecticut River Valley is unlikely. If the wind speed in the Connecticut River Valley is greater than 10 knots, winds are organized and transport of pollution is likely. With a persistent southwest wind of 10 knots the emissions from metropolitan New York can reach central Connecticut in about 8 to 10 hours. Obviously, wind speeds in excess of 10 knots can result in even more rapid pollution transport.

The remainder of this section of the report will be devoted to discussions of the 7 days selected for detailed analysis.

JULY 18, 1975

July 18, 1975, was a hot, humid, hazy day in the Connecticut River Valley. A high pressure ridge began to build over New England during the day and a weak upper level subsidence set in. Wind flow below 5000 feet was from the Southwest throughout most of the region. Figures A-1 and A-2 in Appendix A show calculated air mass trajectories\* for Simsbury and Groton, Connecticut,\*\* for several hours during this day. A description of the techniques used to derive these trajectories may be found elsewhere<sup>(25)</sup>. A discussion on interpretation of the trajectories is included in Appendix A. It is clear from the trajectories that the flow throughout the day was from the southwest. The air arriving at Groton during the daylight hours had generally passed over the northern New Jersey-New York City area within the previous 5-7 hours. The air arriving at Simsbury passed well to the north of the New York metropolitan area during most of the day, but by evening air arriving at Simsbury had passed very near the urban boundaries.

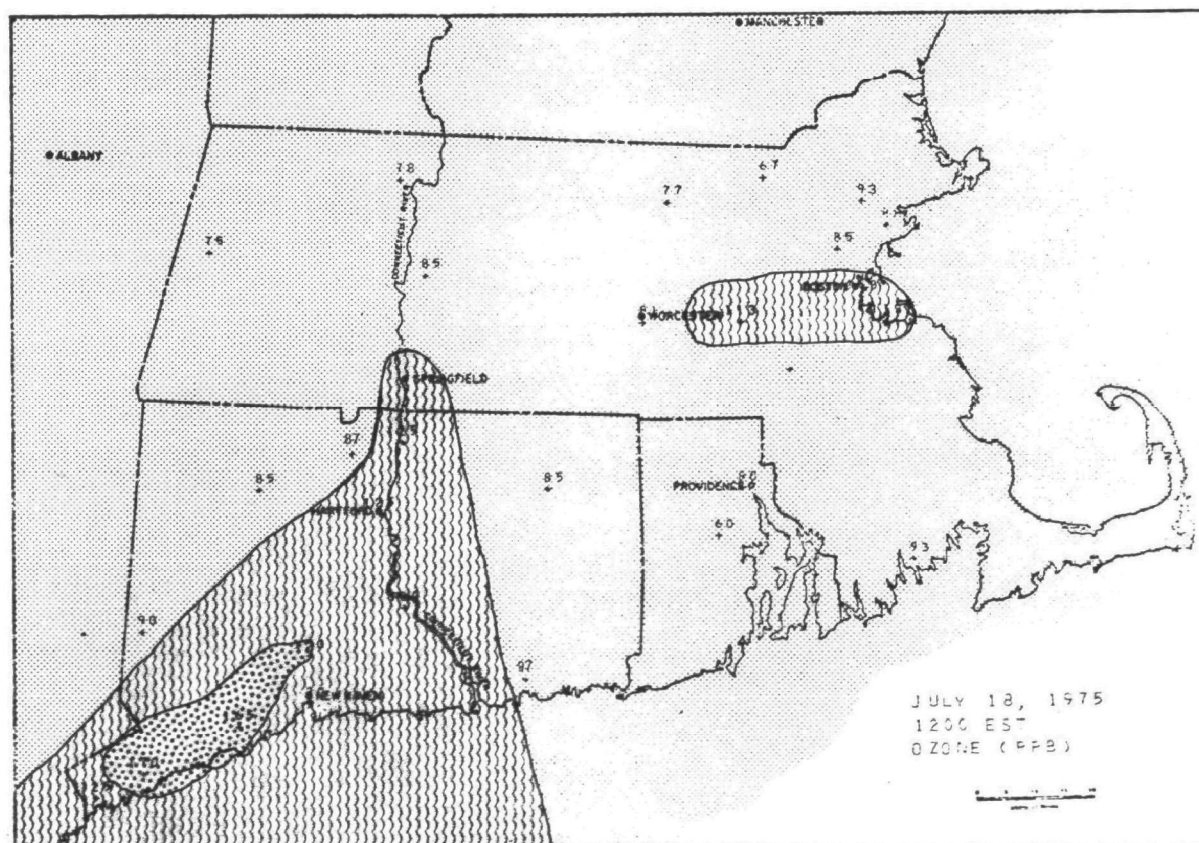
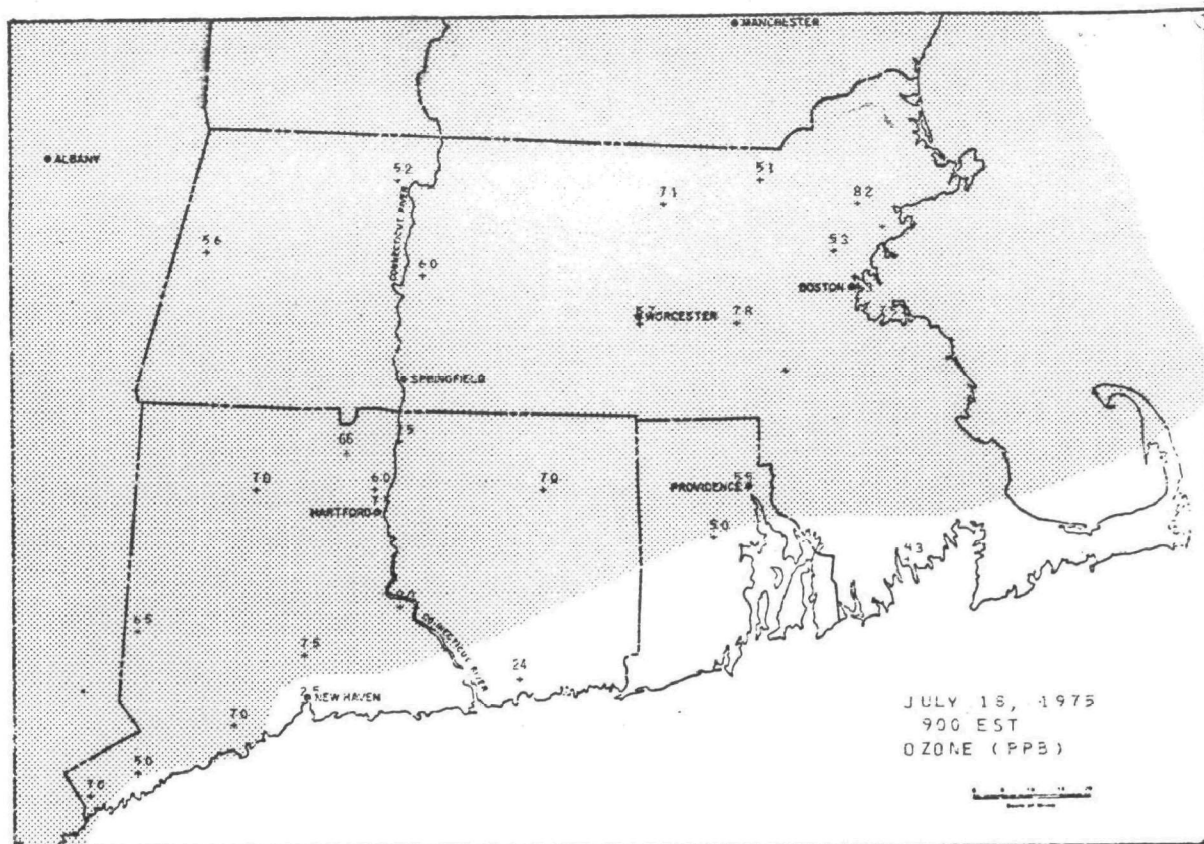
In order to discuss the origin of high ozone within the Connecticut River Valley, we have derived maps which display the ozone distribution throughout southern New England. The maps for July 18 are shown in Figure 1 a-c. The ozone data shown by these maps are primarily from the more than 30 ground-level monitoring stations in Connecticut, Massachusetts, and Rhode Island. The data from these stations are shown in the maps in ppb. Where available, aircraft ozone data have been used to fill in questionable portions of the maps. Since the aircraft data were taken at 1000 feet above ground, there is a risk of inconsistency; to minimize this risk we have generally used aircraft data taken over nonurban areas. Ozone data from New York State has also been used in deriving the maps when the ozone patterns in the western portion of the region were unresolved.

---

\*Trajectories courtesy of Stanford Research Institute.

\*\*Simsbury and Groton were two of the special study sites during the Northeast Oxidant Study. Approximately 38 days of continuous chemical and meteorological data were collected at these sites by heavily instrumented mobile laboratories.





#### Density

- 0-50 ppb
- ▤ 50-100 ppb
- ▥ 100-150 ppb
- ▧ 150-200 ppb
- ▨ 200-250 ppb
- ▩ 250-300 ppb
- > 300 ppb

Figure 1a. Ozone distribution in southern New England on July 18, 1975.

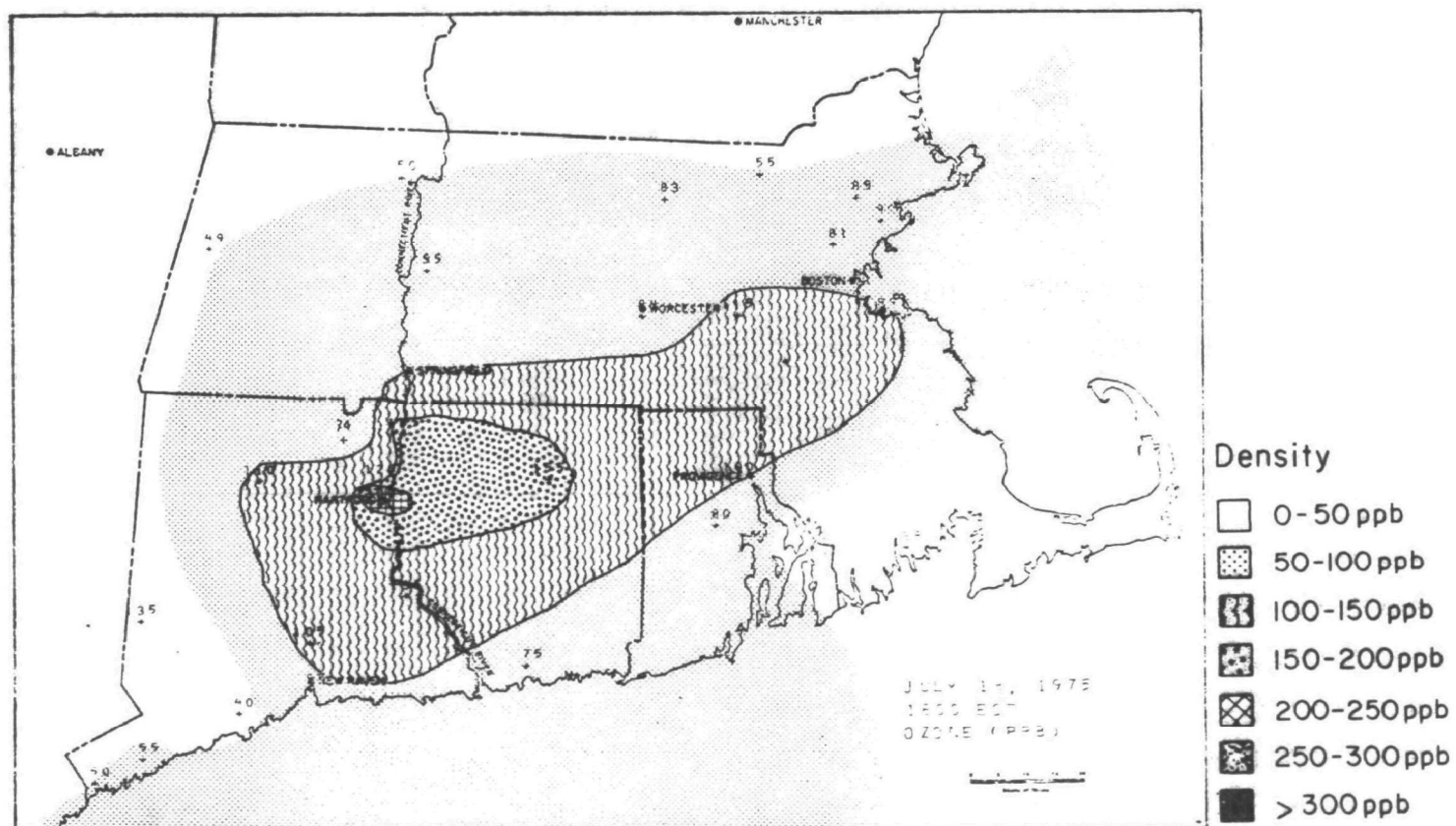
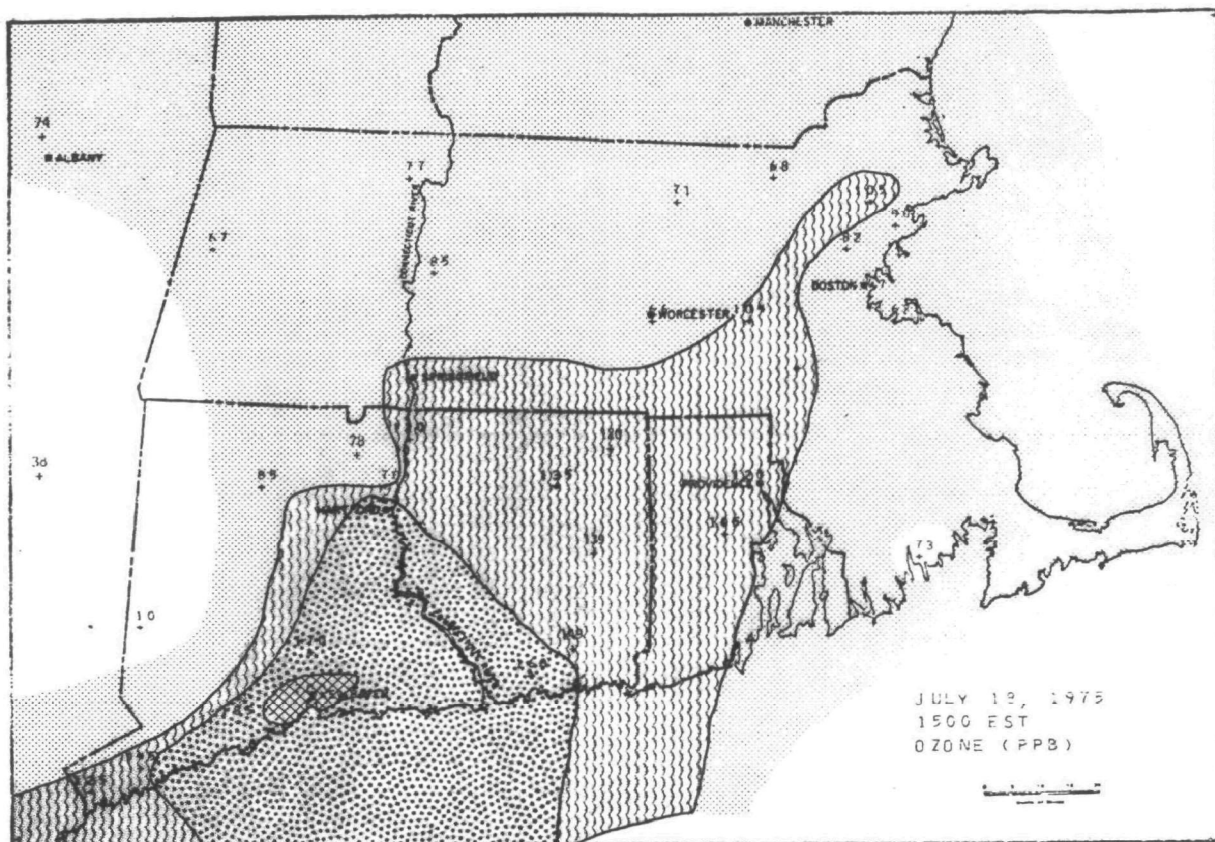


Figure 1b. Ozone distribution in southern New England on July 18, 1975.

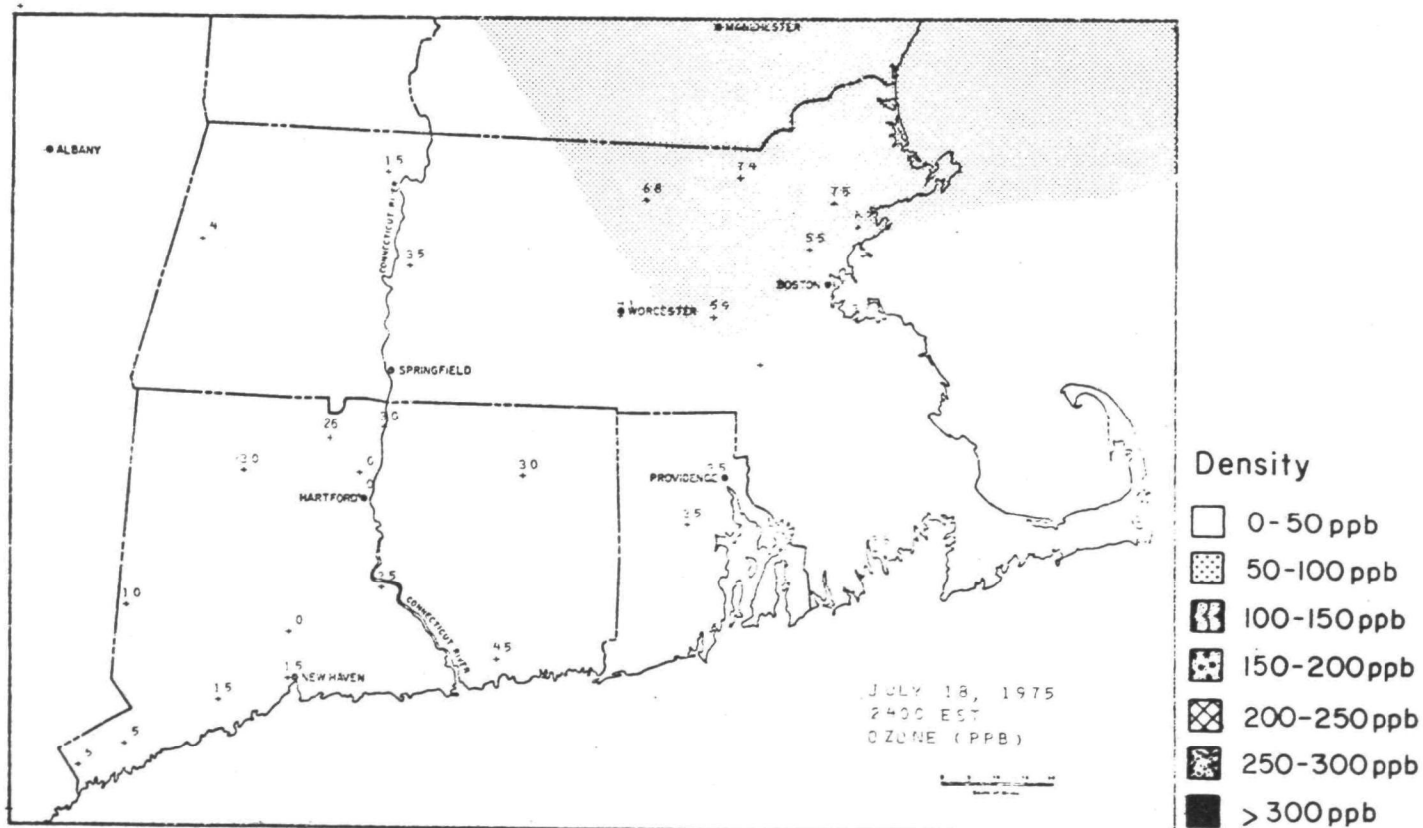
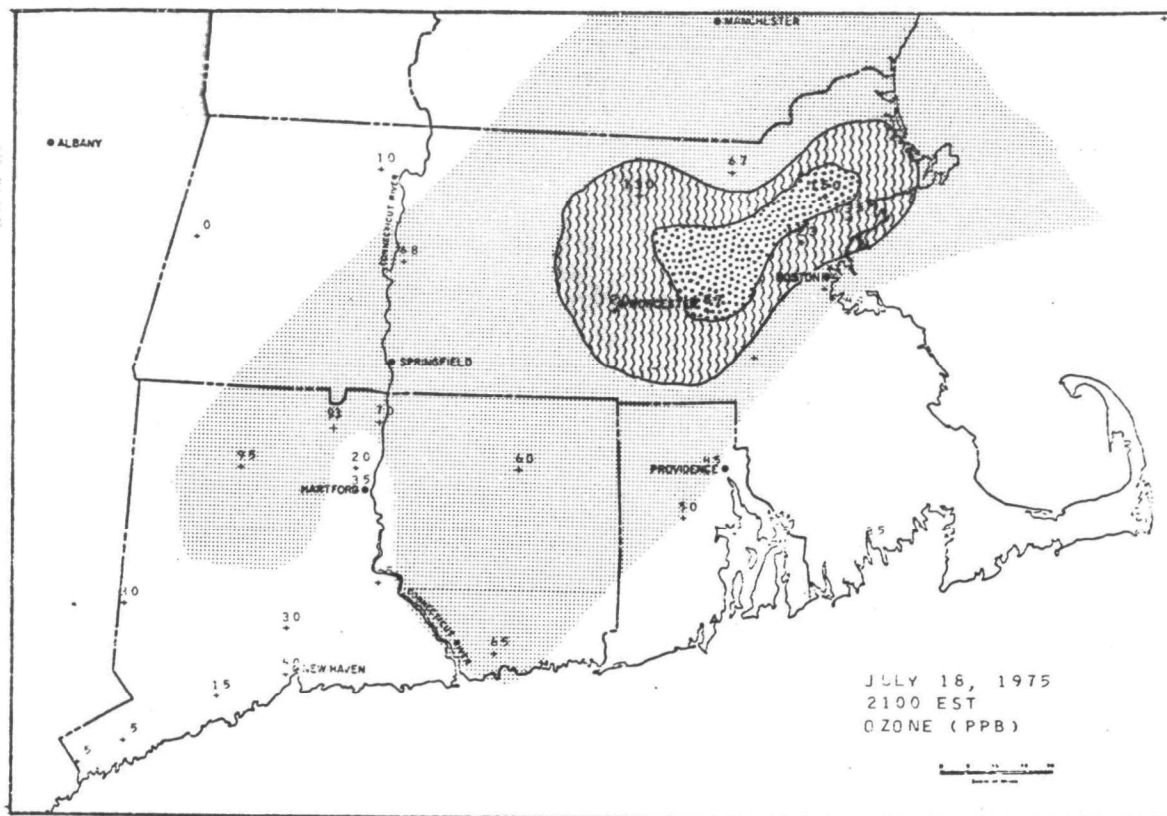


Figure 1c. Ozone distribution in southern New England on July 18, 1975.

The map shading shows ozone concentrations in 50 ppb increments, from zero to >300 ppb. A legend which categorizes the shading is provided on each page. For the most part the data shown on the maps for each station was followed rigorously in determining the concentration contours; however, where data looked suspicious or led to highly complex patterns, some smoothing was done. The need to smooth the contours by ignoring a station's data was very rare with three exceptions. The Springfield, Mass., and Litchfield, Conn., results were often completely inconsistent with the rest of the data, and have been ignored in drawing the contours. In addition, the results from Windsor, Conn., were frequently much lower than the surrounding area. To avoid highly complex contour patterns some of the Windsor data were excluded.

Ozone data over Long Island Sound and the Atlantic Ocean were not usually available so that shading in these areas is by inference. In most cases the shading patterns have been terminated in these areas (extreme right side and bottom of the maps); lack of shading in these areas does not indicate low ozone but rather lack of data.

The ozone distribution plots for July 18, 1975, are shown in Figure 1. Plots were constructed for every third hour from 0900 to 2400 EST. Referring to the maps, the concentration of  $O_3$  along the southern New England coast at 0900 EST was generally about 50 ppb, with inland concentrations of 50-80 ppb. By noon some areas of very high ozone had developed in Connecticut. The trajectories mentioned earlier, and the general meteorological data both suggest that the air mass moving into Connecticut at noon was located over the New York metropolitan area during the 6-9 a.m. rush hour period, when ozone precursor emissions are highest. By 1500, areas of high ozone extend from southern and eastern Connecticut through Rhode Island and up into the vicinity of Boston. The area of particular concern to this study, the Connecticut River Valley, shows high levels of  $O_3$  from New Haven up to about Springfield, Mass. However, there is nothing unique about the river valley in terms of high  $O_3$  concentrations; high levels of ozone also exist outside of the valley. This is a very important point in terms of whether a "channeling" effect occurs in the valley. If ozone concentrations outside the valley are similar to those within, it is very difficult to build a case that the valley funnels pollution into itself or is in any way unique. As mentioned earlier, channeling is one mechanism which has been suggested to explain high  $O_3$  in the valley.

By 1800 EST elevated  $O_3$  concentrations exist from west-central Connecticut to the Boston area, with the highest values extending eastward about 35 miles from Hartford. At 2100 the area of high  $O_3$  is in eastern Massachusetts and by midnight only the northeast portion of the region has ozone levels >50 ppb.

It is apparent from these maps that an air mass of high ozone/precursor concentration entered southern New England from the southwest on the morning of July 18 and moved through the region from southwest to northeast during the remainder of the day. Emissions from the urban areas of Connecticut undoubtedly contributed to this air mass and may be largely responsible for the elevated ozone in eastern Connecticut, Rhode Island, and east-central Massachusetts at 1500 EST. In terms of the Connecticut River Valley situation, it seems clear that a polluted air mass moving across the valley from the southwest resulted in high valley  $O_3$ , and that nothing unique to the valley's topography or meteorology led to the high values. The lack of evidence for a channeling effect is consistent with our analysis of the valley's topography and meteorology presented in a previous section.

It is initially surprising that an air mass moves rapidly enough to traverse the approximately 200 miles between New York and Boston during the course of a single day, as these maps seem to suggest. Table 2 shows the 1000-foot wind directions and speeds at several locations during July 18. Higher altitude winds are generally even higher in speed. During much of the day the winds averaged at least 15 mph within the important surface-to-5000-foot transport layer. At this speed, a polluted air mass could easily travel 200 miles over a single day.

TABLE 2. WINDS AT 1000 FEET ON JULY 18, 1975

Time	Location	Speed, mph	Direction, degrees
0700	Chatham, Mass.	8	210
	Springfield, Mass.	2	180
	Putnam, Conn.	8	271
1300	Chatham, Mass.	23	250
	Springfield, Mass.	15	177
	Putnam, Conn.	14	243
1430	Avery Point, Conn.	17	260
1900	Chatham, Mass.	29	245
	Putnam, Conn.	14	220



Some additional interesting features of the ozone patterns on July 18 are apparent from the shaded maps. The pattern of rapid  $O_3$  depletion in southwestern Connecticut between 1500-2100 EST is suggestive of the rapid scavenging of  $O_3$  by NO emitted in the evening traffic rush. We have observed this effect elsewhere<sup>(4,5)</sup>. The NO responsible for  $O_3$  depletion in this case is probably a combination of local emissions and emissions transported from the New York metropolitan area.

Another interesting feature is the seemingly anomalous behavior of ozone in the Simsbury area. The  $O_3$  remains comparatively low during the afternoon at Simsbury, even while concentrations of 200 ppb were recorded only 15 miles to the southeast in Hartford. By 2100 EST however, the higher concentrations of  $O_3$  had reached Simsbury. Recall that the trajectories showed Groton receiving urban air most of the day but Simsbury not until evening. The late arrival of the urban air at Simsbury may explain the unusual  $O_3$  behavior. A plot of the fluorocarbon-11 profiles at Simsbury and Groton shown in Figure 2, confirms this.\* The F-11 concentration increases to very high levels during late morning and early afternoon at Groton, indicating a direct influx of polluted urban air. As might be expected, the concentration of  $O_3$  also reached very high values by 1500 that afternoon.\*\* Based on the F-11 profile in Figure 2, Simsbury did not receive its infusion of urban air until 1900-2000 EST. For this reason the Simsbury  $O_3$  peak did not occur until well after dark (132 ppb at 2000 EST). Since the reactions forming  $O_3$  are completed by this time, the peak  $O_3$  and F-11 concentrations occur simultaneously at 2000 EST at Simsbury. The occurrence of such high levels of  $O_3$  after dark in a rural area like Simsbury, combined with the simultaneous peak in the urban air tracer, F-11, is very strong evidence of the transport of urban pollution to rural areas.

JULY 19, 1975

The meteorological situation on July 19, 1975, was very similar to July 18. Wind flow was still from the southwest throughout most of the day, but the wind speed was somewhat greater. The Simsbury and Groton trajectories from

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\* Fluorocarbon-11 emissions are related to population density and are used here to distinguish rural air from air which has passed over urban areas. A later section will discuss the F-11 data in more detail.

\*\* Due to the reaction time necessary to generate  $O_3$  we should not always expect the F-11 and  $O_3$  peaks to occur simultaneously.

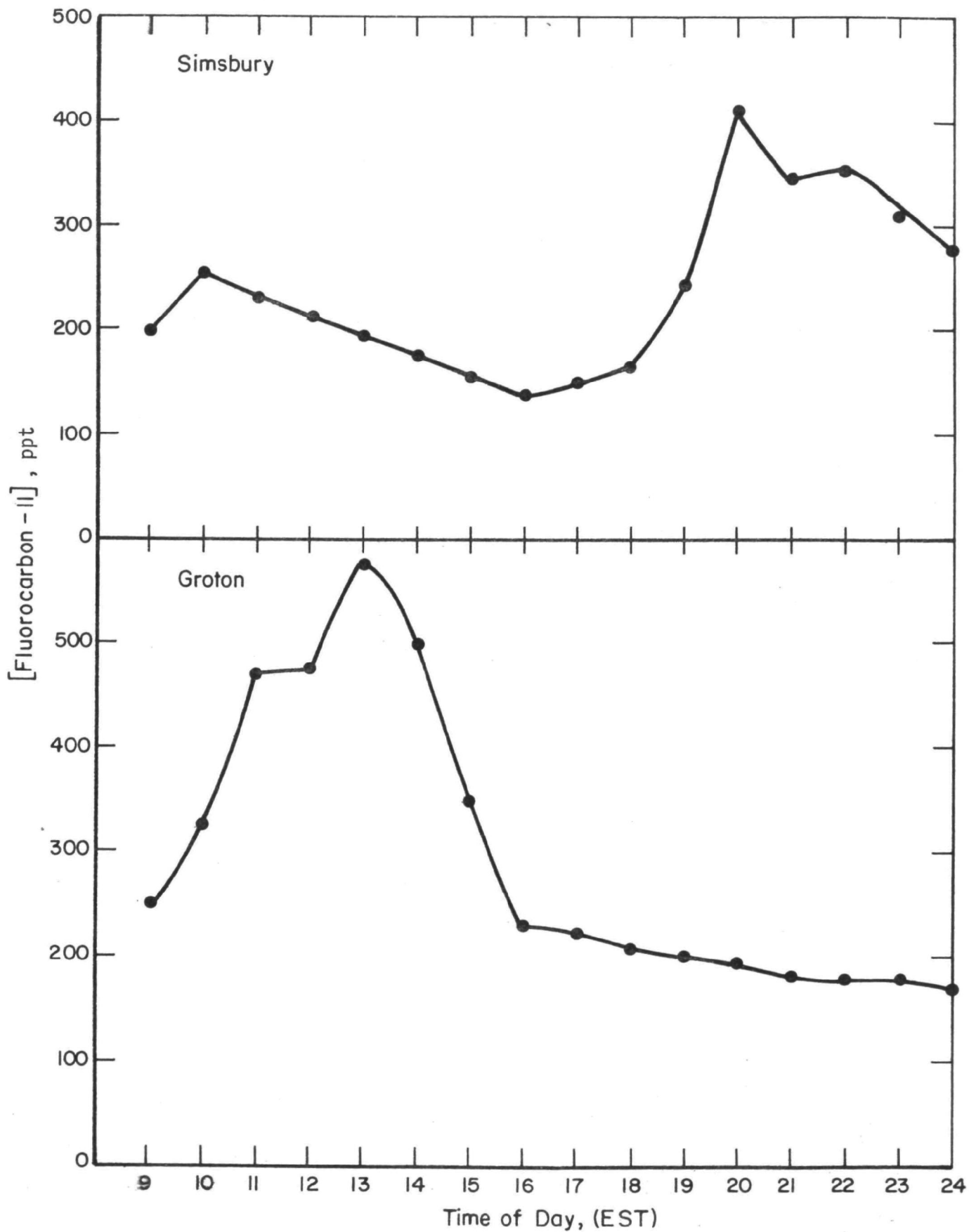


Figure 2. Fluorocarbon-11 profiles for July 18, 1975.

Figures A-2 and A-3 in Appendix A are also very similar to the trajectories on July 18. Flow into Connecticut during most of the day was from the southwest; the direction of the New Jersey-New York urban complex.

The ozone shading maps for July 19 may be found in Figure 3 a-c. The ozone patterns at 0900 EST still show the effect of the previous evening's high ozone in the northeastern part of the region. It is uncertain how much of this ozone is truly residual, that is, surviving from the previous evening, and how much is a result of an increase in the morning rate of ozone formation due to a more favorable  $\text{NO}_2/\text{NO}$  ratio caused by nighttime reaction of residual  $\text{O}_3$  with  $\text{NO}$ . The diurnal ozone profiles from such sites as Fitchburg and Lowell, Mass., indicate that significant surface concentrations of  $\text{O}_3$  did exist overnight at these locations. Since the overnight concentration of ozone within stable layers aloft was probably even higher than the surface concentration, it seems plausible that much of this morning ozone is actually left over from the previous evening.

The concentration of  $\text{O}_3$  within the Connecticut River Valley at 0900 is generally low. By noon however, there is a definite intrusion of ozone-rich air into Connecticut from the southwest. The greatest concentrations exist around Bridgeport, but it is clear that the entire southern portion of the Connecticut River Valley from New Haven to Hartford is affected. At 1500 the highest levels of  $\text{O}_3$  are in the vicinity of Hartford, about 40 miles northeast of Bridgeport. However, high concentrations of  $\text{O}_3$  (>100 ppb) exist within a band from southwestern Connecticut to northeastern Massachusetts. The fact that wind speeds averaged more than 30 mph throughout the day is entirely consistent with the hypothesis that this band of high ozone represents the smeared-out urban plume from the urban complexes in New Jersey, New York, and southwestern Connecticut. Table 3 shows representative wind information for July 19. The band of high  $\text{O}_3$  at 1500 EST extends across the Connecticut River Valley, with high levels found within and on either side of the valley. As on July 18, there is no indication of any unique feature of the valley which accounts for the observed high  $\text{O}_3$ ; rather the high  $\text{O}_3$  in the valley seems to relate to the geographical location of the valley downwind of major urban centers.

The band of high  $\text{O}_3$  is somewhat smaller and has moved north and slightly eastward by 1800 EST. Simsbury data show a shift in the wind from southwesterly to southerly starting around 1600 EST. This probably explains the northward

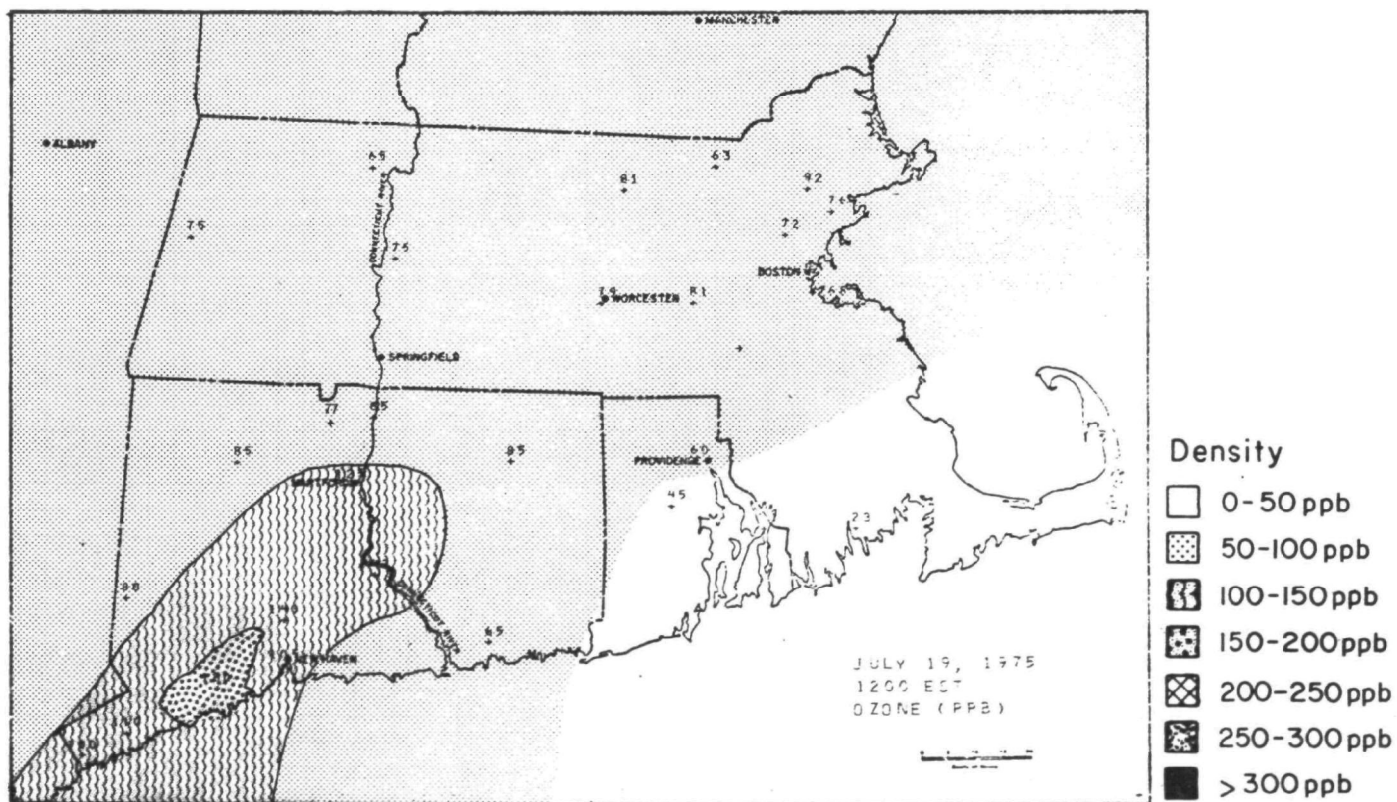
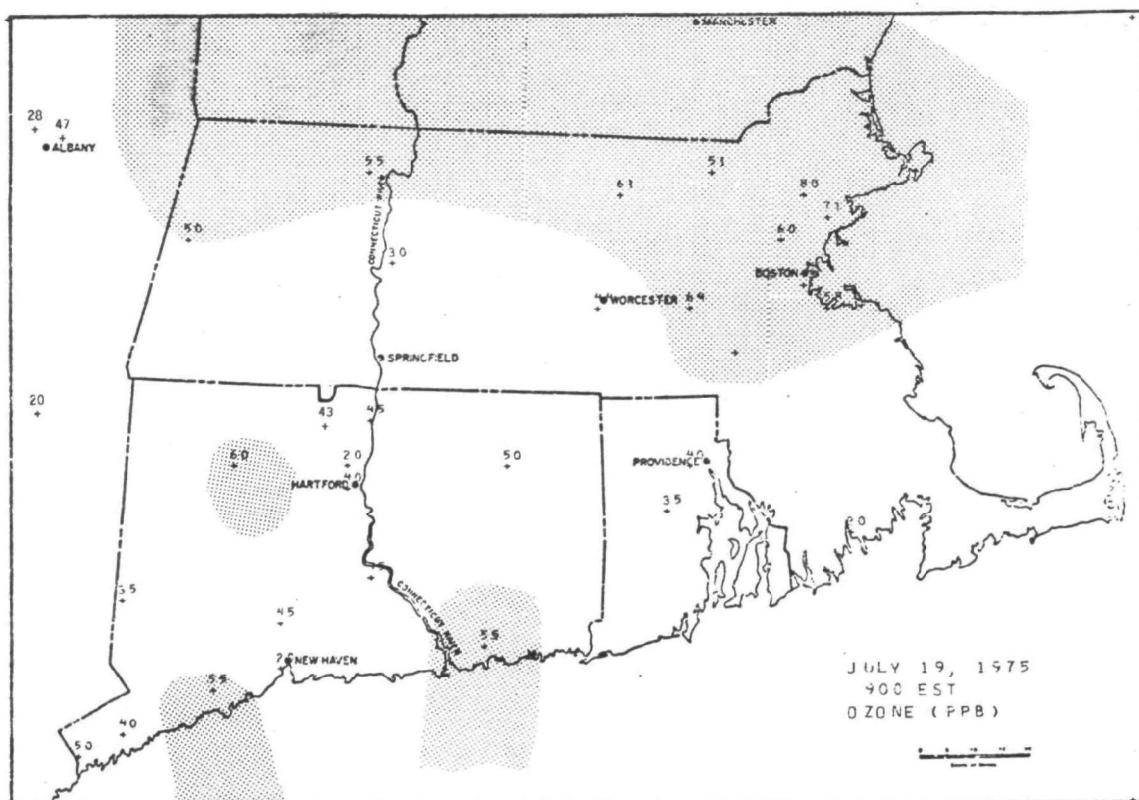


Figure 3a. Ozone distribution in southern New England on July 19, 1975.

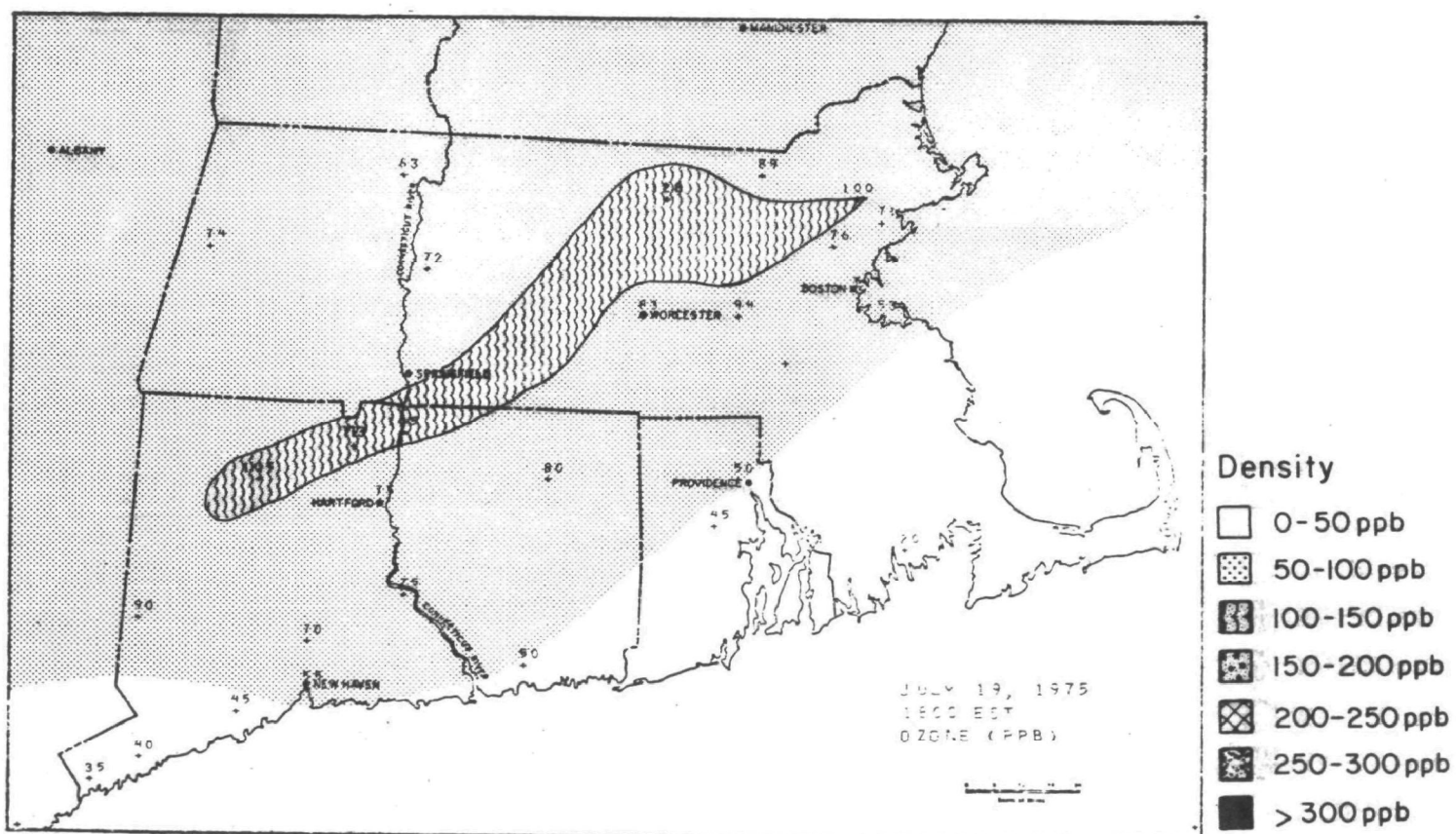
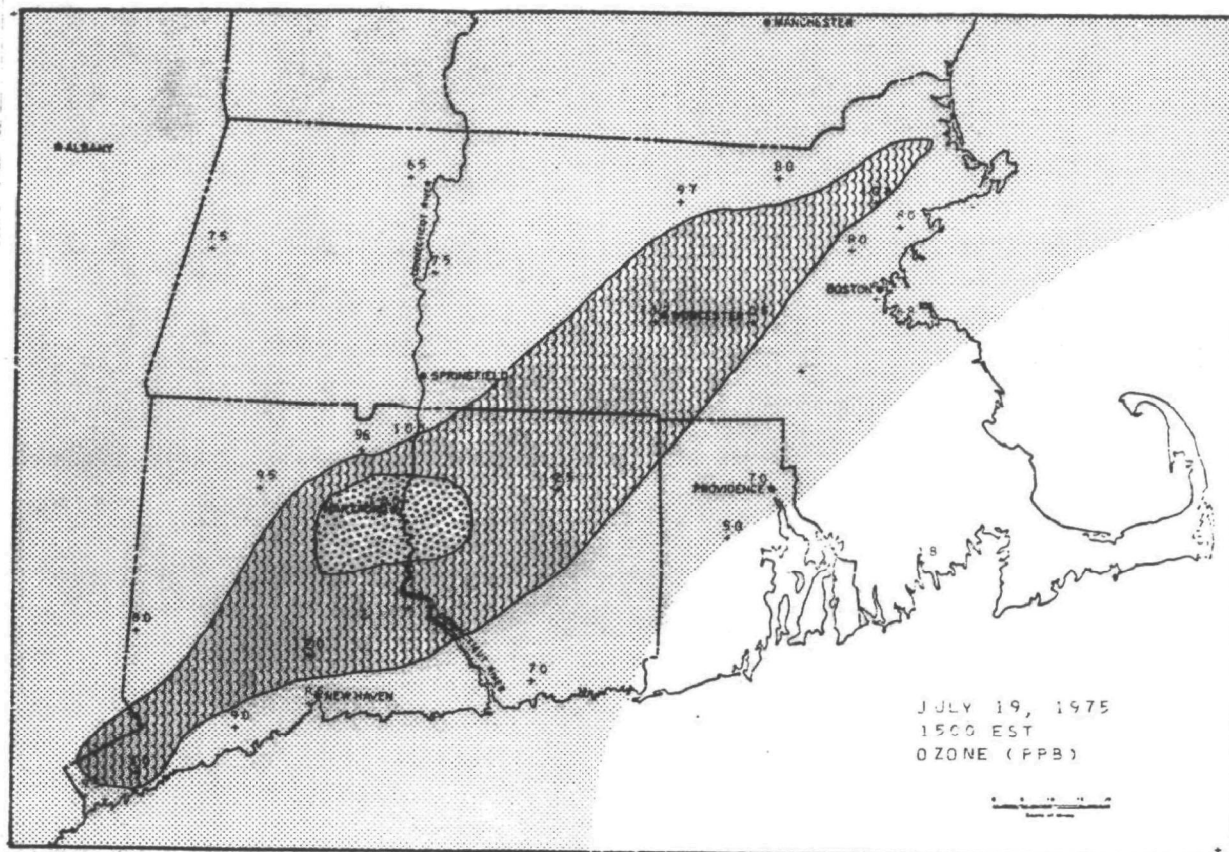


Figure 3b. Ozone distribution in southern New England on July 19, 1975.

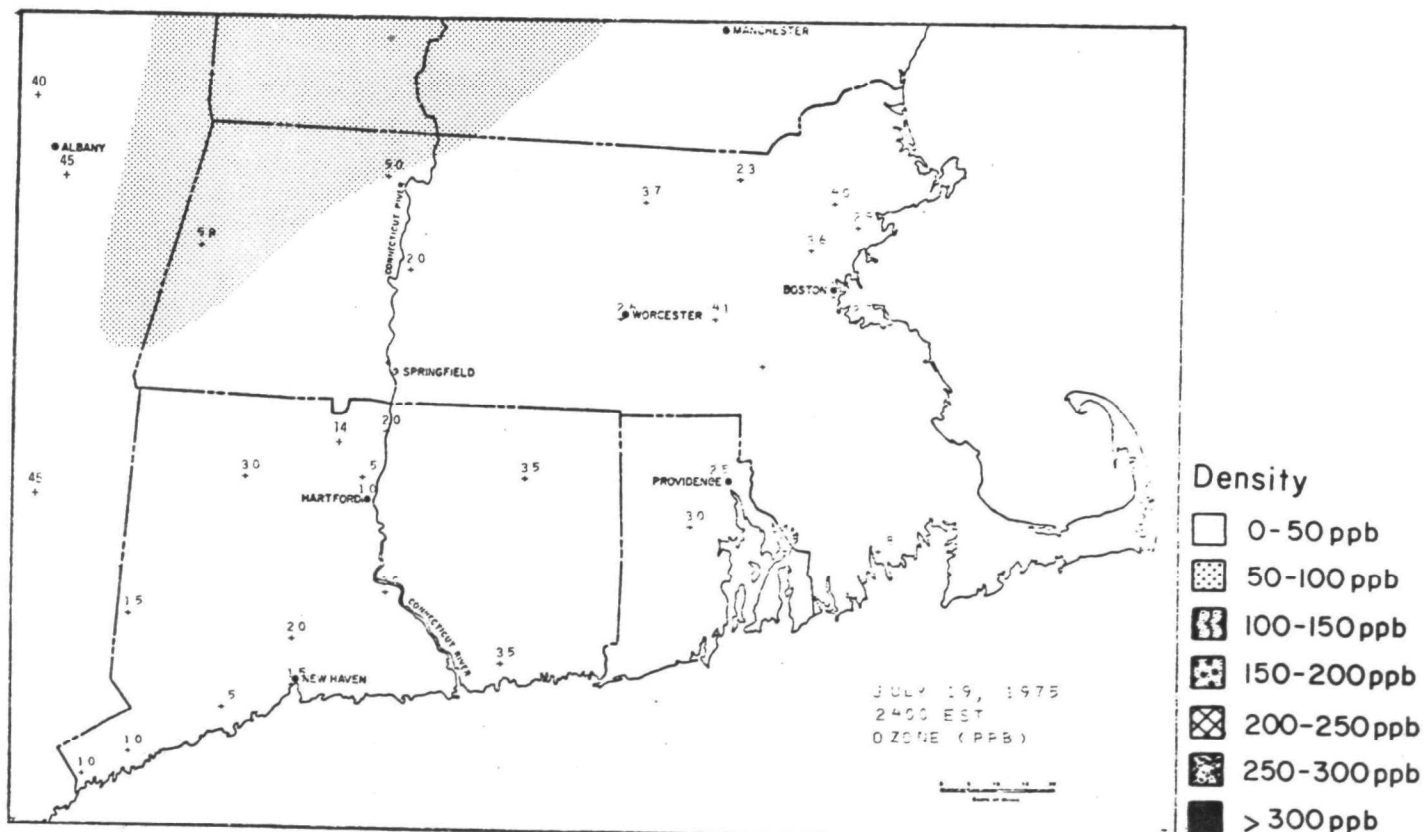
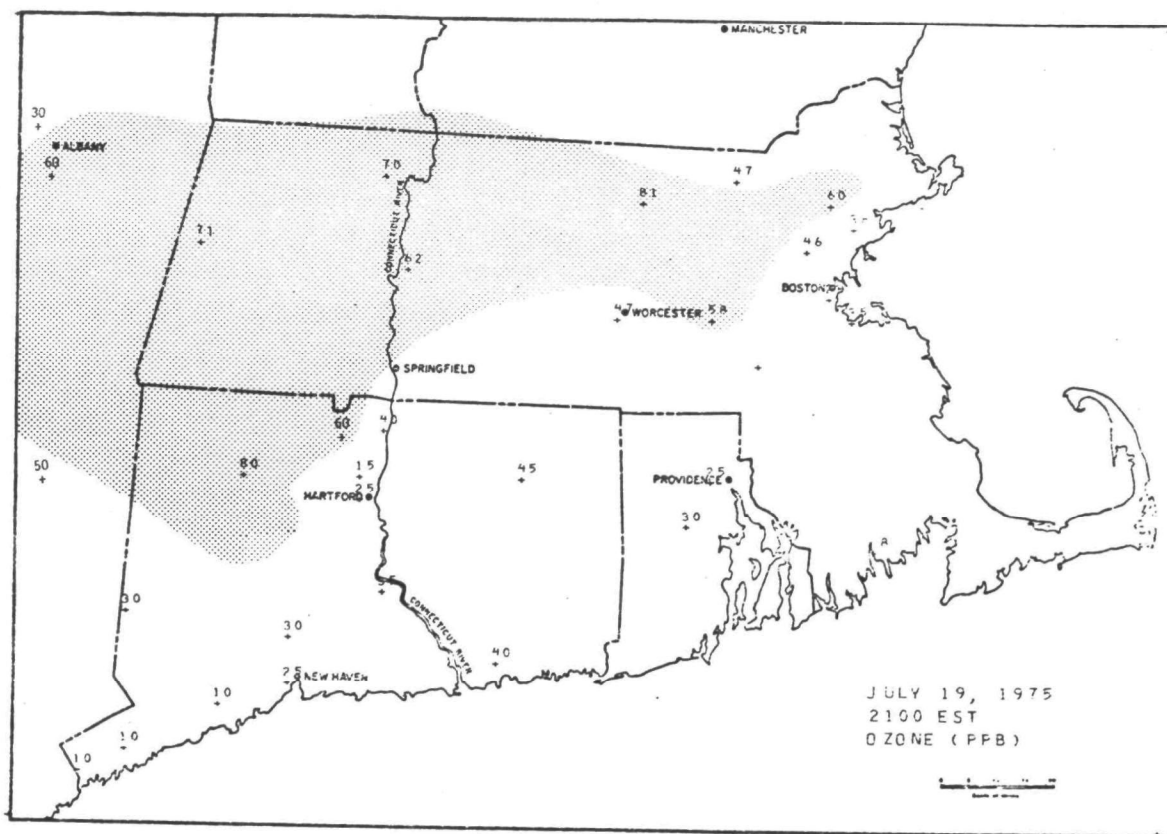


Figure 3c. Ozone distribution in southern New England on July 19, 1975.

TABLE 3 . WINDS AT 1000 FEET ON JULY 19, 1975

Time	Location	Speed, mph	Direction, degrees
0700	Chatham, Mass.	30	250
0900	Avery Point, Conn.	25	247
1700	Avery Point, Conn.	33	247
1900	Chatham, Mass.	41	230

movement. The highest  $O_3$  at this time is at Fitchburg, Mass. Since the photochemical reactions which generate  $O_3$  are essentially terminated by this time in the evening, some scavenging and decay of  $O_3$  are undoubtedly occurring; thus the band of high concentrations is shrinking. By 2100, all of the surface stations report concentrations less than 100 ppb. The highest concentrations in the region are in the rural areas of central Massachusetts and northwestern Connecticut, and are clearly the residue of the ozone band observed entering these areas at 1800. By midnight, concentrations throughout the region are less than 60 ppb.

The daily average fluorocarbon-11 concentration at Simsbury was the same on the 19th as on the 18th. However, the profiles differ markedly. The fluorocarbon-11 concentration on the 19th, as shown in Figure 4, was virtually constant throughout the day, as opposed to the late evening surge which occurred on July 18. The constant F-11 profile suggests a steady influx of dilute urban air throughout the day at Simsbury. This is consistent with the  $O_3$  shading maps, which show no unusual  $O_3$  contours or gradients near Simsbury on the 19th (as were observed on the 18th). Judging from the F-11 patterns, the input of urban  $O_3$  precursors to Groton is less than Simsbury on the 19th and considerably less than Groton on the 18th. This undoubtedly explains the much lower  $O_3$  at Groton on this day.

In summarizing the  $O_3$  patterns of July 19 in terms of the Connecticut River Valley situation, it is important to emphasize the cross-valley nature of the high  $O_3$  area (especially visible at 1500 and 1800 EST). It seems apparent that the high  $O_3$  in the valley on this day was not related to the valley itself, but the fact that a portion of the valley was located directly downwind of a major emissions complex to the southwest. Under the meteorological conditions which existed on this day, a smeared-out urban plume extended across

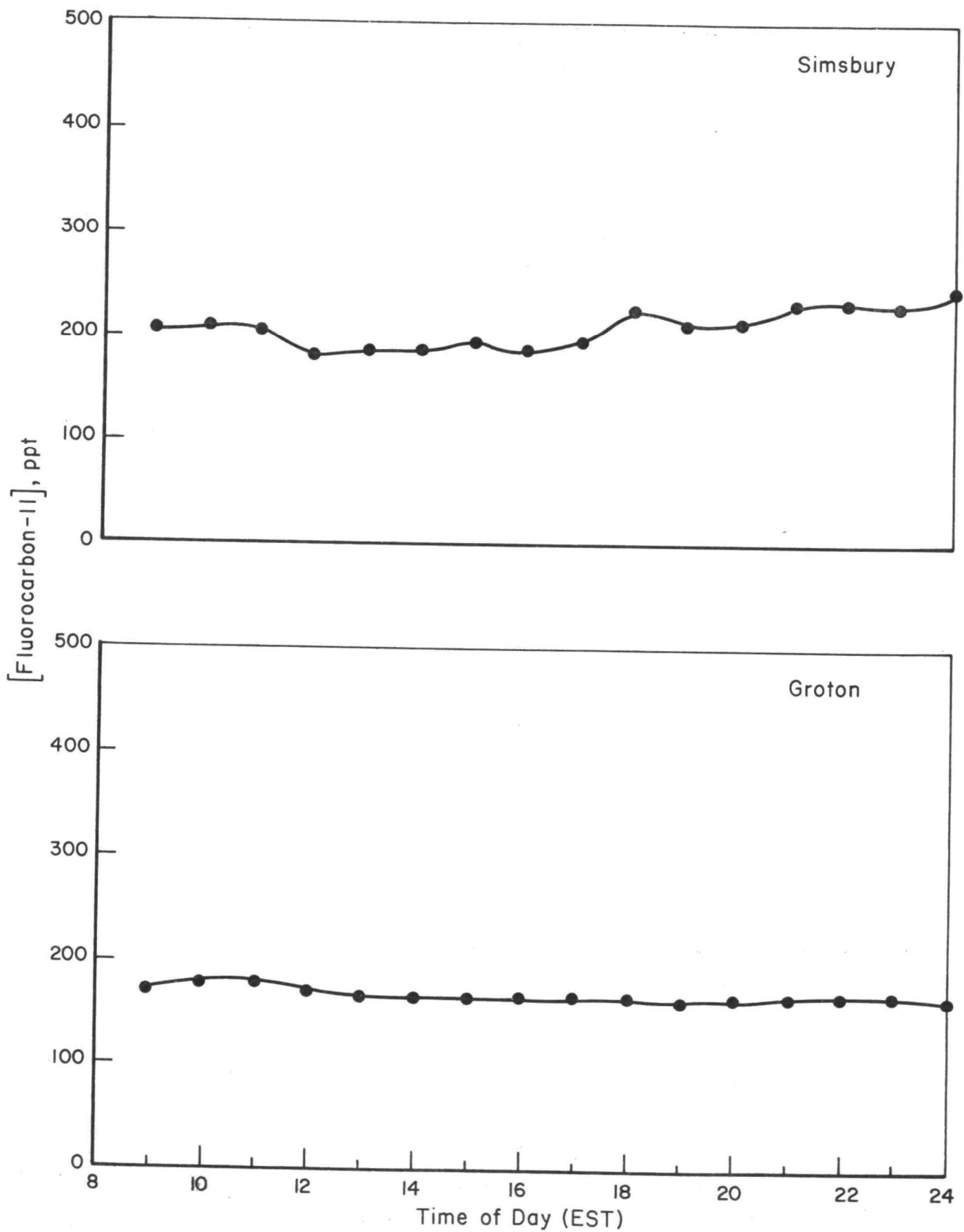


Figure 4. Fluorocarbon-11 profiles for July 19, 1975.



the valley; high levels of ozone were observed both within and on either side of the valley. The  $O_3$  levels within the urban plume are superimposed on the  $O_3$  which would form in the absence of the plume (about 70 ppb judging from the concentrations on either side of the plume). The ozone which exists outside the urban plume may result from local precursor emissions, long range transport (i.e., associated with a high pressure system), natural sources or some combination of the three. The interaction and superposition of  $O_3$  and precursors from these sources was discussed in our 1974 midwest study report<sup>(4,5)</sup>.

Some feeling for the spatial extent of urban plumes can be gained from the ozone maps for July 18 and 19. On July 18 the maximum diameter (perpendicular to the wind flow) of the urban plume ( $O_3 > 100$  ppb) was between 50 and 80 miles. The length of the plume was in excess of 100 miles. On the 19th, with considerably higher wind speeds, the plume diameter was only 30-40 miles, with a length greater than 175 miles. Of course, the spacing between the urban centers contributing to this plume undoubtedly contributes to its overall length.

#### JULY 23 AND 24, 1975

July 23 and 24 will be treated as a single episode here for clarity. A high pressure system moved eastward through the region on July 23 causing a southwest to west-southwest surface flow pattern. By July 24 the high began to diffuse and winds became more southerly. Representative wind data at 1000 feet are presented in Table 4.

Air mass trajectories for these 2 days are shown in Figures A-4 - A-5 in Appendix A. The air parcels arriving in Simsbury and Groton during the early part of July 23 had passed through the fairly rural south-central areas of New York State. By midafternoon however, the flow had shifted to the southwest, and the 1900 EST trajectory at Groton passed directly over the New Jersey-New York-Connecticut urban complex known as the New York metropolitan area. The air arriving in Simsbury passed well north of the urban complex. A set of forward trajectories for New York City and Philadelphia were reported by Wolff, et al.<sup>(20)</sup> and are included here as Figures 5 and 6. The New York City trajectories show that air leaving the city after 0800 moves into Connecticut from the southwest. Air leaving the metropolitan area during the morning peak traffic period (trajectory B) arrives in the Bridgeport-New Haven area by midafternoon. Air from Philadelphia (Figure 6) has little impact on

TABLE 4. WINDS AT 1000 FEET ON JULY 23-24, 1975

Time	Location	Speed, mph	Direction, degrees
<u>Winds at 1000 Feet on July 23, 1975</u>			
0700	Chatham, Mass.	14	270
0800	Springfield, Mass.	8	255
0822	Putnam, Conn.	7	267
0830	Avery Point, Conn.	16	305
1300	Chatham, Mass.	17	250
1355	Avery Point, Conn.	17	262
1400	Springfield, Mass.	17	205
1900	Chatham, Mass.	20	260
<u>Winds at 1000 Feet on July 24, 1975</u>			
0700	Chatham, Mass.	28	250
0809	Springfield, Mass.	15	228
0183	Putnam, Conn.	13	230
1340	Avery Point, Conn.	15	240
1400	Springfield, Mass.	25	184
1900	Chatham, Mass.	36	205

Connecticut during July 23, but does enter the state early on the morning of the 24th after passing through the New York metropolitan area.

Figure 7 a-c shows the ozone distribution maps for July 23. Ozone at 0900 is less than about 60 ppb throughout southern New England. At noon, very high levels of  $O_3$  are observed entering the region from the southwest. By 1500 a plume of elevated  $O_3$  (>100 ppb) is found from southwestern Connecticut to eastern Massachusetts. The highest concentrations, and these were the highest levels observed during the 1975 Northeast Oxidant Study, are found near New Haven. Recall that the New York forward trajectories predicted that the air over the city during the morning rush hours would arrive in New Haven by midafternoon. This corresponds precisely with the New Haven ozone maximum. Note also that the band of high  $O_3$  extends across the Connecticut River Valley, with very high levels of  $O_3$  found within and on either side of the valley. It seems very likely that the high  $O_3$  in the Connecticut River Valley results from the geographical fact that the valley lies downwind of a complex of major urban emissions sources, and at an optimum downwind distance which permits extensive photochemical reaction and  $O_3$  generation within the pollutant-laden morning air mass. The combination of these factors allows extensive  $O_3$  formation

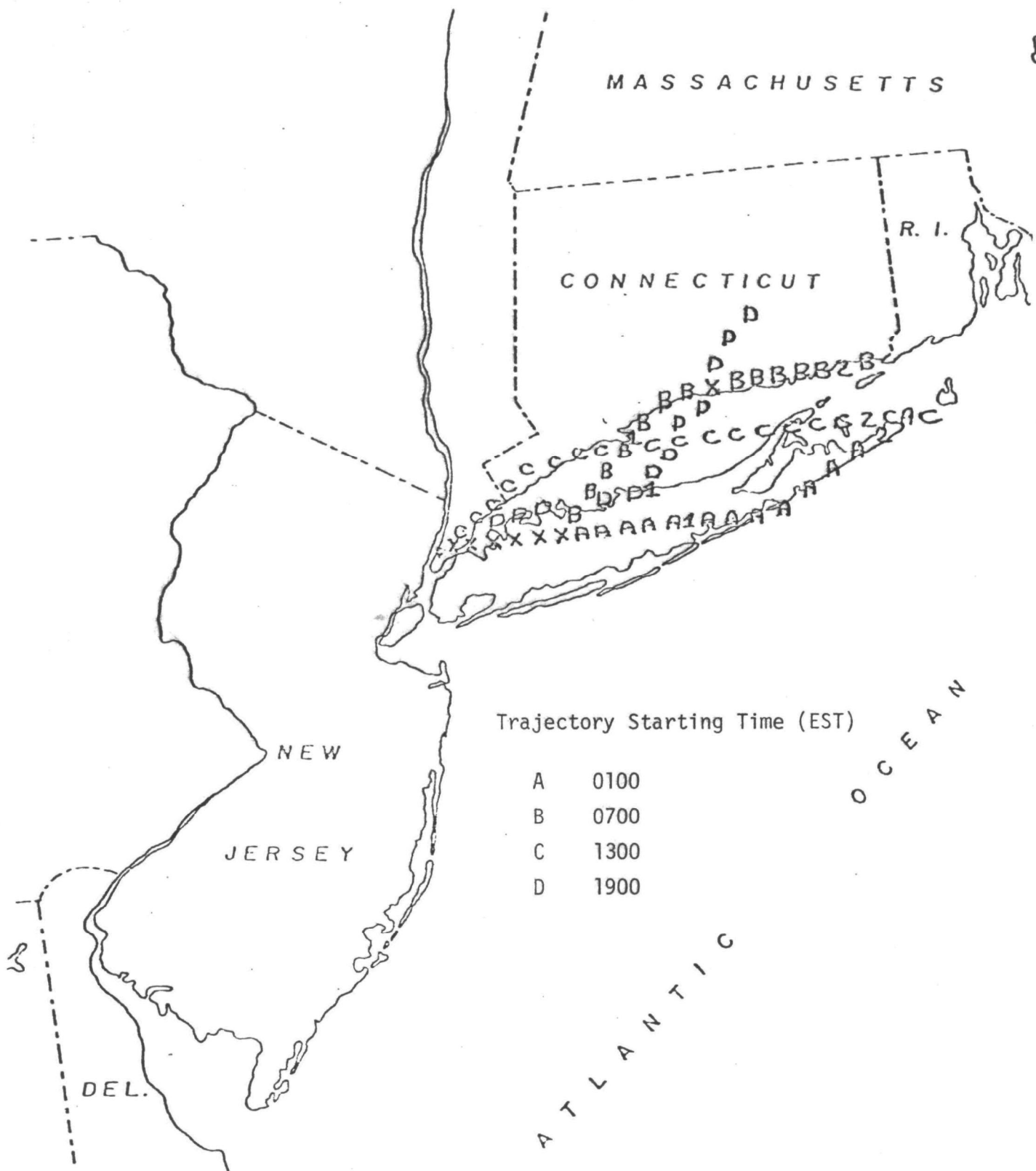


Figure 5. Forward trajectories for New York City on July 23, 1975.

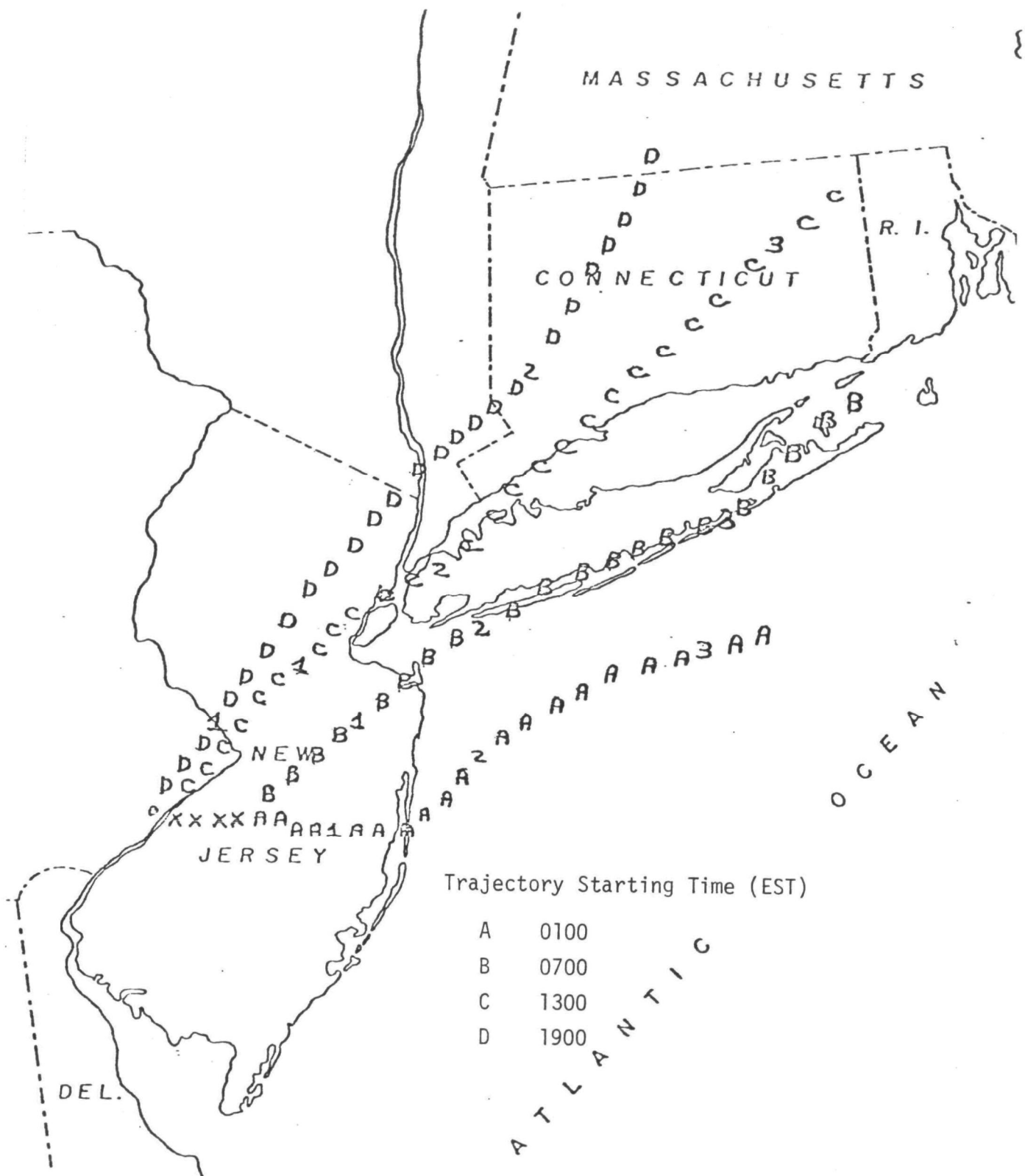


Figure 6. Forward trajectories for Philadelphia on July 23, 1975.

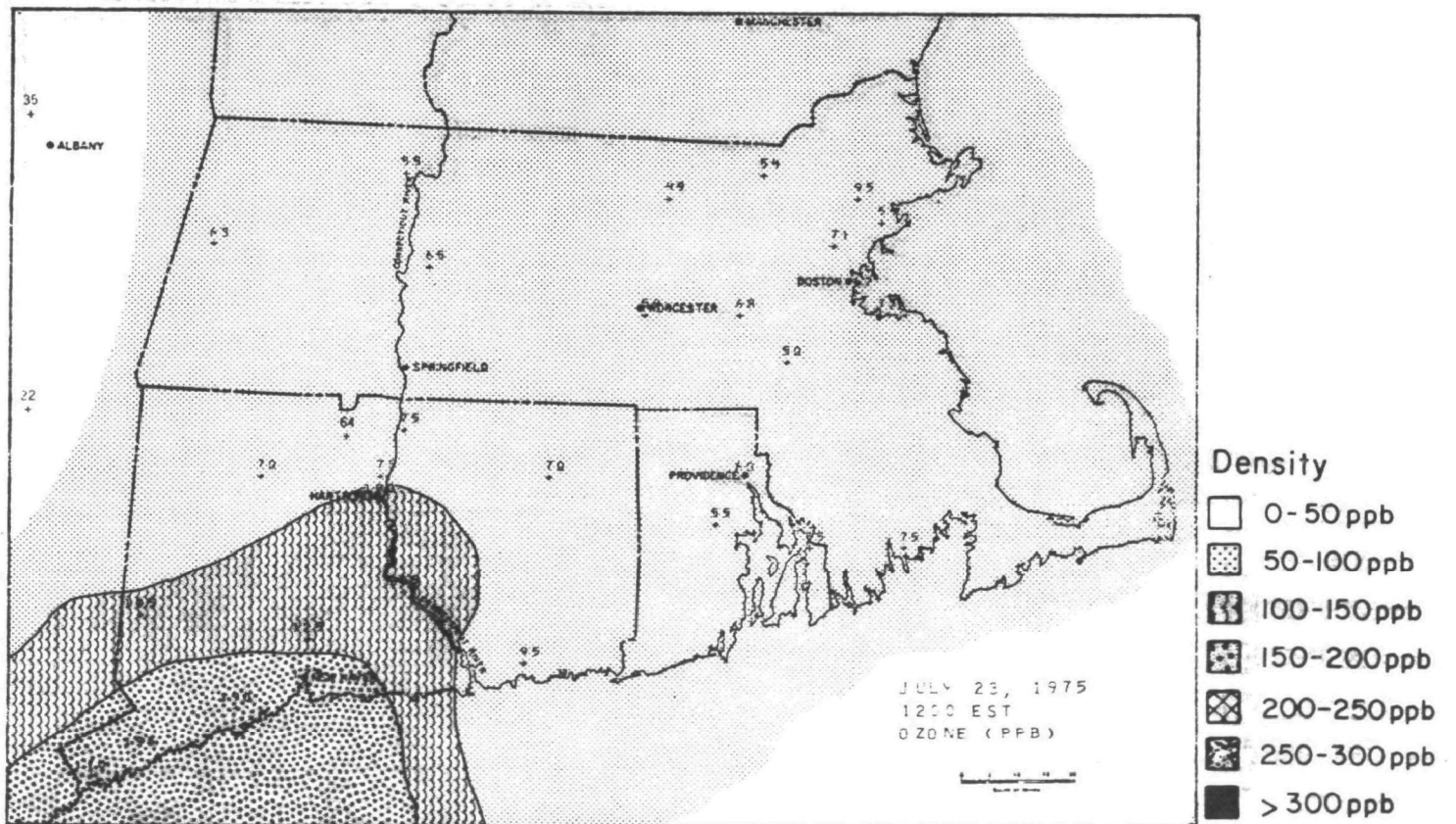
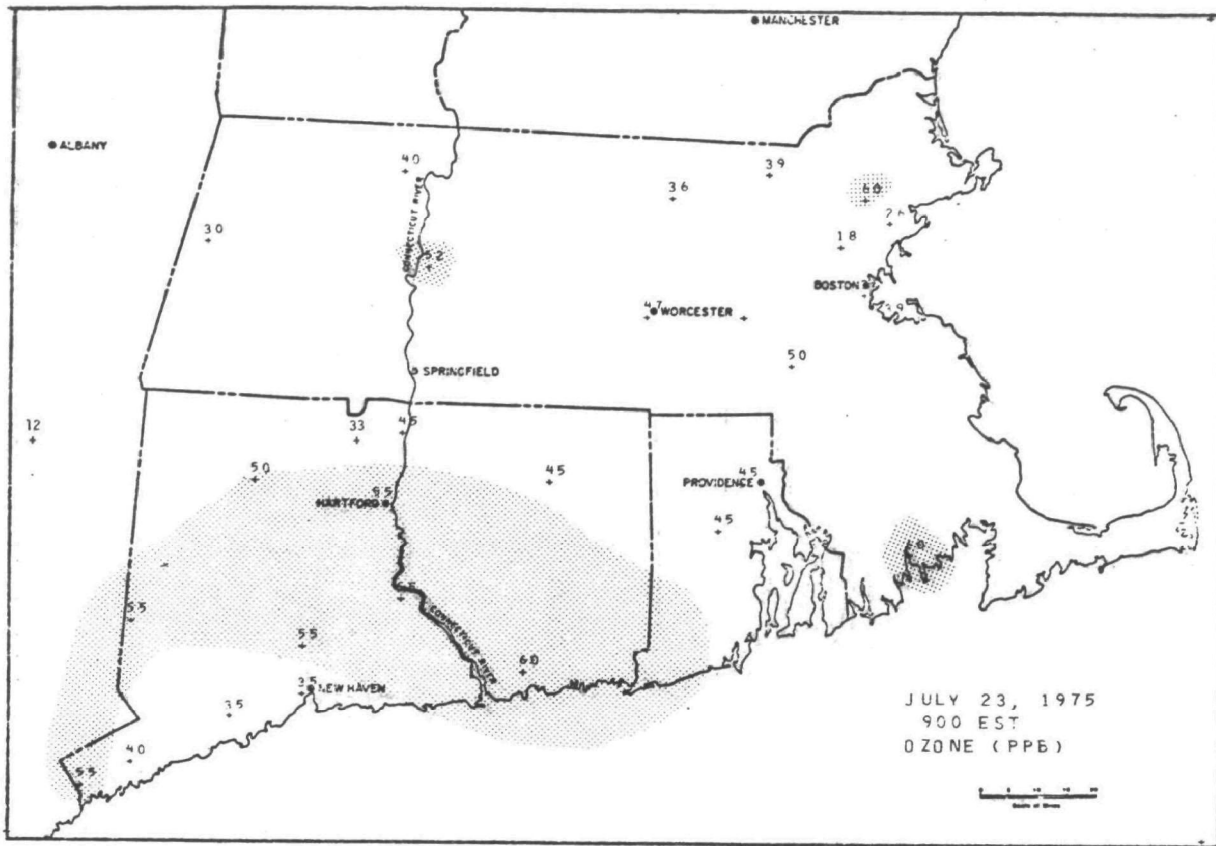


Figure 7a. Ozone distribution in southern New England on July 23, 1975.

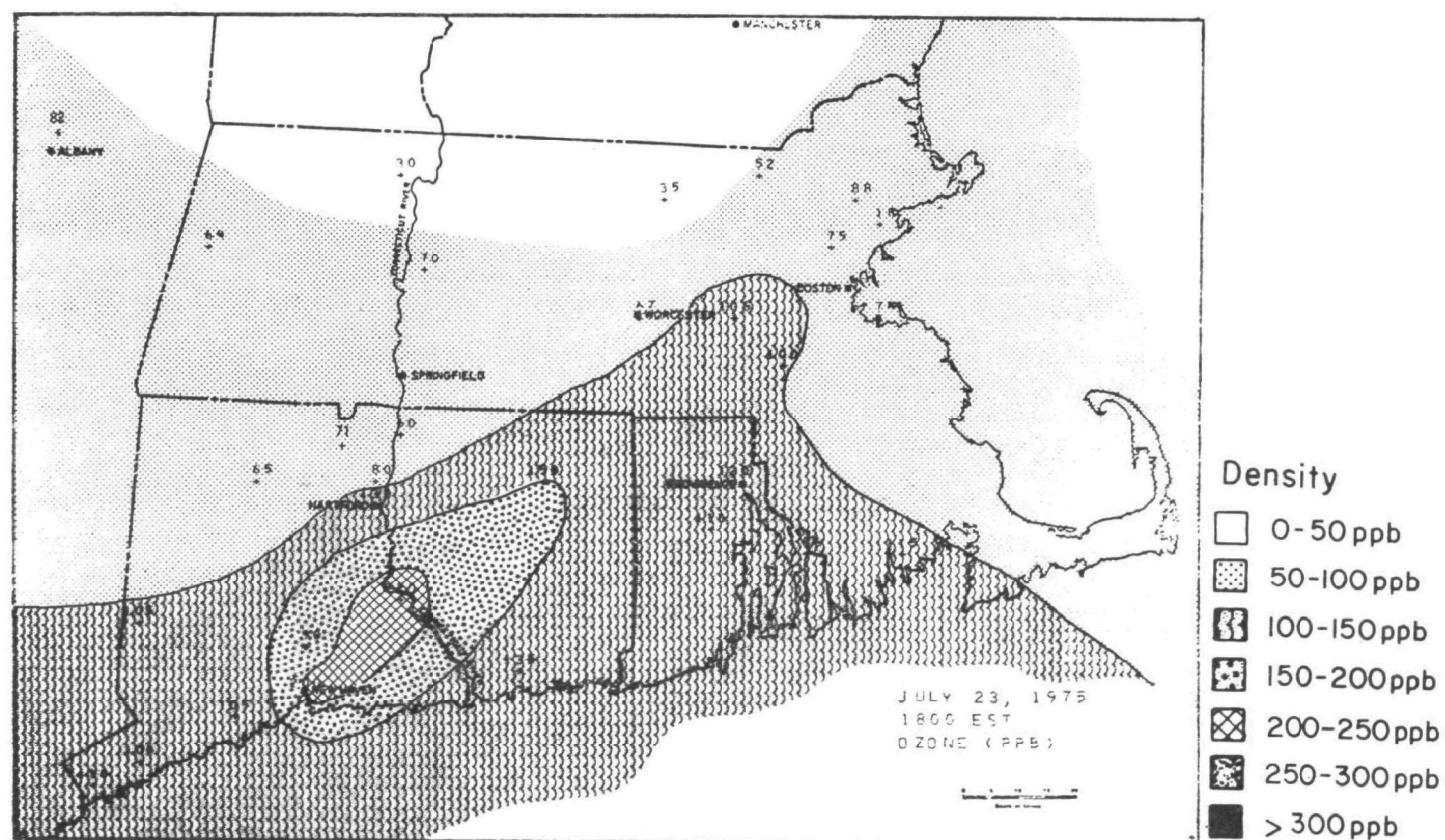
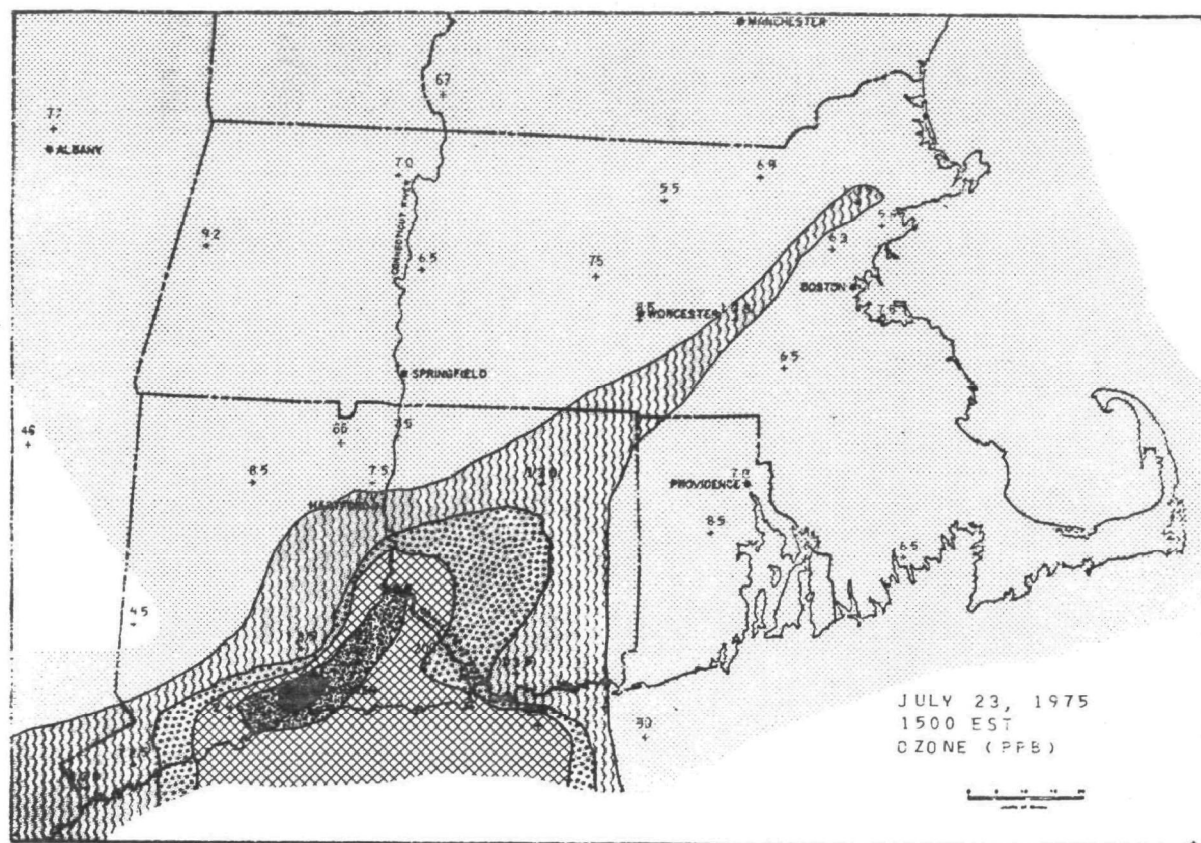


Figure 7b. Ozone distribution in southern New England on July 23, 1975.



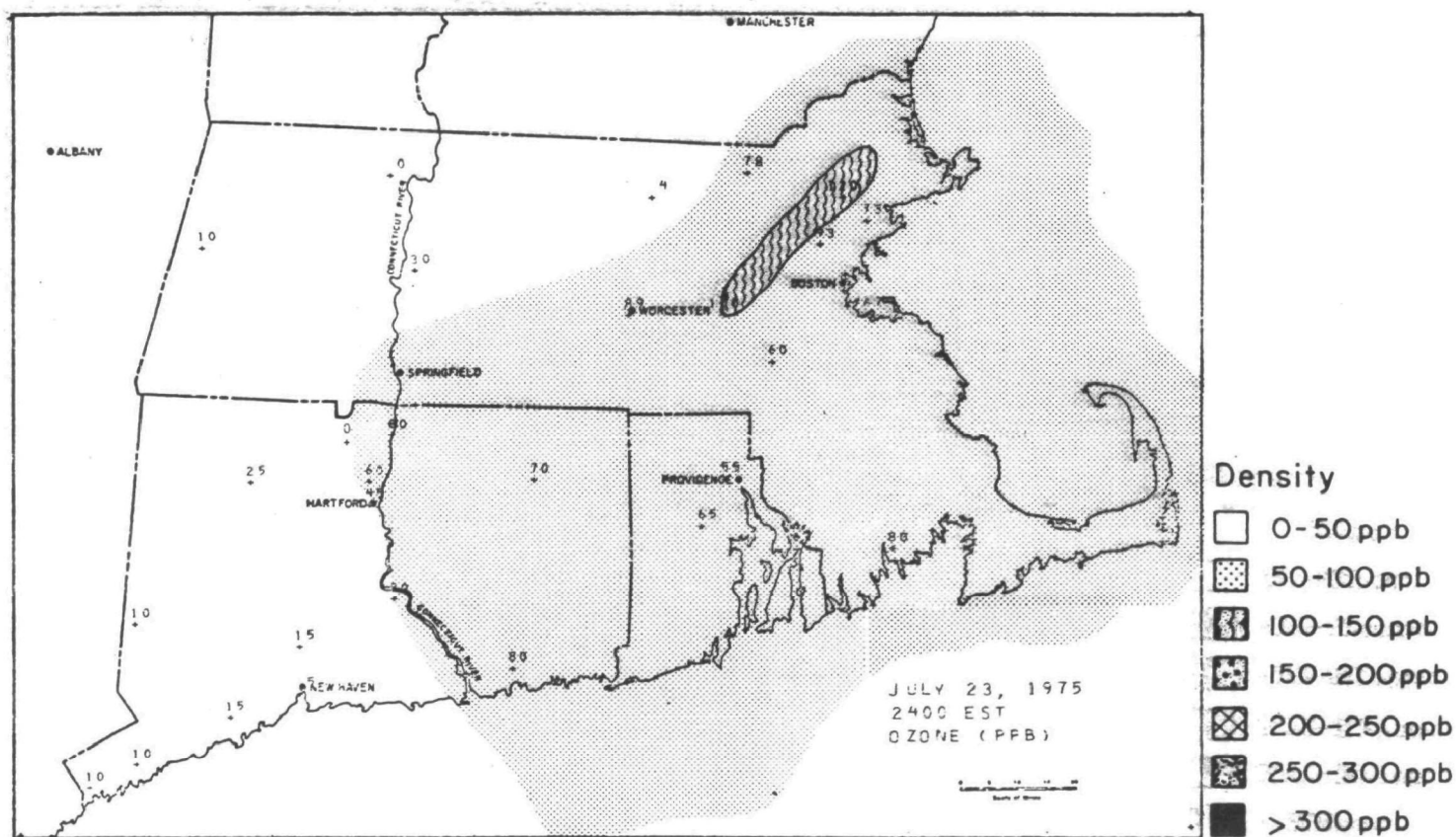
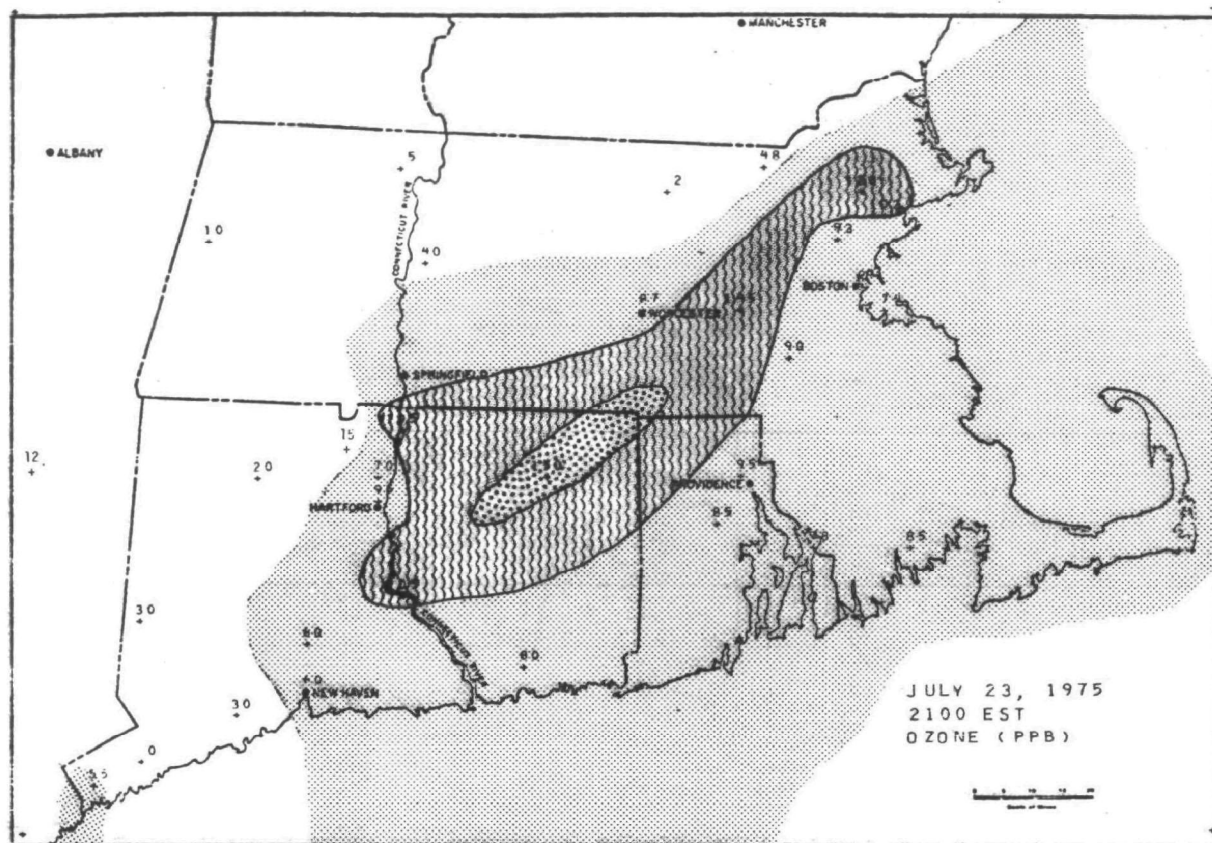


Figure 7c. Ozone distribution in southern New England on July 23, 1975.

to occur by the time the air parcel reaches the river valley. Obviously the  $O_3$  and precursors moving into the source area (New Jersey-New York) in the morning contribute to the ultimate ozone burden within the urban plume. On some days this contribution can be significant, for example, when the Philadelphia urban plume overlaps the New York metropolitan area. The trajectories suggest this is not occurring on the afternoon of July 23. This topic will be discussed again shortly.

Other sources of  $O_3$  and precursors such as regional  $O_3$  associated with high pressure cells also contribute to the ultimate concentration within the plume. However, judging from the  $O_3$  levels outside of the urban plume during the afternoon of July 23 (70-85 ppb), it is clear that the dominant source of the very high (>200 ppb)  $O_3$  within the plume is upwind urban emissions.

By 1800 (7 p.m. local time) the photochemical reactions producing  $O_3$  are terminated, yet extensive portions of Connecticut, Rhode Island, and parts of Massachusetts are still experiencing high  $O_3$ . The center of the  $O_3$  distribution extends across the Connecticut valley from New Haven to the northeast corner of the state. Note that Groton experiences high levels of  $O_3$  during the afternoon, levels about twice those found at Simsbury. These observations are consistent with the trajectory analysis, which showed Groton receiving direct input of urban air, in contrast to Simsbury which experienced relatively clean rural emissions.

By 2100 EST the urban plume extends from the eastern Connecticut valley up to northeastern Massachusetts. Three hours later, at midnight, high concentrations exist only in eastern Massachusetts north and west of Boston. This is about the distance that the wind speed data from Table 4 predict the morning New York air mass would travel in the intervening 15-16 hours.

We will shortly use aircraft data to track this air mass further north and east of Massachusetts. Before doing so however, we will first discuss the fluorocarbon data for July 23 and the July 24  $O_3$  distribution maps.

The fluorocarbon-11 profiles for Simsbury and Groton are presented in Figure 8. The F-11 concentration in Simsbury was near the tropospheric background level (~90-120 ppt) during most of the day, confirming the absence of urban air influx to Simsbury. After 1800 there apparently was an infusion of urban air; at about this same time  $O_3$  reached its maximum at Simsbury. The F-11 concentrations at Groton were higher than at Simsbury during most of the day, consistent with the trajectory analysis and the higher  $O_3$  levels at Groton.



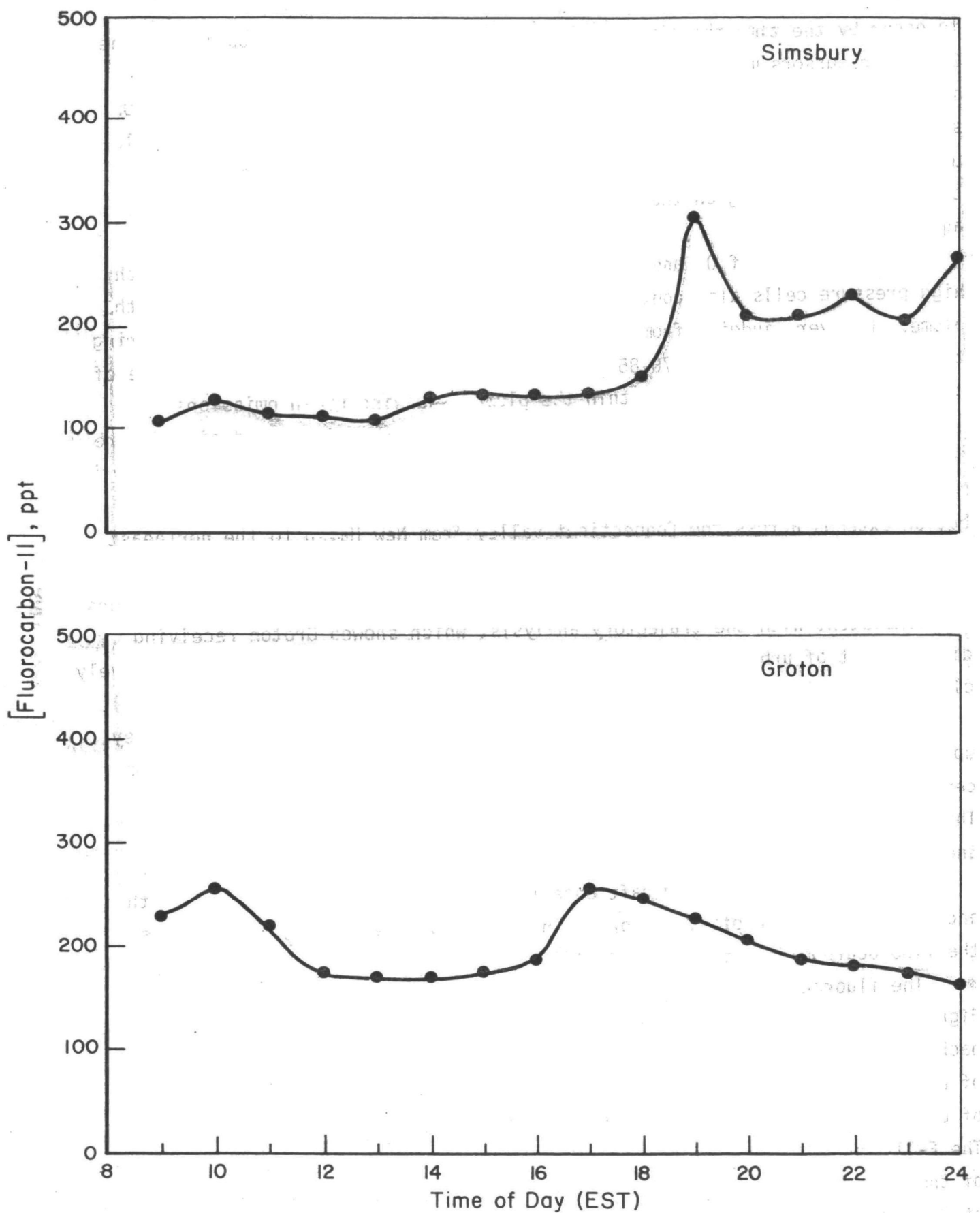


Figure 8. Fluorocarbon-11 profiles for July 23, 1975.

Turning our attention now to the following day, the Simsbury and Groton air mass trajectories for July 24, 1975, are shown in Figure A-5 in the Appendix. The trajectories indicate that the air arriving at Simsbury during most of the day had passed over the major metropolitan complexes of New York and Philadelphia, and to some extent even Washington and Baltimore. The air arriving in Groton during the daytime and evening hours has passed near Baltimore, up the Atlantic coast of New Jersey and across eastern Long Island. Groton apparently receives very little input from New York and Philadelphia on July 24. The forward trajectories from Philadelphia, shown earlier in Figure 6, are in substantial agreement. Air which left Philadelphia at 1400 on July 23 passes over New York in the middle of the night and enters Connecticut in the early morning hours of July 24. On a day such as this it is very possible that an overlapping of urban plumes within the Washington-Boston corridor could occur. Thus,  $O_3$  entering southern New England on July 24 could be the result of emissions from several upwind urban areas. These overlapping urban plumes will be superimposed on any regional  $O_3$  which might result from emissions several hundred miles upwind (e.g., the midwest).

The ozone distribution maps for July 24 are pictured in Figure 9 a-c. At 0900 we can see what are probably the remains of the previous day's high ozone band. Ozone from one day frequently survives overnight by being trapped aloft above the nocturnal inversion away from scavenging surfaces and surface-based scavenging emissions. This ozone aloft then fumigates the surface after the inversion breakup the next day. That this phenomenon occurred on July 23-24 can be seen from vertical  $O_3$  profiles during the evening of July 23 and the morning of July 24. These profiles are shown in Figure 10 a and b. Figure 10a shows a very concentrated layer of  $O_3$  at 2000 feet MSL above Groton at 1600 hours. The  $O_3$  values in this layer aloft (elevated urban plume) are nearly twice the surface concentrations. Thus a reservoir of  $O_3$  exists aloft for possible isolation and survival overnight. A profile obtained at 0855 the next morning over Putnam, in the remote northeast corner of Connecticut, is shown in Figure 10b. It is evident that a reservoir of  $O_3$  still exists aloft (2000-2500 feet MSL) and, because of the early hour, this  $O_3$  must have survived from the previous day. It is highly probable that the high  $O_3$  concentrations observed in east-central Massachusetts at 0900 on the morning of July 24 are the remains of the previous day's urban plume, which was "stored" aloft overnight.

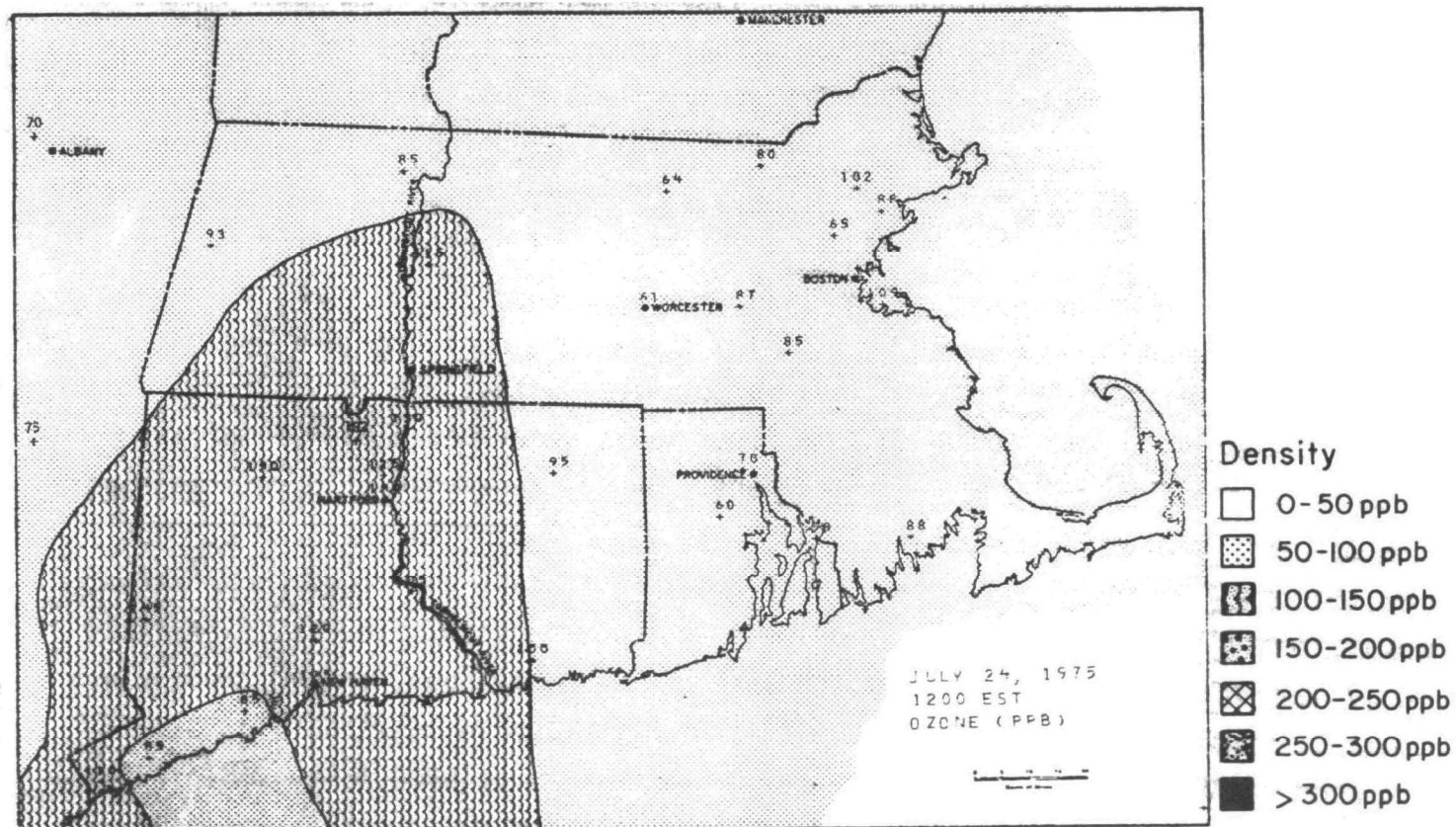
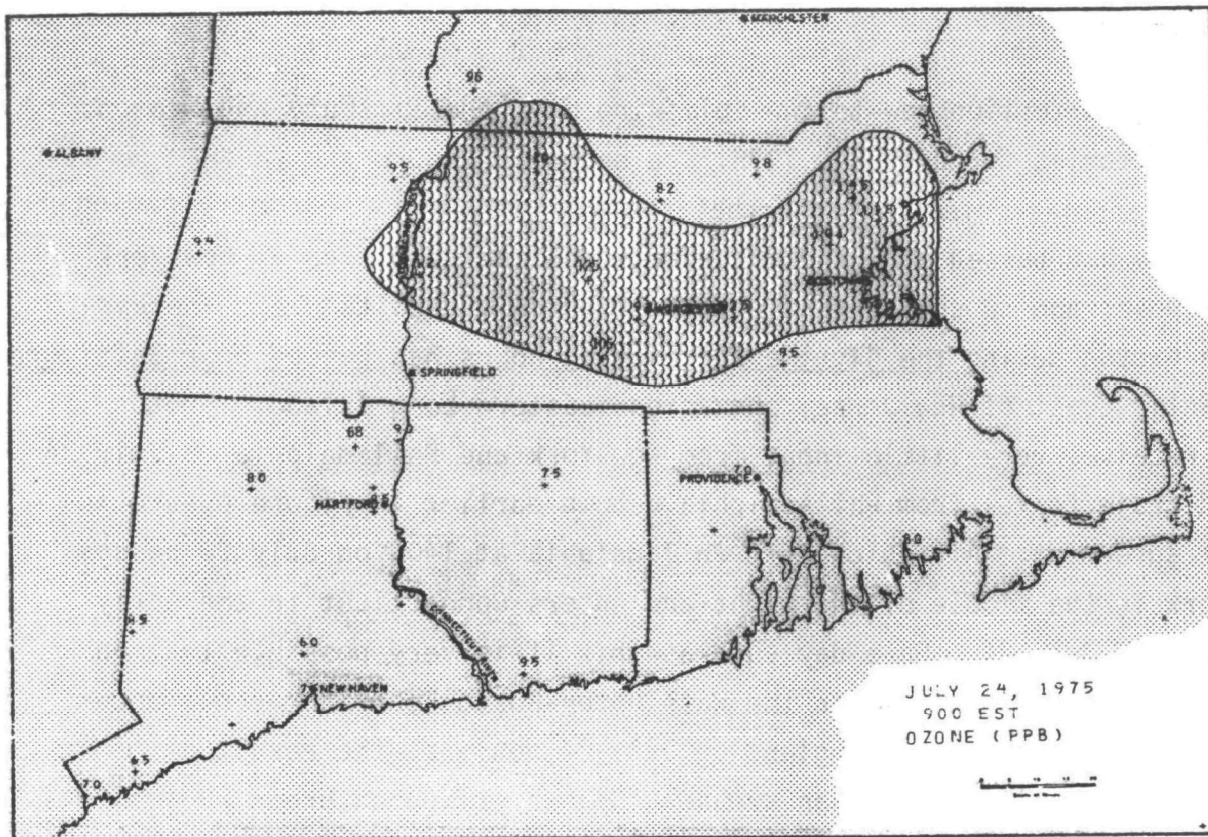


Figure 9a. Ozone distribution in southern New England on July 24, 1975.

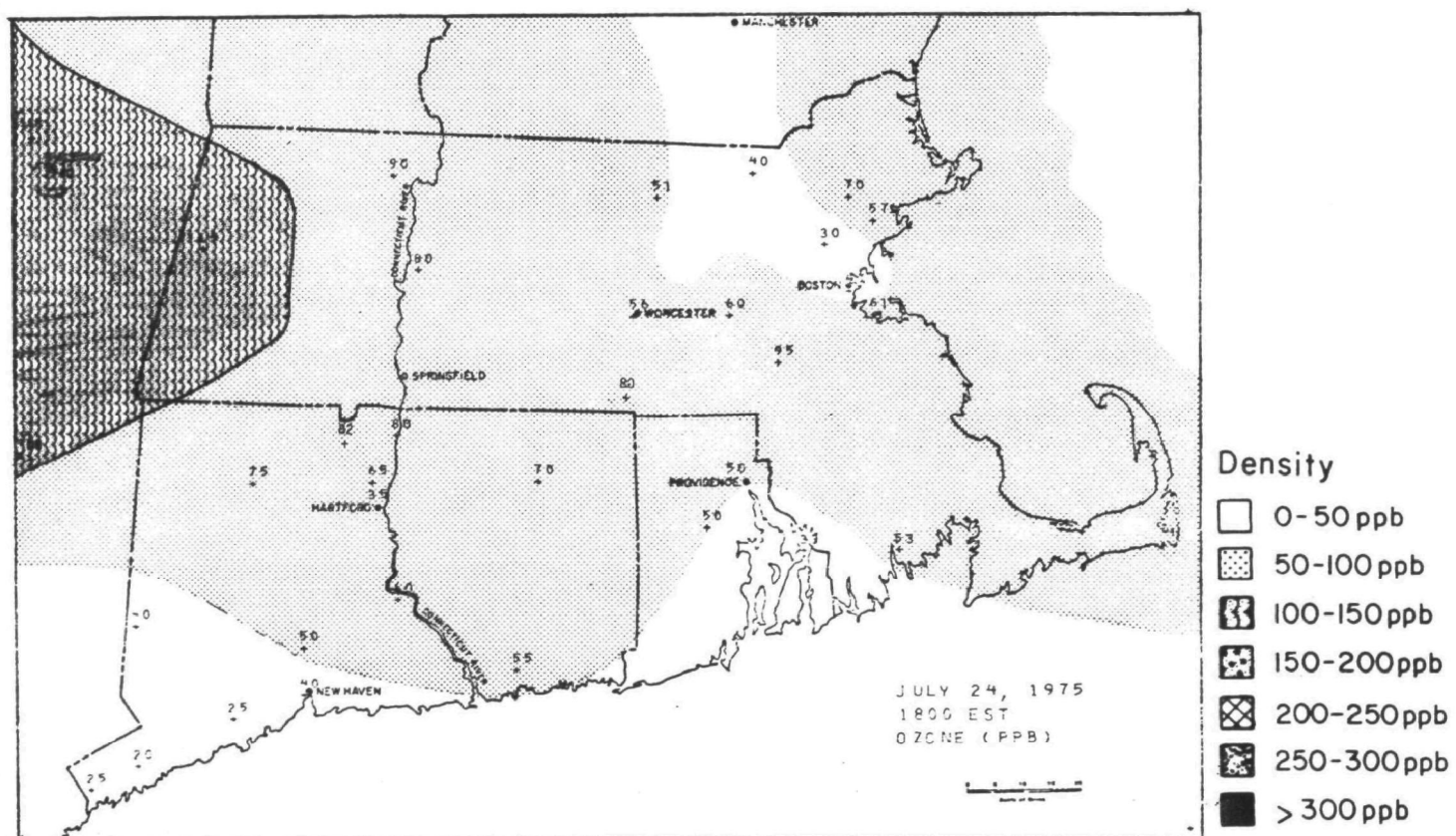
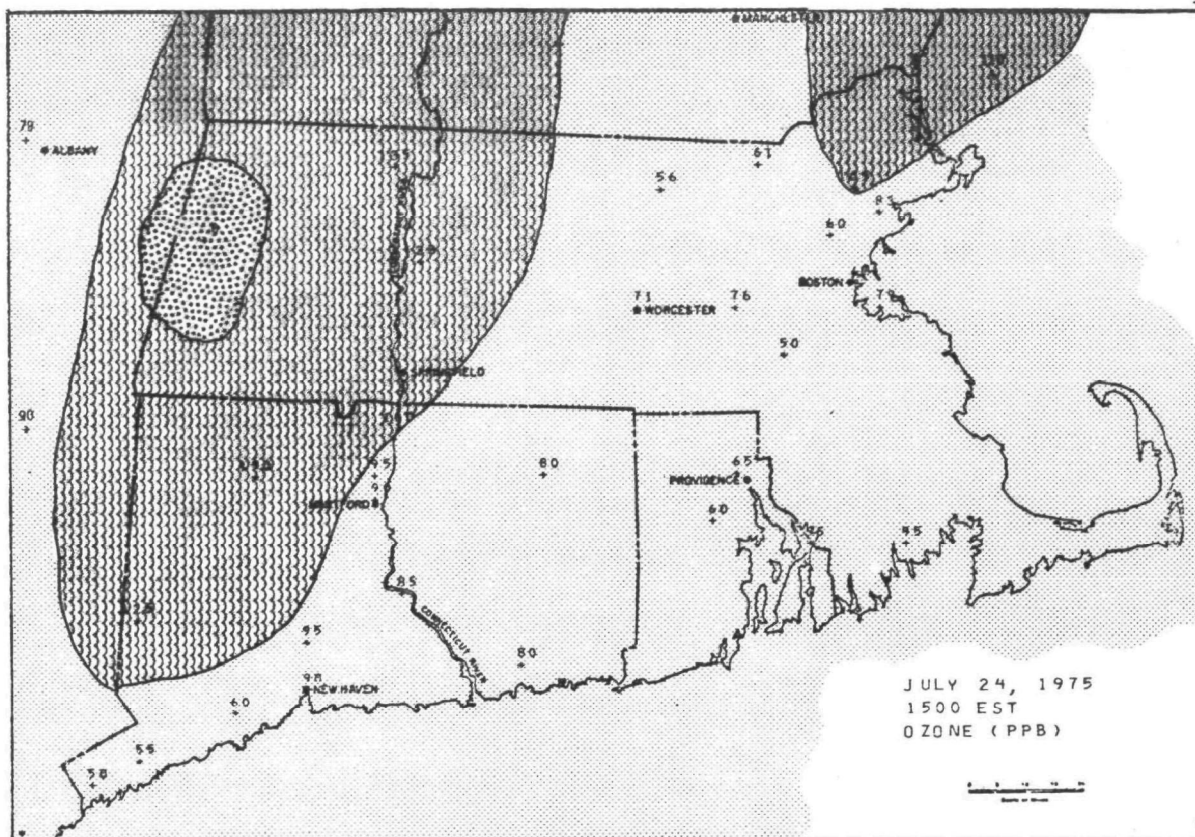


Figure 9b. Ozone distribution in southern New England on July 24, 1975.

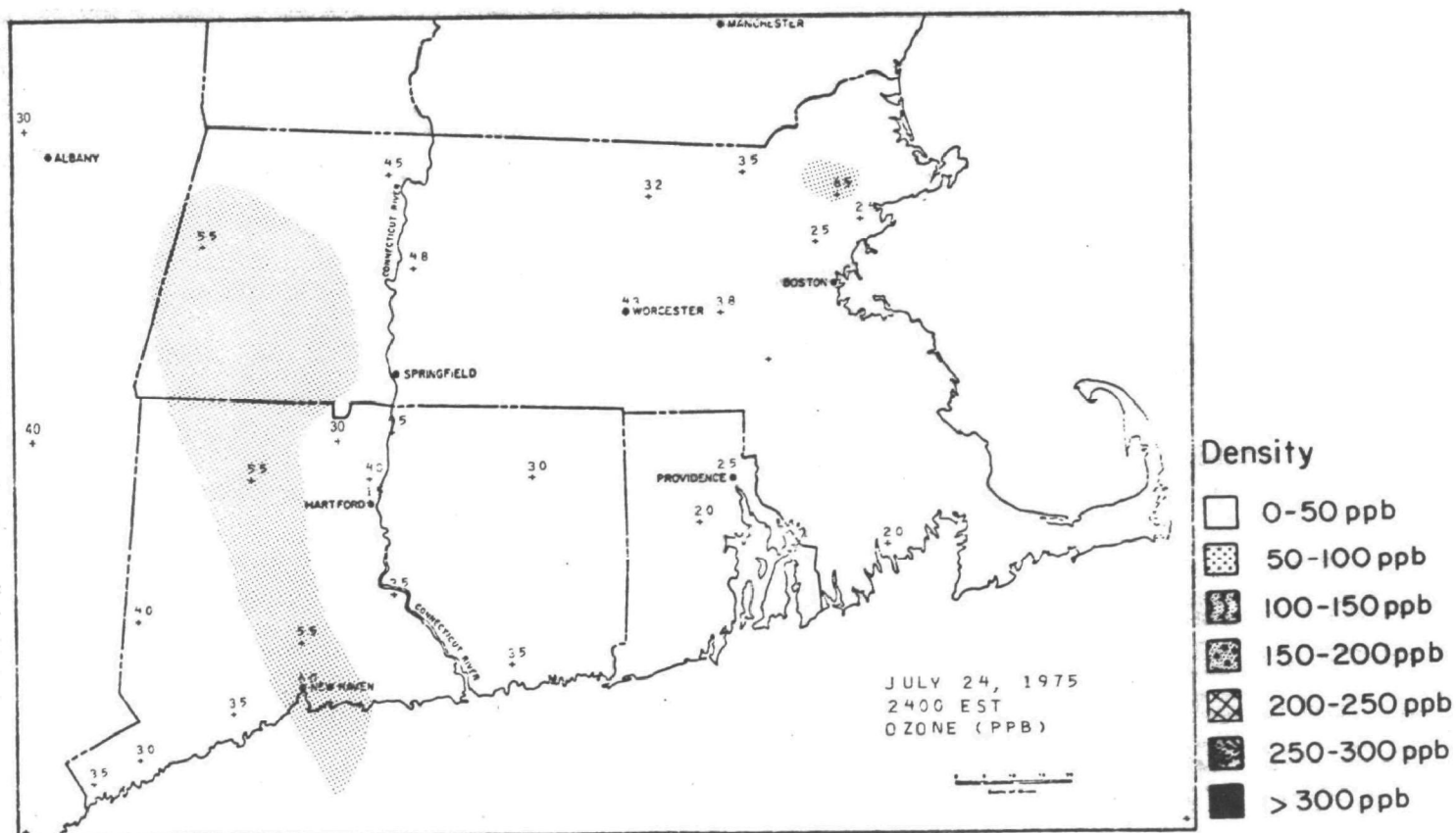
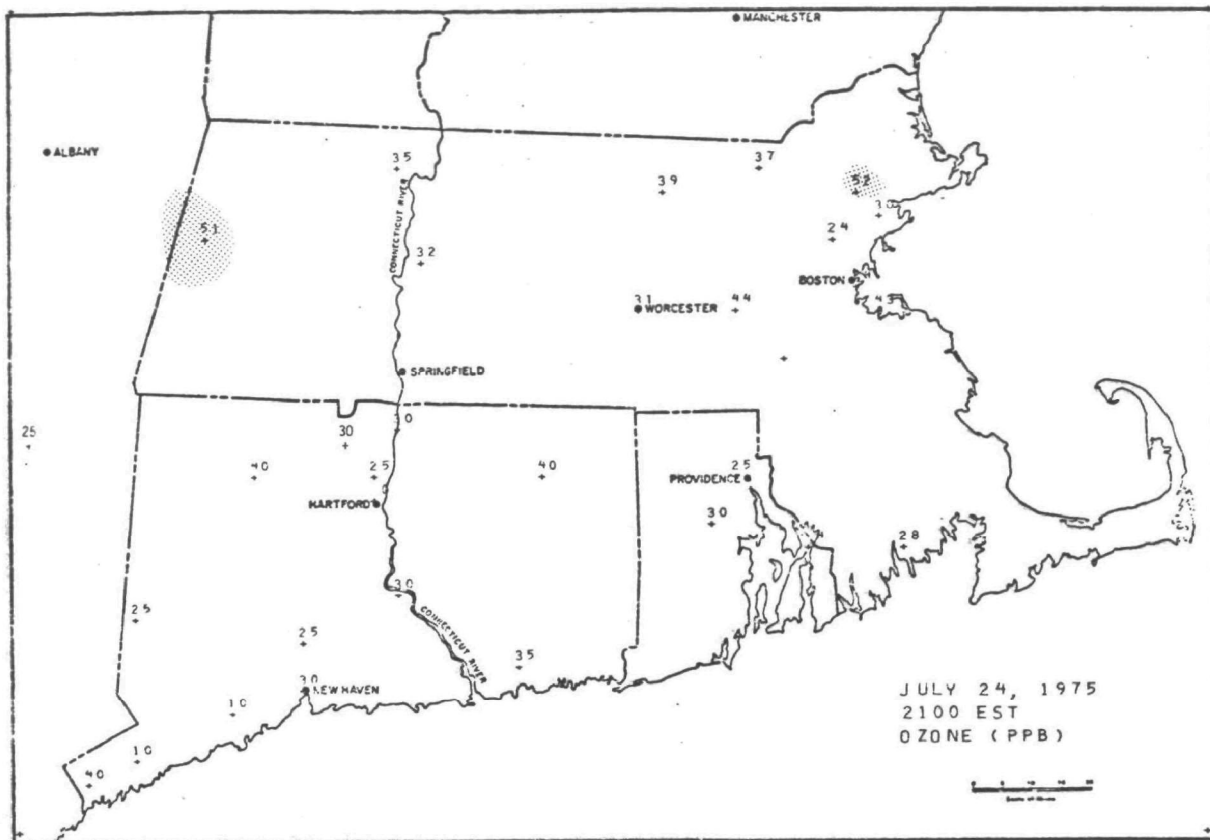


Figure 9c. Ozone distribution in southern New England on July 24, 1975.

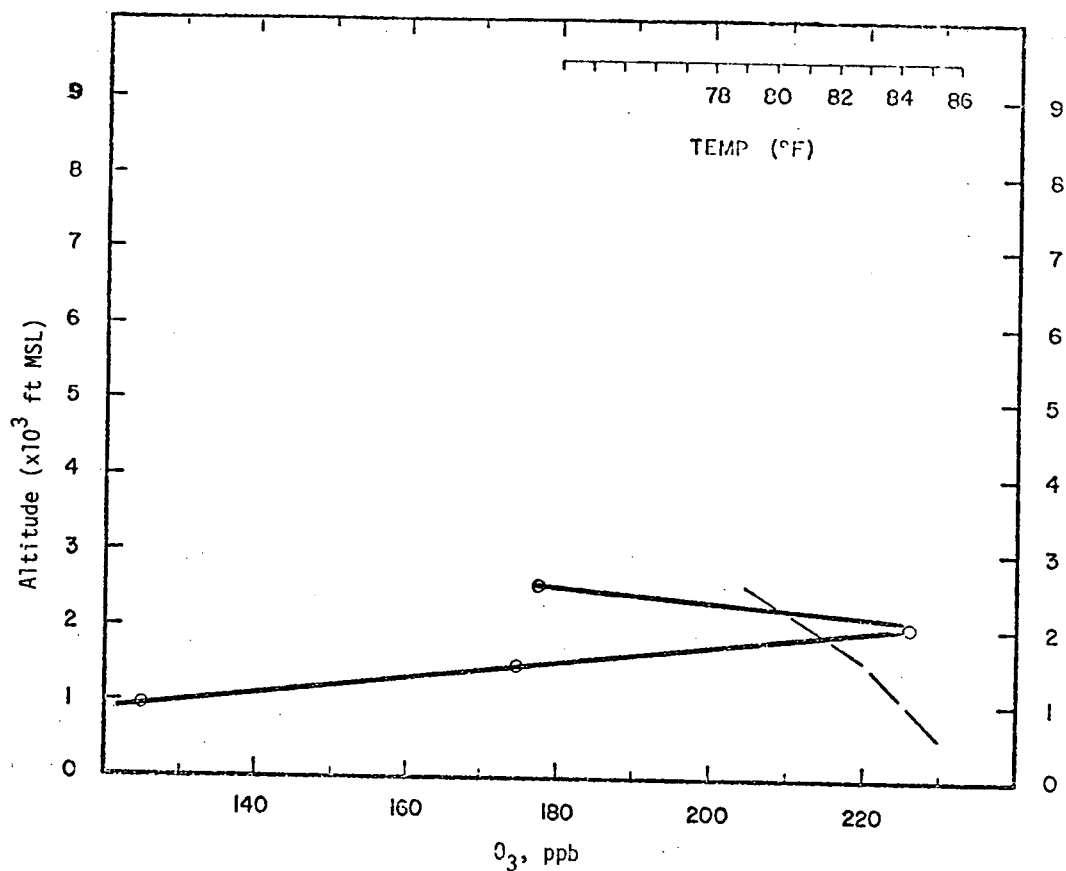


Figure 10a. Vertical ozone and temperature profiles at Groton, Conn., at 1710 EDT, July 23, 1975.

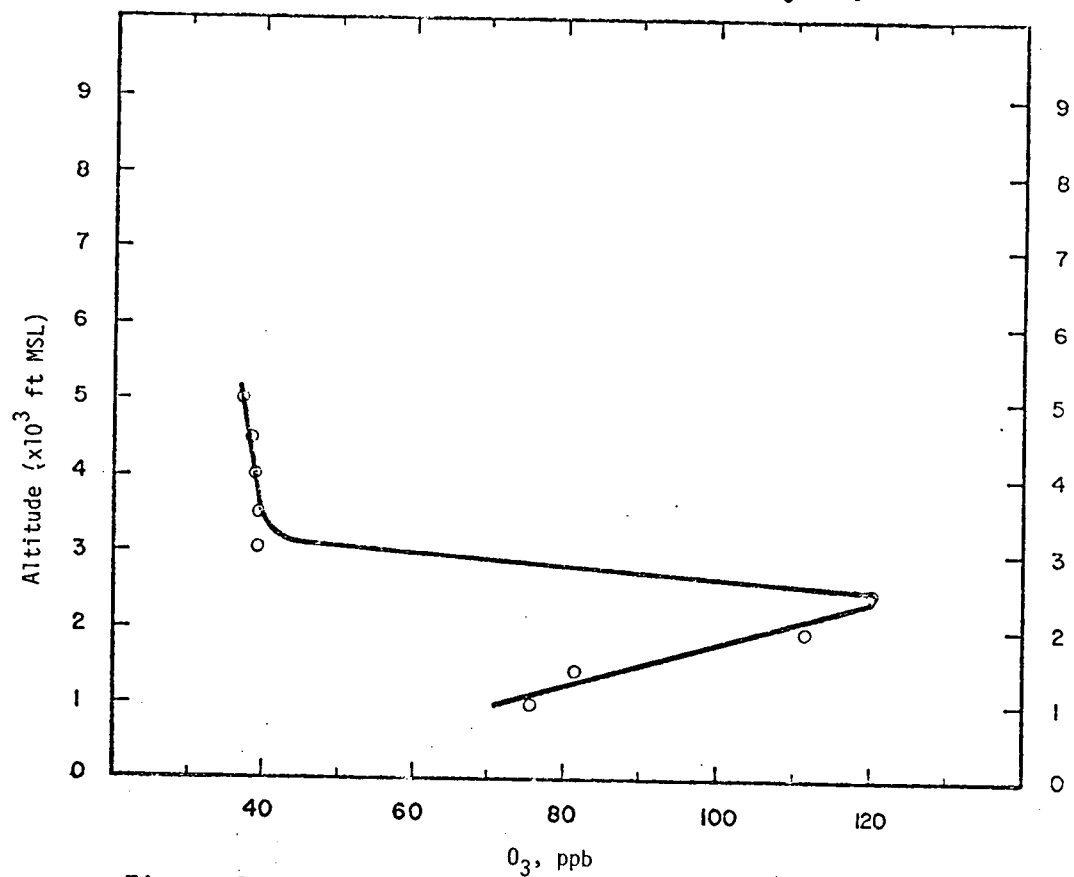


Figure 10b. Vertical ozone profile NE of Putnam, Conn., at 0955 EDT July 24, 1975.



Referring to the  $O_3$  distribution maps, we see that by noon on the 24th, high concentrations of  $O_3$  exist throughout western Connecticut and southwestern Massachusetts. This is consistent with the trajectories and our earlier observation of a shift toward more southerly flow on the 24th. High concentrations of ozone are found within the Connecticut River Valley and also to the west of the valley (e.g., Torrington and Danbury).

By 1500 the area of high ozone concentration has spread further northward, with fairly remote areas of northwest Massachusetts exceeding the federal standard by wide margins. At 1800 only far western Massachusetts and part of eastern New York showed  $O_3$  in excess of 100 ppb. Subsequent to 1800 EST, the  $O_3$  levels throughout the region dropped to well below the 80 ppb standard.

As on the previous days that we have discussed, no special effect of the Connecticut River Valley is evident from the  $O_3$  distribution data. Levels of  $O_3$  found within the valley were no greater than those found outside. A tabulation of ozone concentrations across the valley illustrates this point and is included in Table 5. Once again the high concentration of ozone found within the valley in early afternoon and in remote northwestern Connecticut and western Massachusetts later in the day seems to originate from a source upwind (southwest) of the region. As discussed earlier, the source of precursors could be any one of several upwind urban areas. More likely several upwind urban areas each contributed in different degrees to the ultimate burden of  $O_3$  in the air mass.

TABLE 5. EAST-WEST OZONE CROSS-SECTIONS ACROSS THE CONNECTICUT RIVER VALLEY - JULY 24, 1975

Time	West of Valley (Station)	Within Valley (Station)	East of Valley (Station)
1200	145 ppb (Danbury)	120 ppb (Hamden)	100 ppb (Groton)
1200	140 ppb (Torrington)	125 ppb (Windsor)	95 ppb (Eastford)
1500	168 ppb (Pittsfield)	135 ppb (Greenfield)	120 ppb (Aircraft)

The fluorocarbon profiles from Groton and Simsbury on July 24, shown in Figure 11, are not very revealing due to lack of structure.

A somewhat different perspective on  $O_3$  transport during the July 23-24 episode may be gained from combining the aircraft data collected by Battelle-

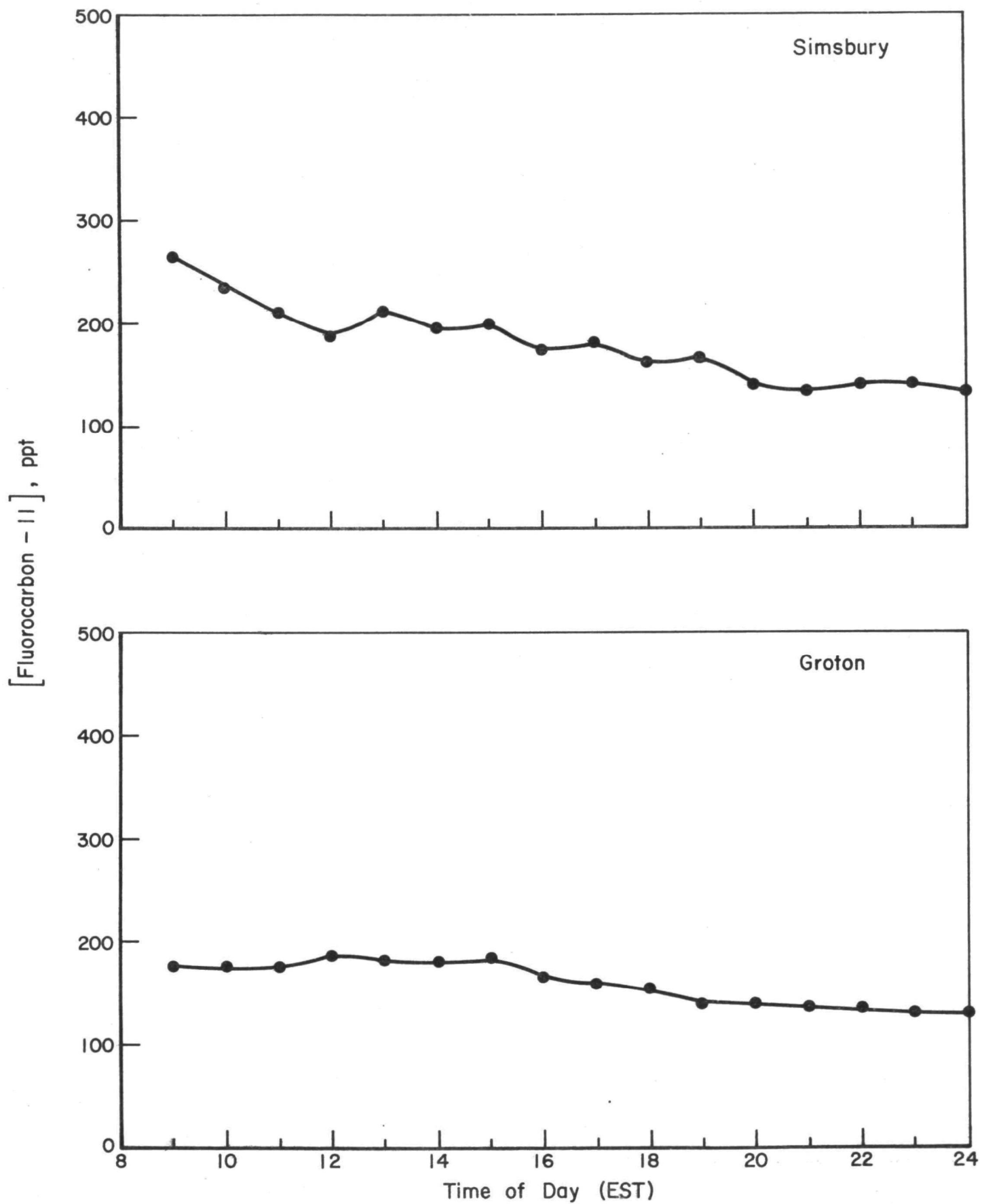


Figure 11. Fluorocarbon-11 profiles for July 24, 1975.



Columbus and Washington State on these days. Using area averages to represent different segments of the flight patterns, we obtain the maps of  $O_3$  distribution at 1000 feet AGL shown in Figure 12 a-d. Referring to these maps we see that  $O_3$  concentrations were moderate throughout the region during the morning of July 23. By the afternoon of the 23rd the concentration of  $O_3$  over southern Connecticut and Long Island Sound reached extremely high values (Figure 12b), in agreement with the surface  $O_3$  distribution maps shown earlier. On the morning of July 24, Figure 12c shows the  $O_3$ -rich air mass residing over northern and northeastern Massachusetts. We have already demonstrated the likelihood that this morning's  $O_3$  resulted from the previous afternoon's urban plume which survived aloft overnight.

The aircraft data on the afternoon of July 24 are found in Figure 12d and are quite interesting. Recall from the  $O_3$  maps in Figure 9 that a new urban plume has formed during the afternoon on the 24th, causing high levels of  $O_3$  in western Connecticut and Massachusetts. The aircraft data do not show the new urban plume because the planes were still tracking the plume from the previous day. It is clear from Figure 12 that high concentrations of  $O_3$  had moved northeastward up the Atlantic coast to areas northeast of Portland, Maine. Vertical profiles during the flight over the ocean showed the maximum  $O_3$  was concentrated in a fairly thin layer about 2000 feet above the sea. With southwest to south-southwest winds of about 20 mph existing throughout the region on July 24 (Table 4) the  $O_3$ -rich air mass residing over northeastern Massachusetts in the morning would require about 8 hours to reach the area northeast of Portland in late afternoon. Eight hours is about the time difference between Figure 12c and Figure 12d. Thus it seems likely that the high  $O_3$  in the air mass found off the coast of Maine in late afternoon was from the same  $O_3$ -rich air observed in northeast Massachusetts in the morning and was partly the remnants of the metropolitan New York urban plume from the previous day. Urban areas along the trajectory, most notably Boston, probably contributed significantly to the precursor burden of the air mass (the effect of overlapping urban plumes discussed earlier). However, the existence of high levels of  $O_3$  early in the morning in northeastern Massachusetts, observed before locally emitted precursors could have generated significant  $O_3$ , suggests that the contribution of the previous day's urban plume is significant. The interaction between the aged plume from the previous day and fresh local emissions can also be an important factor in the rate of  $O_3$  generation (e.g., by affecting the  $NO_2/NO_x$  ratio) as the overlapping plumes move downwind.



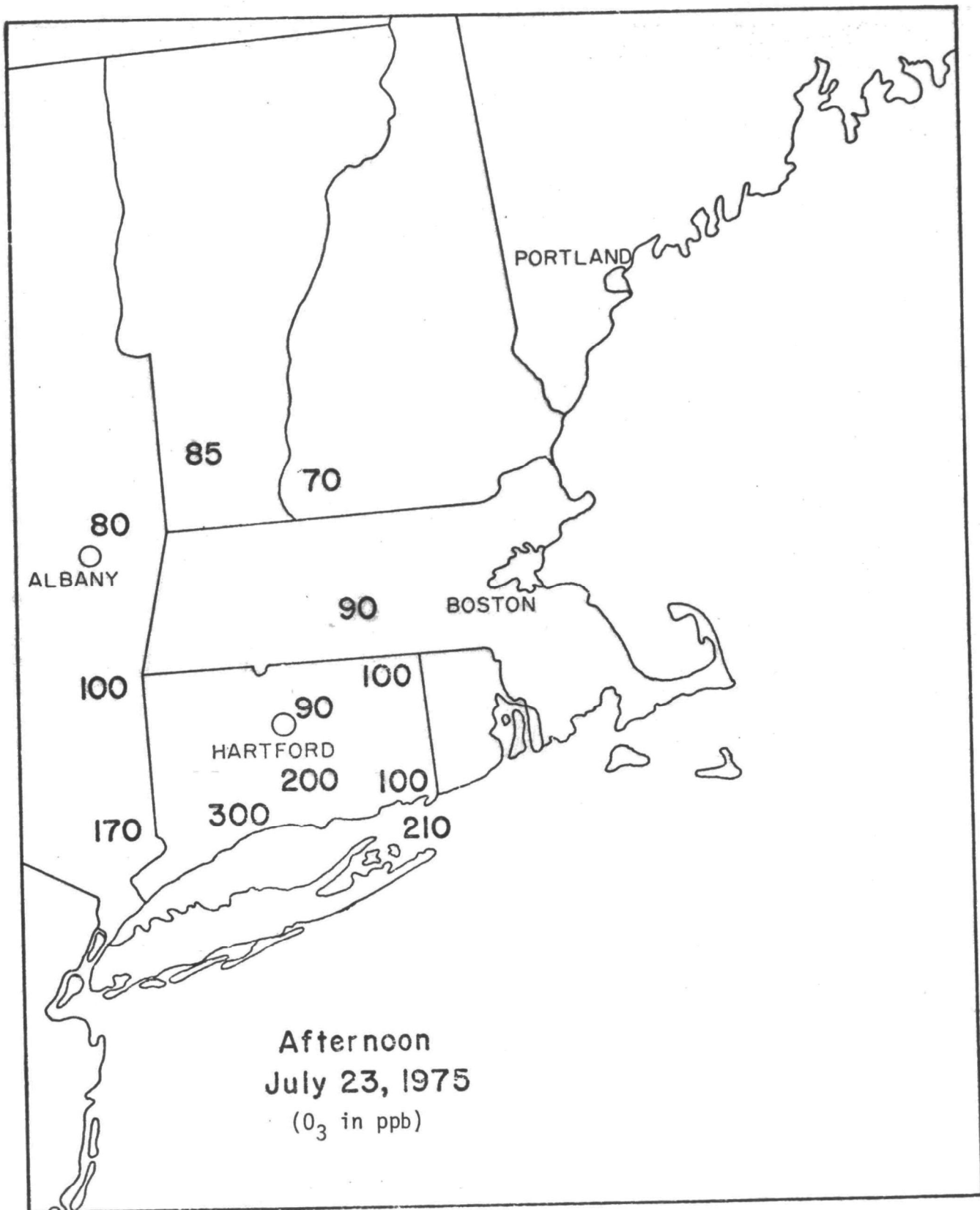


Figure 12b. Ozone concentrations at 1000 feet AGL from aircraft.

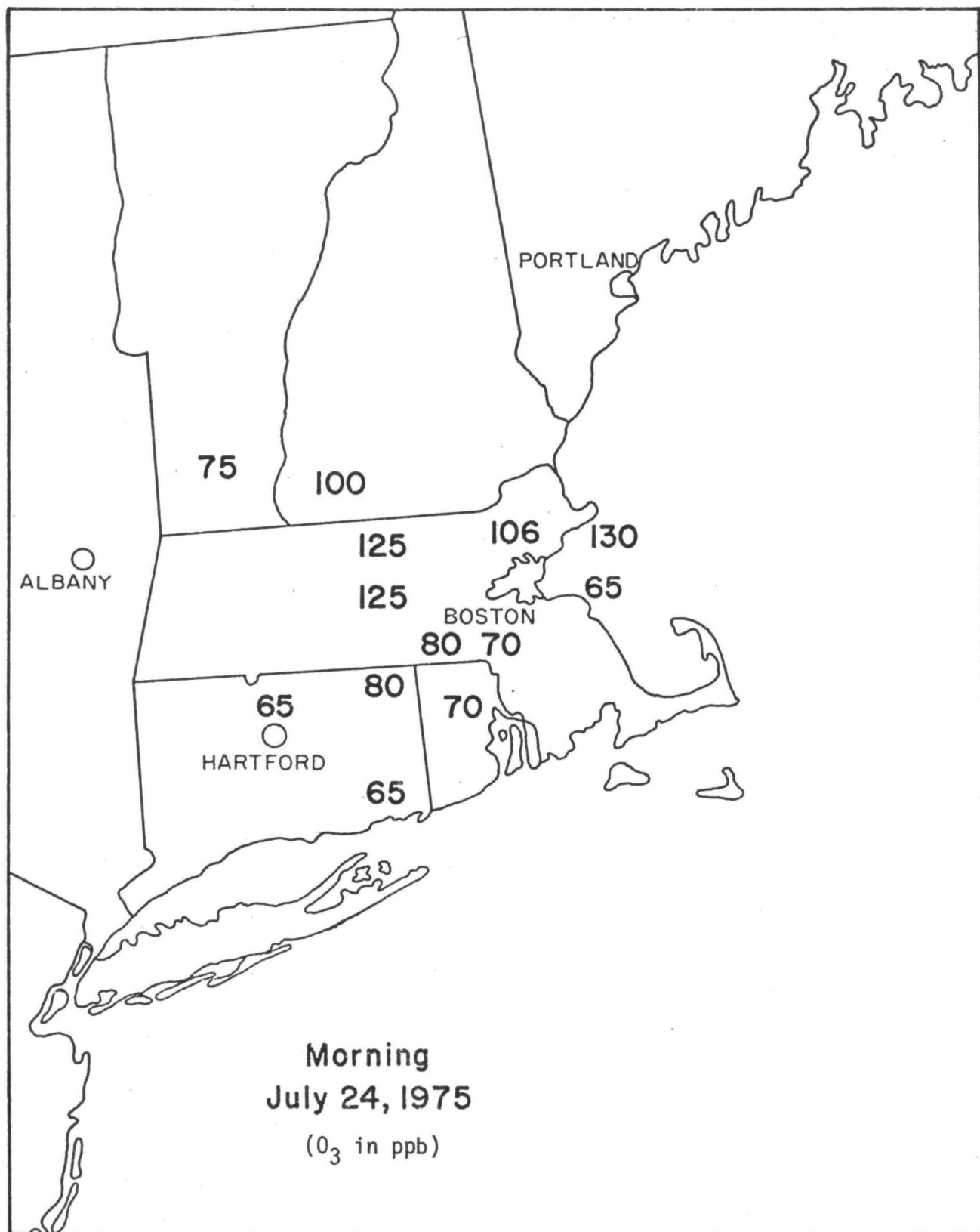


Figure 12c. Ozone concentrations at 1000 feet AGL from aircraft.

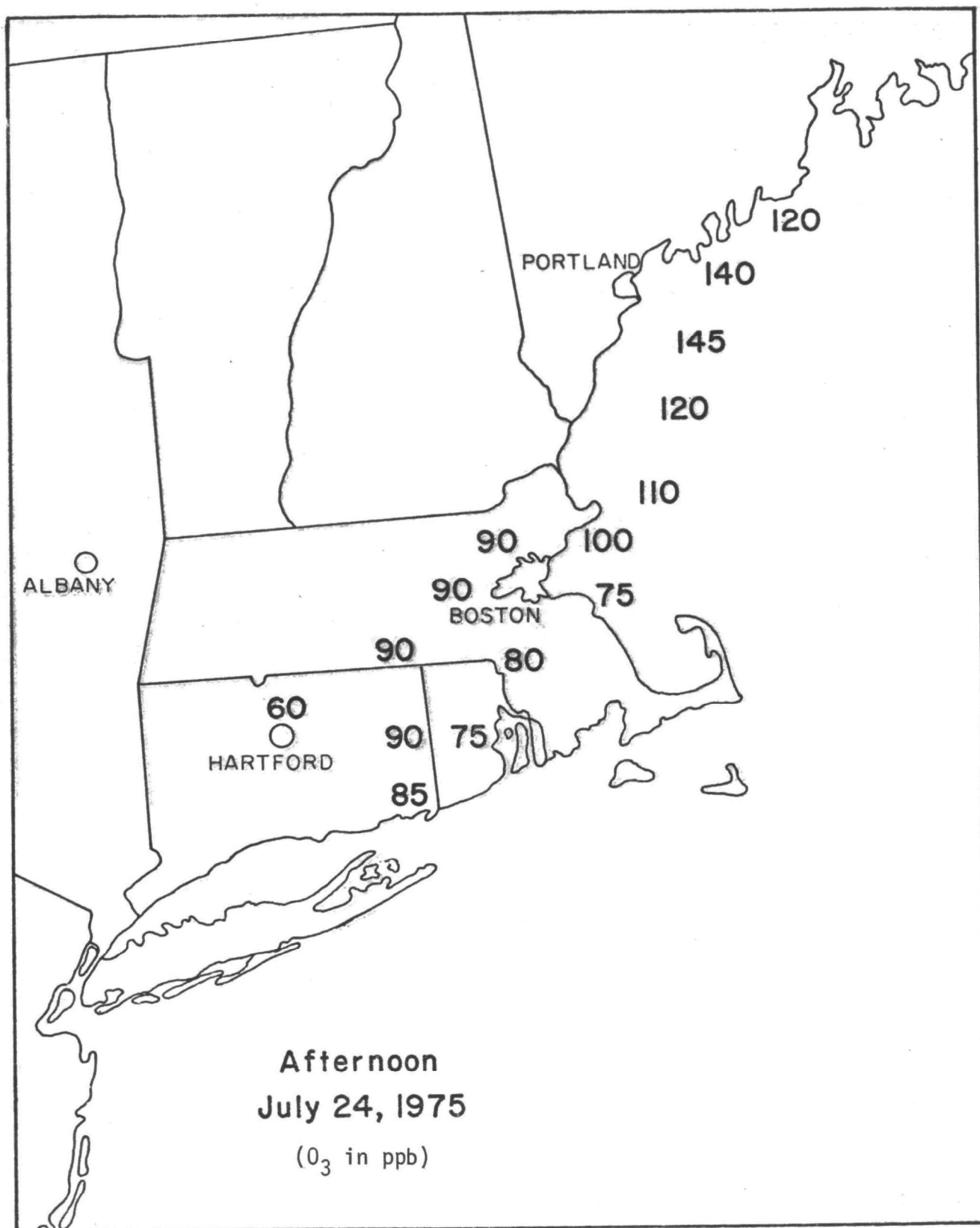


Figure 12d. Ozone concentrations at 1000 feet AGL from aircraft.

One final demonstration of ozone transport during this 2-day episode can be obtained from the diurnal ozone profiles from the surface stations. Profiles of  $O_3$  from stations along the southwest-to-northeast air mass trajectory between southwestern Connecticut and northeastern Massachusetts should show progressively later  $O_3$  maxima. Profiles from several ground stations have been plotted together in Figure 13. Stations from southwestern Connecticut (Bridgeport at the top of the figure) to northeastern Massachusetts (Salem near the bottom of the figure) are shown, along with a background site (Pittsfield) from western Massachusetts which is well out of the path of the July 23 urban plume (Pittsfield is in the path of the July 24 plume, as shown earlier). Lines have been drawn through each profile at the 80 ppb level for reference. It is clear from the figure that there is a progression in the time of maximum  $O_3$  along a southwest to northeast trajectory. Since these are surface data, the nighttime readings may be misleading due to scavenging below the nocturnal inversion. However, the occurrence of the  $O_3$  maximum early on the morning of July 24 in Framingham, Cambridge, and Salem, suggests that this  $O_3$  originated on the previous day and was transported into the area.

To summarize briefly, the July 23-24 ozone episode in southern New England can be attributed to the combination of (1) urban plumes entering the region from the southwest, (2) regional  $O_3$  associated with the residing high pressure system, and (3)  $O_3$  generated from local emissions. During this particular period, urban plumes seem to be the predominant contributor. No special effects of the Connecticut River Valley were apparent; high ozone in the valley resulted from the addition of  $O_3$  generated by local emissions to  $O_3$  in the urban plume crossing the valley. Evidence was also presented for the overnight survival of  $O_3$  aloft, with subsequent fumigation of the surface when the inversion broke the next day. An  $O_3$ -rich air mass which entered the region from the southwest early in the afternoon of July 23 was observed the following morning over northeast Massachusetts and late that same afternoon off the coast of Maine. These observations suggest that transport of  $O_3$  within urban plumes over distances of nearly 400 miles may be possible. It was not possible to define the role played by the overlapping of urban plumes in such long distance transport.

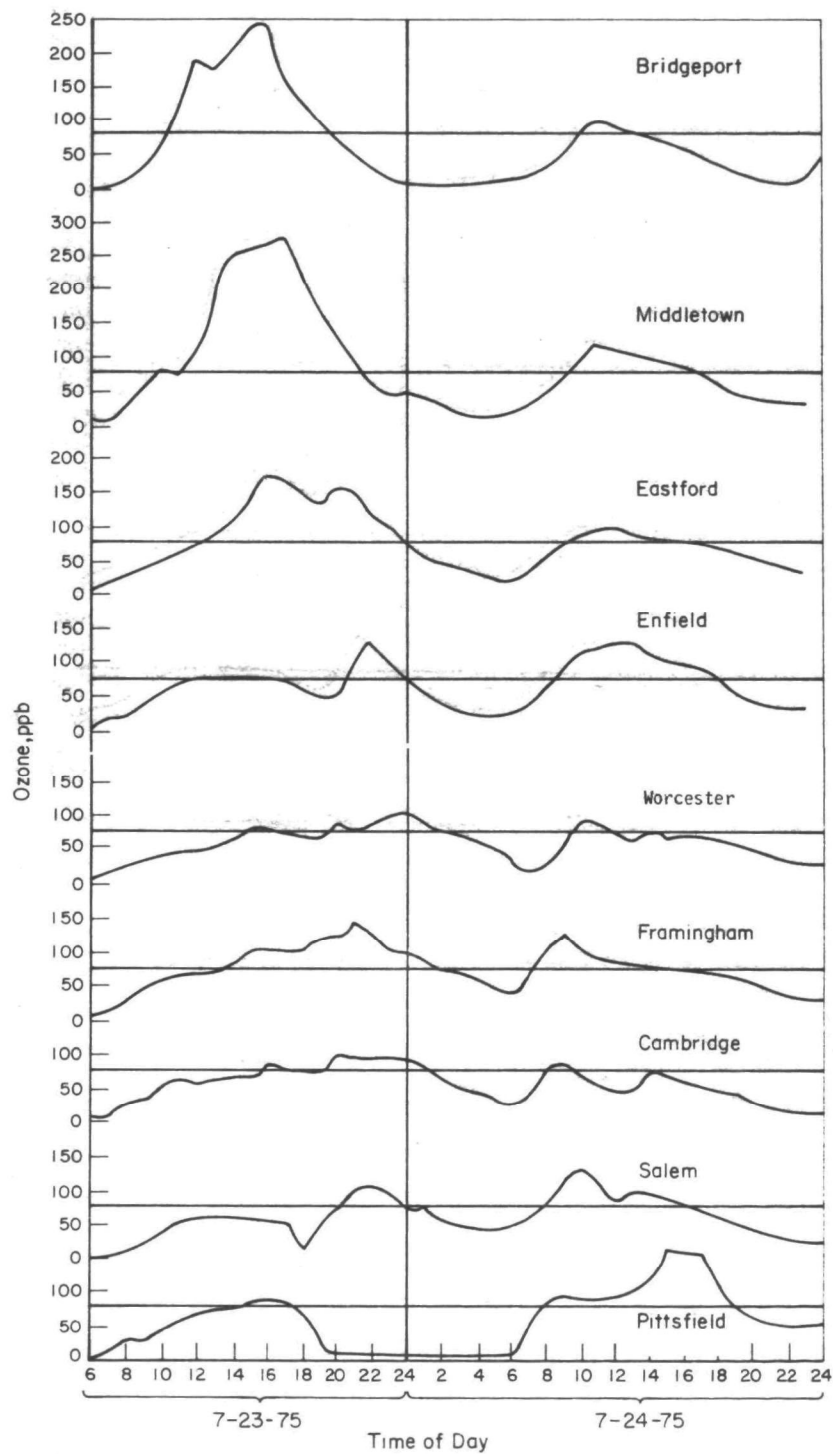


Figure 13. Selected New England ground level ozone profiles-July 23-24, 1975.

AUGUST 10, 1975

August 10, 1975, was a hot hazy day in the Connecticut River Valley. A high pressure system centered near North Carolina and a low northeast of the region influenced conditions on this day. A surface trough extended along much of the east coast of the United States. Figures A-6 and A-7 in Appendix A show the calculated trajectories for Simsbury and Groton. Flows were generally from the west to northwest. The speed and direction of the winds at 1000 feet for several representative locations within the region are given in Table 6. These data indicate northwesterly winds in the morning shifting to westerly sometime before noon.

TABLE 6. WINDS AT 1000 FEET ON AUGUST 10, 1975

Time	Location	Speed, mph	Direction, degrees
0700	Chatham, Mass.	22	295
0755	Boston, Mass.	17	329
0807	Springfield, Mass.	10	290
0815	Avery Point, Conn.	23	292
0830	Putnam, Conn.	13	307
1110	Avery Point, Conn.	12	267
1408	Springfield, Mass.	16	285
1425	Avery Point, Conn.	23	261
1900	Chatham, Mass.	29	260

The ground level ozone distributions are presented in Figure 14 a-c. The concentrations at 0900 EST throughout the region were similar and moderately high for this time of day, suggesting the possibility that the high pressure system over the region may be having a region-wide impact on ozone concentrations. This will be discussed shortly.

At noon high concentrations of  $O_3$  exist throughout western Connecticut and Massachusetts; indeed the entire portion of the Connecticut River Valley within Connecticut and Massachusetts is experiencing high levels of  $O_3$ . By 1500 EST high  $O_3$  is observed all along the southern New England coast and as far north as Hartford. Ozone levels throughout the rest of the region are generally in excess of the federal standard. Throughout the remainder of the day the area of high  $O_3$  remained along the southern coast.

With westerly and northwesterly winds it seems likely that the high  $O_3$  along the coast (and over Long Island and the Sound, as we will show shortly)



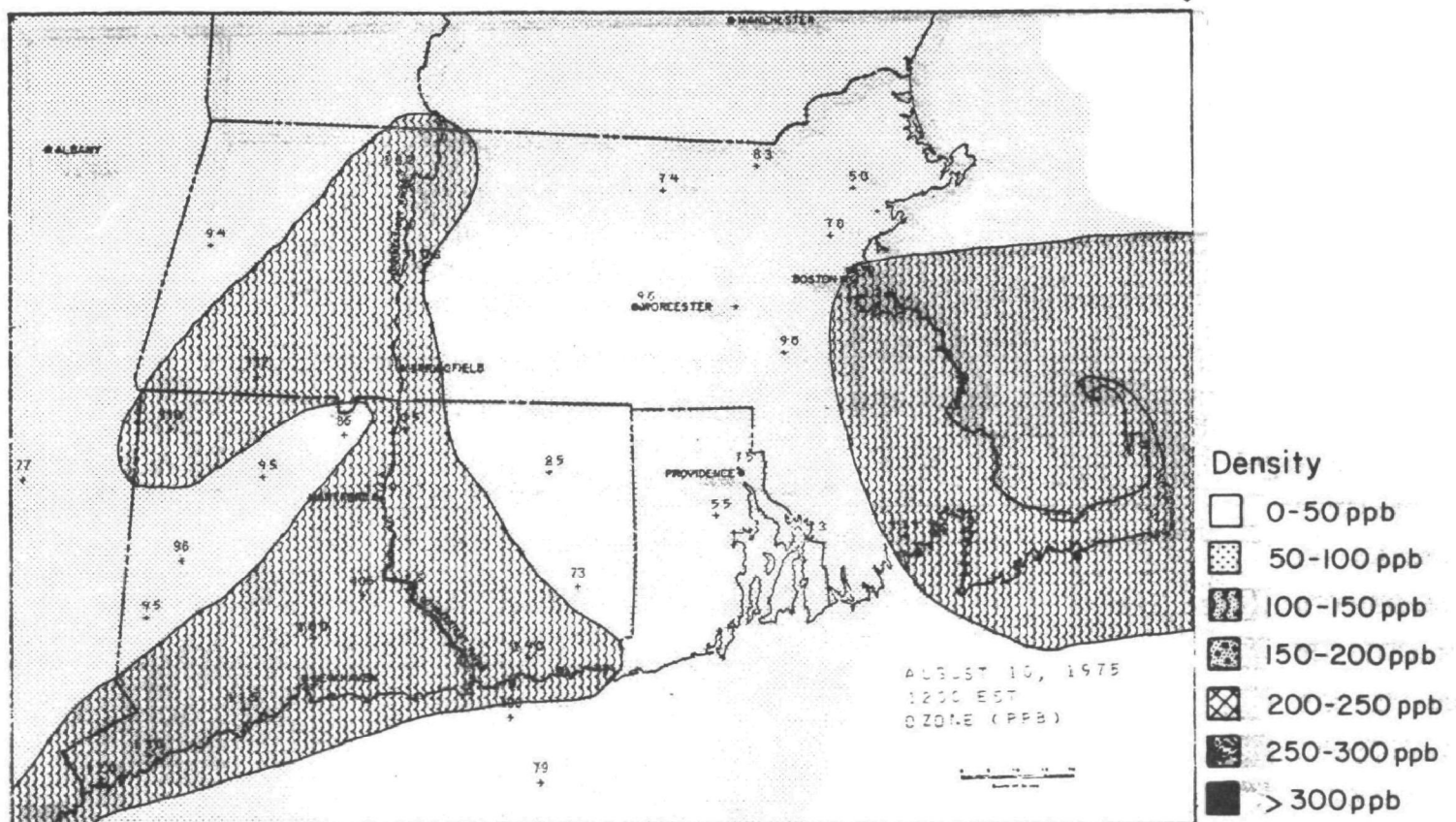
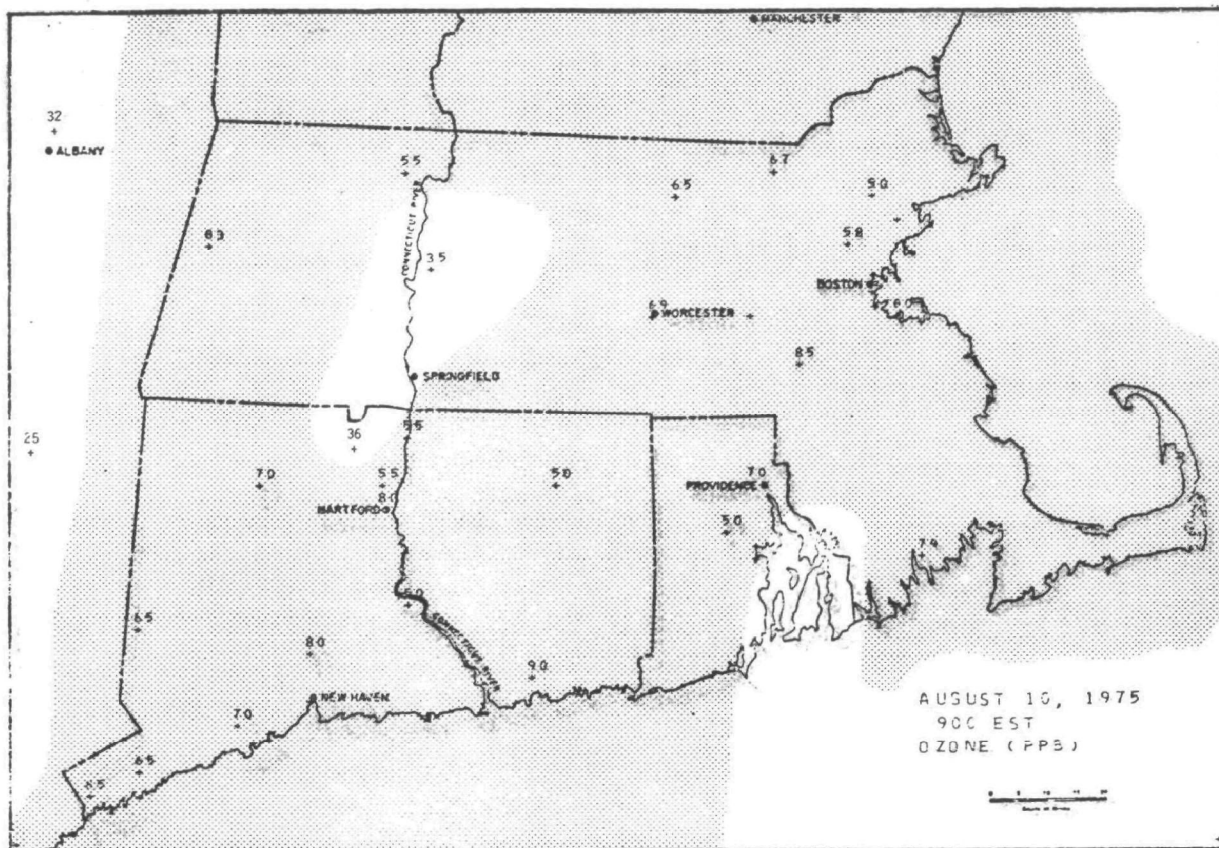


Figure 14a. Ozone distribution in southern New England on August 10, 1975.

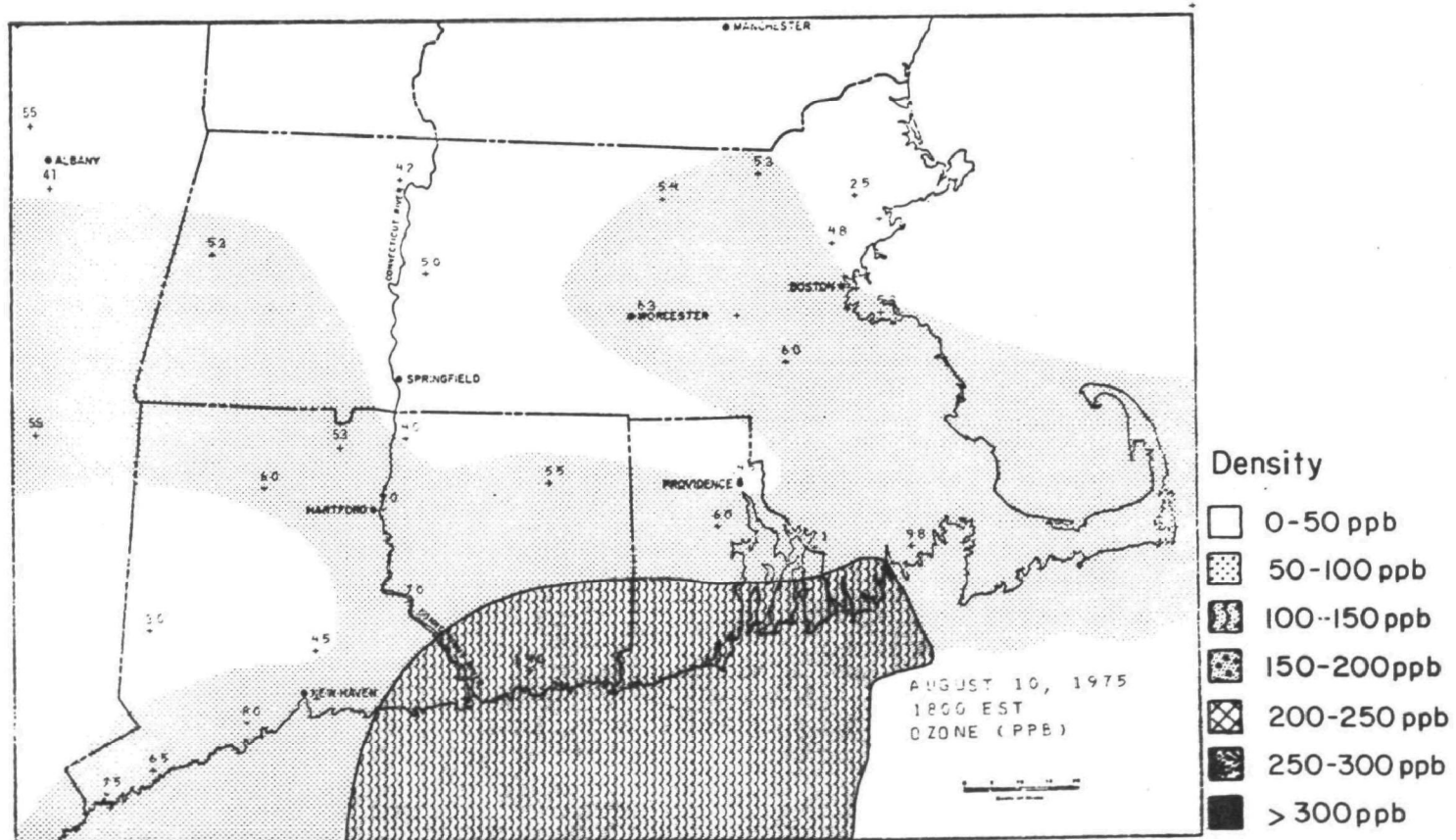
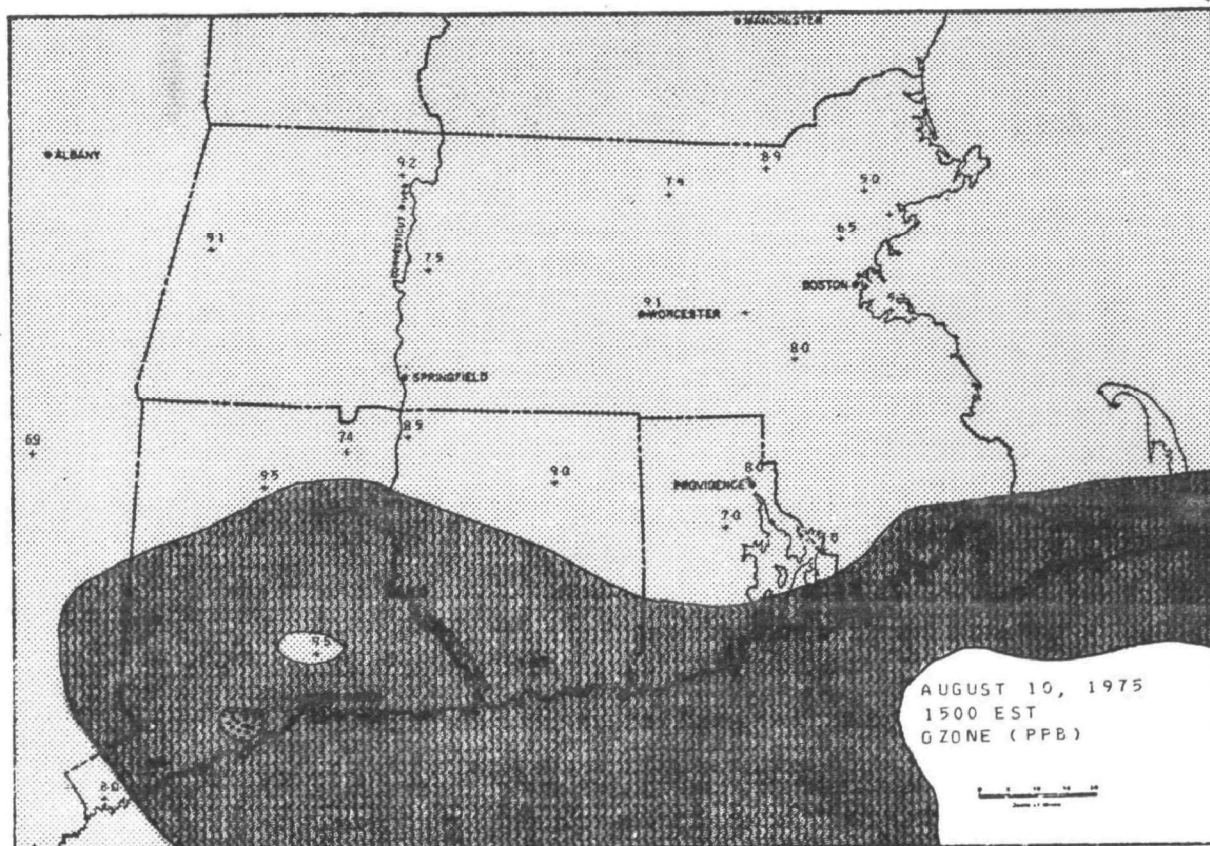


Figure 14b. Ozone distribution in southern New England on August 10, 1975.

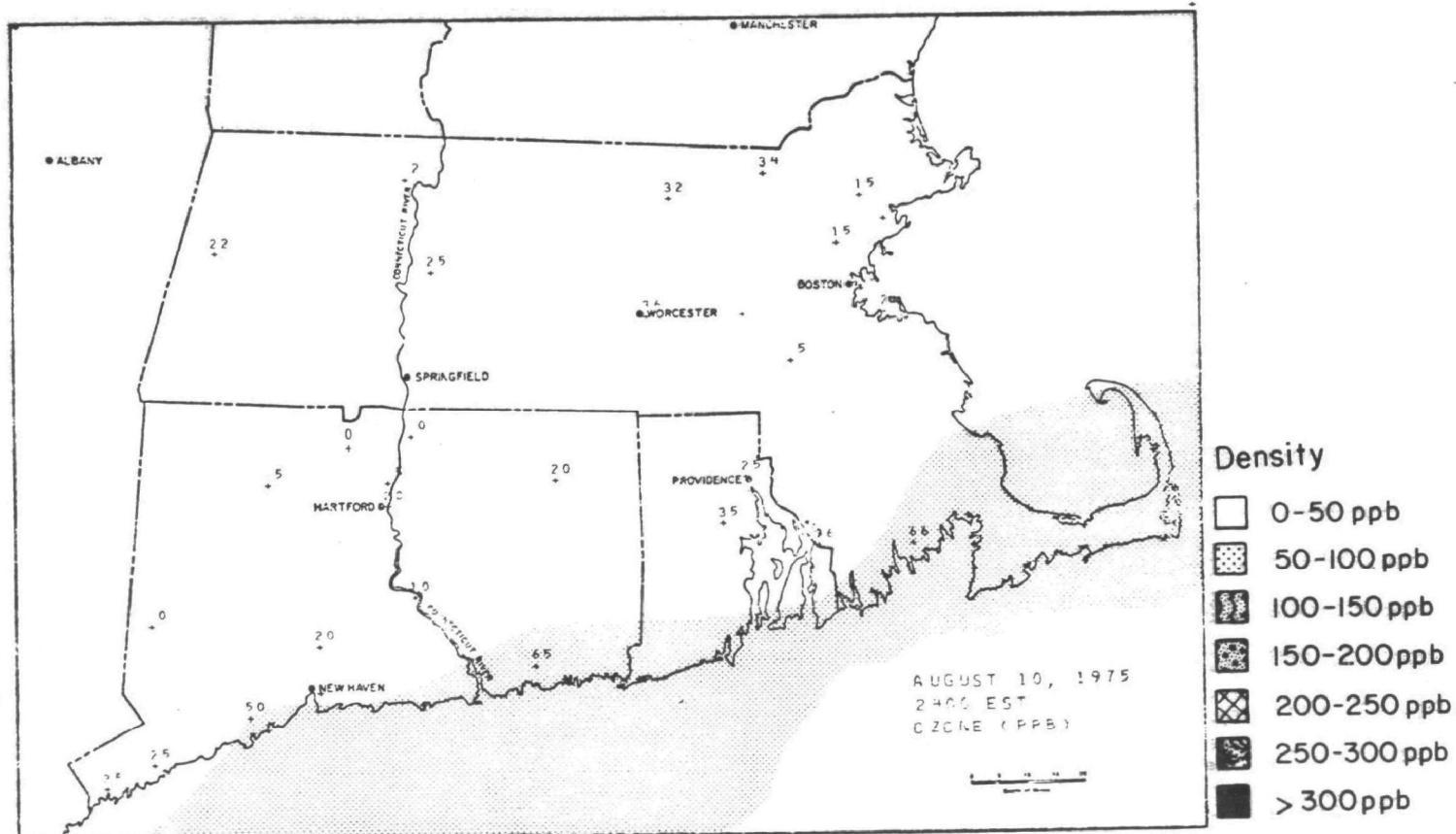
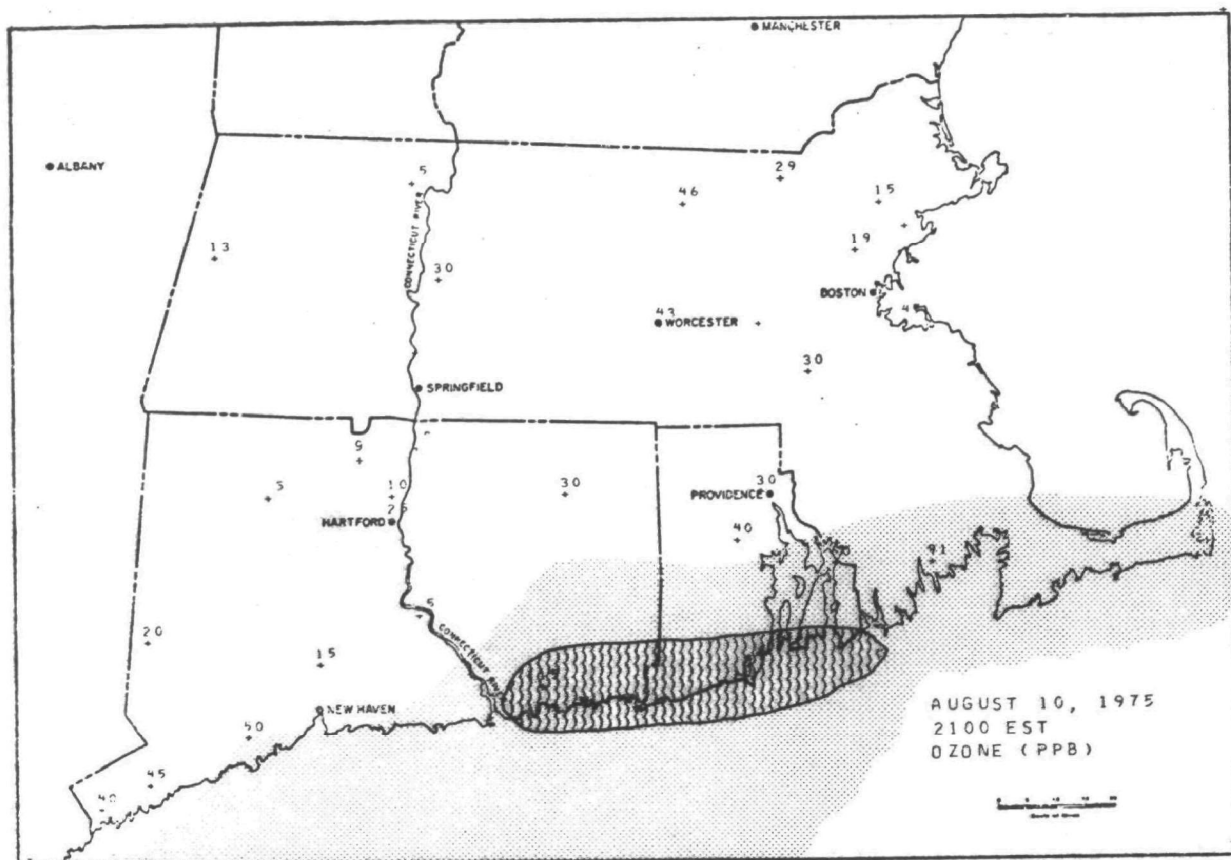


Figure 14c. Ozone distribution in southern New England on August 10, 1975.

is part of the metropolitan New York urban plume. As on previous days, there is no evidence for a unique source of  $O_3$  in the Connecticut River Valley.

The  $O_3$  concentrations in Simsbury and Groton were quite different on August 10. Simsbury experienced only moderate  $O_3$ , consistent with the trajectories which showed a lack of major upwind sources. Groton experienced rather high  $O_3$  concentrations on this day. Early in the day Groton lay directly downwind of Hartford, while later it should be on the fringe of the New Jersey-New York-southern Connecticut urban plume. The fluorocarbon data in Figure 15 also suggest this possibility. Early in the day, the level of F-11 at Groton was more than twice that at Simsbury, and later in the afternoon and evening F-11 at Groton reached very high values consistent with a major urban plume.

Further exploration of the  $O_3$  distribution is possible through the aircraft data shown in Figure 16. This plot represents the results of a cross-sectional pattern flown during the early afternoon of August 10, 1975. Four vertical profiles and horizontal data at 1000 feet AGL were obtained along the approximately north-south line from the south shore of Long Island to the Massachusetts-Connecticut border. With westerly winds the southern portion of this flight should overlap the metropolitan New York urban plume. The vertical and horizontal data along this flight path have been used to construct the computer-derived distribution map of  $O_3$  shown in Figure 17. Horizontal and vertical distances are shown on the abscissa and ordinate, respectively. The ozone concentration is represented by the shading density. The effect of the urban plume is shown quite clearly in the lower right-hand corner of the plot. This part of the study area is directly downwind of metropolitan New York. A similar pattern flown almost simultaneously approximately 70 miles further east (downwind) also shows the highest levels of  $O_3$  just off the southern shore of Long Island<sup>(15)</sup>. The maximum concentration of 140 ppb was observed at the surface. It is interesting that the concentration of  $O_3$  within the urban plume on these two flights was quite similar (140-170 ppb) even though the flight patterns were separated by about 70 miles. It may be that additional generation of  $O_3$  between the two flight paths nearly balanced the dilution and scavenging processes.

Another interesting feature shown in Figure 17 is the region of high ozone concentration aloft at about 3000 feet. This  $O_3$  aloft was also observed during the flight 70 miles to the east and was reported at several locations

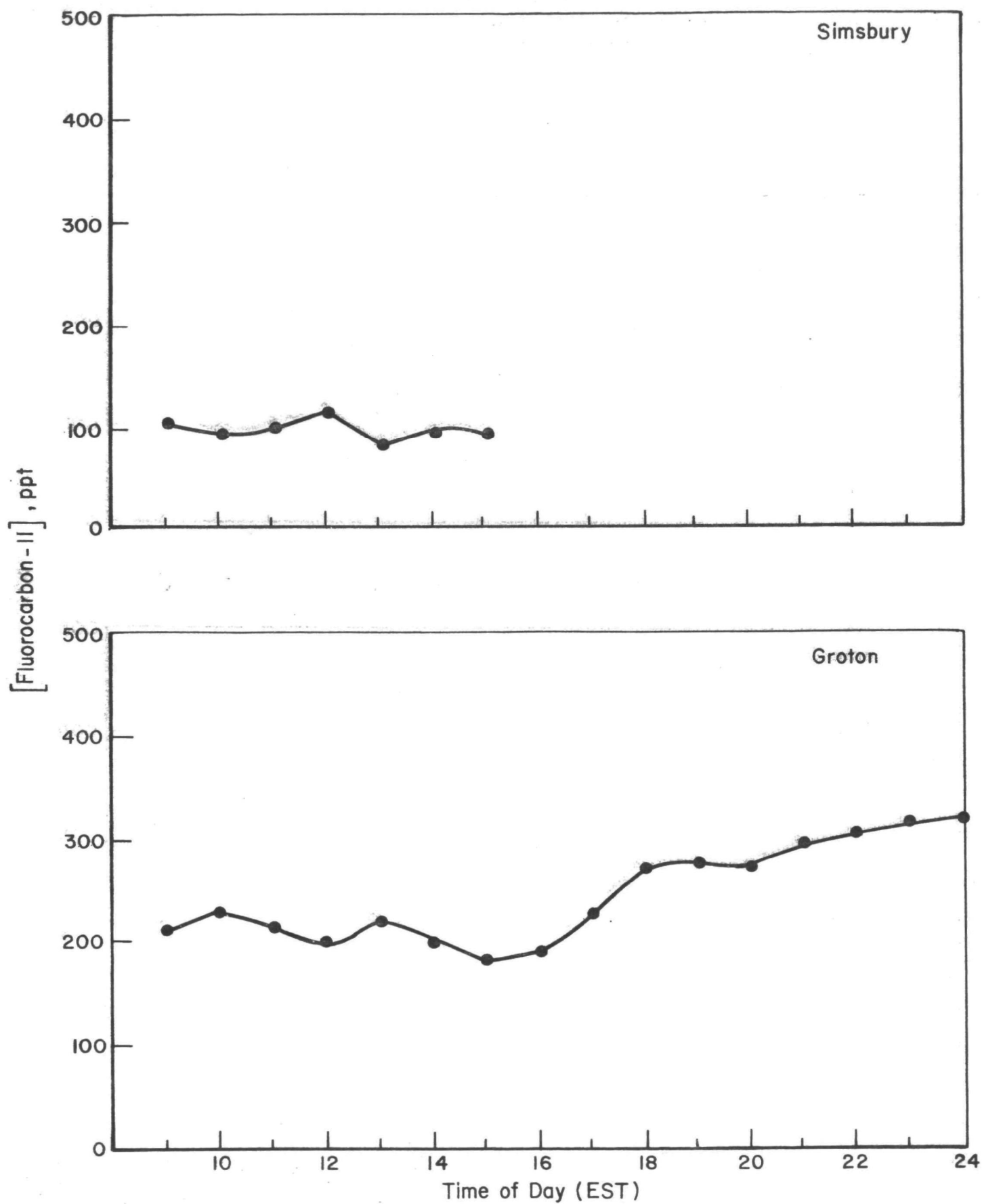


Figure 15. Fluorocarbon-11 profiles for August 10, 1975.

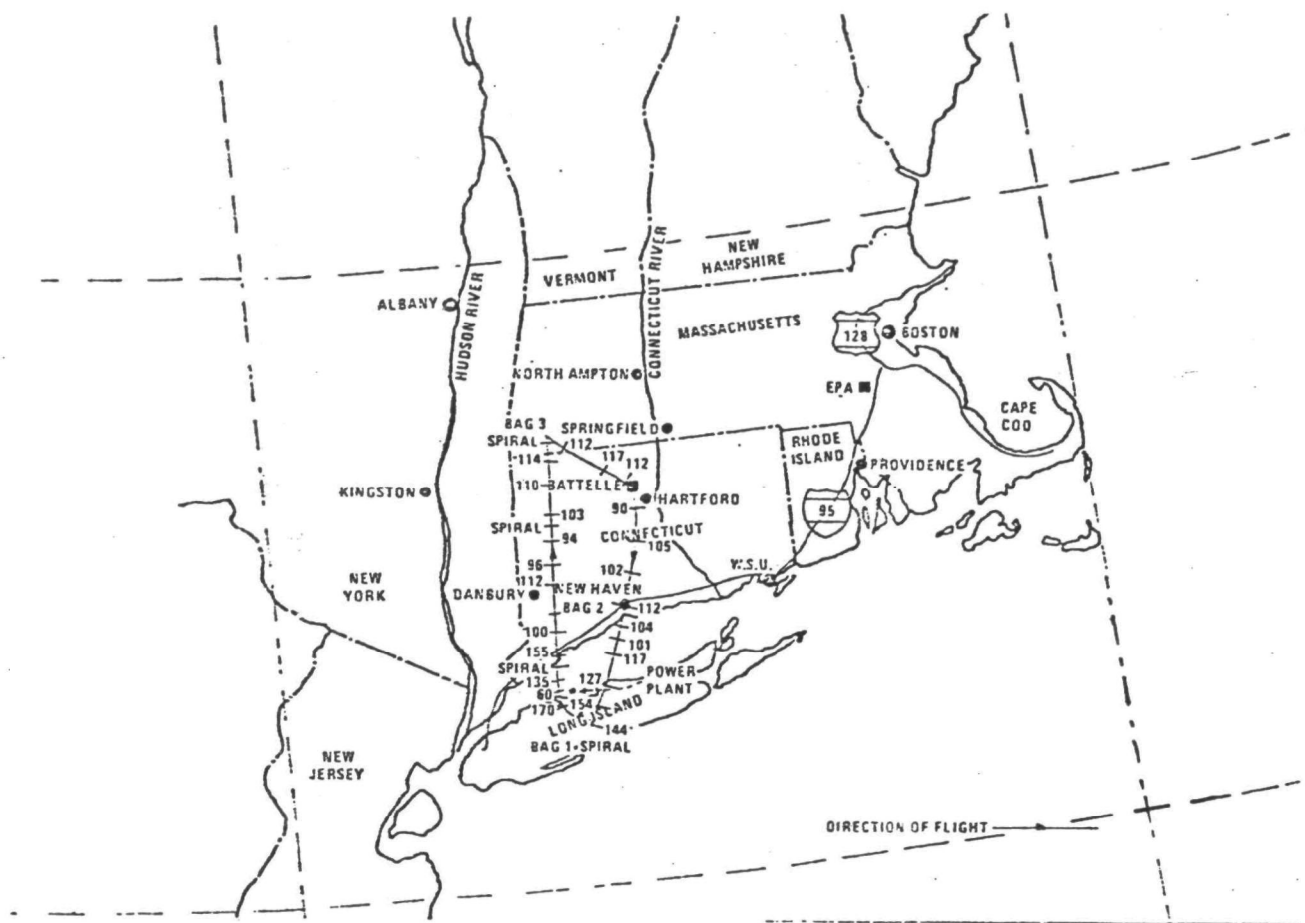


Figure 16. Ozone (in ppb) and other pollutant results for afternoon flight conducted on August 10, 1975.



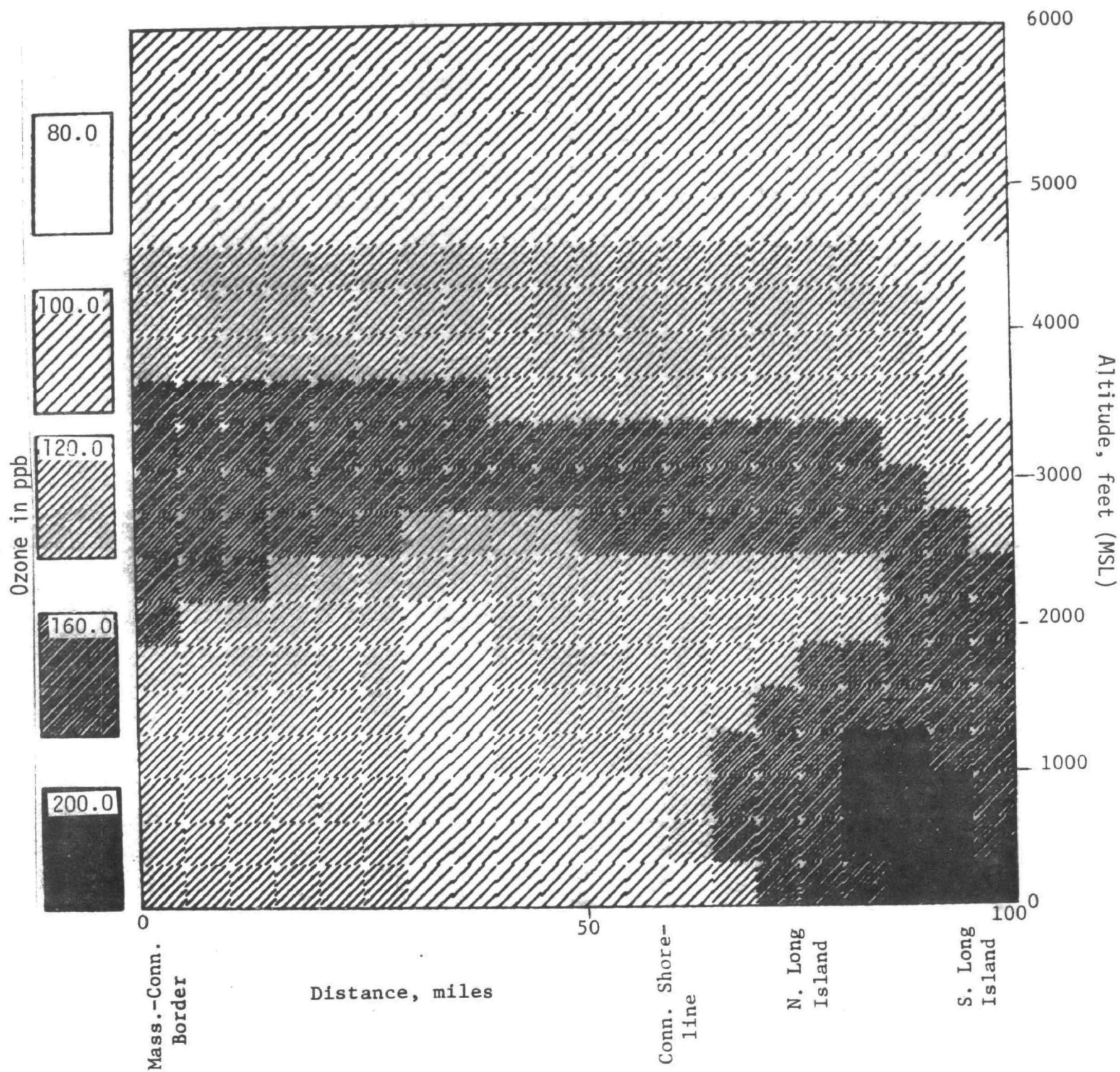


Figure 17. Ozone concentration for cross-section from the Massachusetts-Connecticut border to south shore of Long Island - approximately  $73^{\circ} 10'$  longitude.

in New Jersey<sup>(19)</sup>. It is possible that this layer of O<sub>3</sub>-rich air is associated with the high pressure cell influencing the entire northeastern United States. Ozone throughout the area was high on August 10, with values in New Jersey, Delaware, eastern Pennsylvania, and southern New England exceeding 100 ppb. Such widespread regional O<sub>3</sub> has been related in the past to long distance transport within high pressure systems<sup>(4,5)</sup>. The trajectories discussed earlier show that the air influencing the northeast on August 10 had passed over the industrialized midwest in the previous 2-3 days. The high precursor concentrations picked up at that time may be responsible for the regional O<sub>3</sub> observed on August 10. Obviously any O<sub>3</sub> formed in urban plumes is superimposed on the regional O<sub>3</sub>, leading to the very high concentrations observed downwind of urban centers.

#### AUGUST 13, 1975

Another day which exhibited high levels of O<sub>3</sub> in the Connecticut River Valley was August 13, 1975. Sunny and hazy conditions prevailed on this day, as a weak north-south trough was centered over southern New England. Wind direction varied considerably over the region, but the general flow was from the western quadrants. Wind data from some representative locations in southern New England are listed in Table 7. These data show that a fairly stable southwesterly flow was established by afternoon.

TABLE 7. WINDS AT 1000 FEET ON AUGUST 13, 1975

Time	Location	Speed, mph	Direction, degrees
0700	Chatham, Mass.	2	045
0800	Springfield, Mass.	5	024
0820	Avery Point, Conn.	7	064
1300	Chatham, Mass.	5	180
1405	Avery Point, Conn.	12	231
1414	Springfield, Mass.	10	216
1900	Chatham, Mass.	16	220

The trajectories for Simsbury and Groton are shown in Figures A-8 and A-9 in Appendix A. Until just after noon the air arriving in Simsbury and Groton was from the northwest and had passed diagonally across New York State. It should be noted that this trajectory places Groton directly downwind of Hartford.



By early afternoon the winds had shifted and Groton began receiving air from the metropolitan New York area. At this time Simsbury's air was from north-western New Jersey and southern New York State.

Maps showing the patterns of ozone distribution in southern New England on August 13 are included in Figure 18 a-c. Two regions of elevated  $O_3$  existed at noontime; one from southwest to central Connecticut and one in southeast Massachusetts. By 1500 EST, after the wind shifted to the southwest, a mass of  $O_3$ -enriched air is observed entering Connecticut from the southwest. High ozone is found both within and to the west and south of the Connecticut River Valley. Another area of high  $O_3$  exists in southeastern Massachusetts. Much of the data shown there are from aircraft flights and therefore represent the concentrations at 1000 feet. The morning wind patterns suggest that this high  $O_3$  may be due to an intermingling of the Boston and Providence plumes, although firm evidence for this is not available.

By 1800 the area of high  $O_3$  in Connecticut has moved further eastward and now encompasses Groton. Further eastward and northeastward motion is discernable in the map for 2100 hours, as eastern Connecticut and Rhode Island stations all show increases in the  $O_3$  concentration between 1800-2100 EST. Since these increases occur after dark it is clear that transport rather than photochemistry has caused the increase. The concentrations of  $O_3$  at the Rhode Island and eastern Massachusetts stations increase even further between 2100 hours and midnight, providing further evidence of transport.\*

The fluorocarbon-11 results for August 13 are shown in Figure 19. Until 2200 EST values of F-11 were close to background at Simsbury. At about 2200 the F-11 concentration increased markedly and the maximum  $O_3$  for the day was observed simultaneously. From the ozone distribution maps (Figure 18) it appears that a kind of "backwash" of urban air moved into Simsbury at this time. The concentration of F-11 peaked at 1100 EST in Groton, possibly due to emissions from the Hartford area, and increased again later in the evening

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\*While not pertinent to our discussion of the Connecticut River Valley situation, it is nevertheless noteworthy that a layer of very high  $O_3$  concentration existed aloft during the afternoon over a large portion of southern New England and even into New Hampshire. The altitude of this layer varied between 1000-3000 feet depending on location. It is also interesting that several of the vertical profiles taken during the late morning show ozone concentration increasing with altitude between 6000-11,000 feet. The complex behavior of ozone on this day should be investigated in future studies.

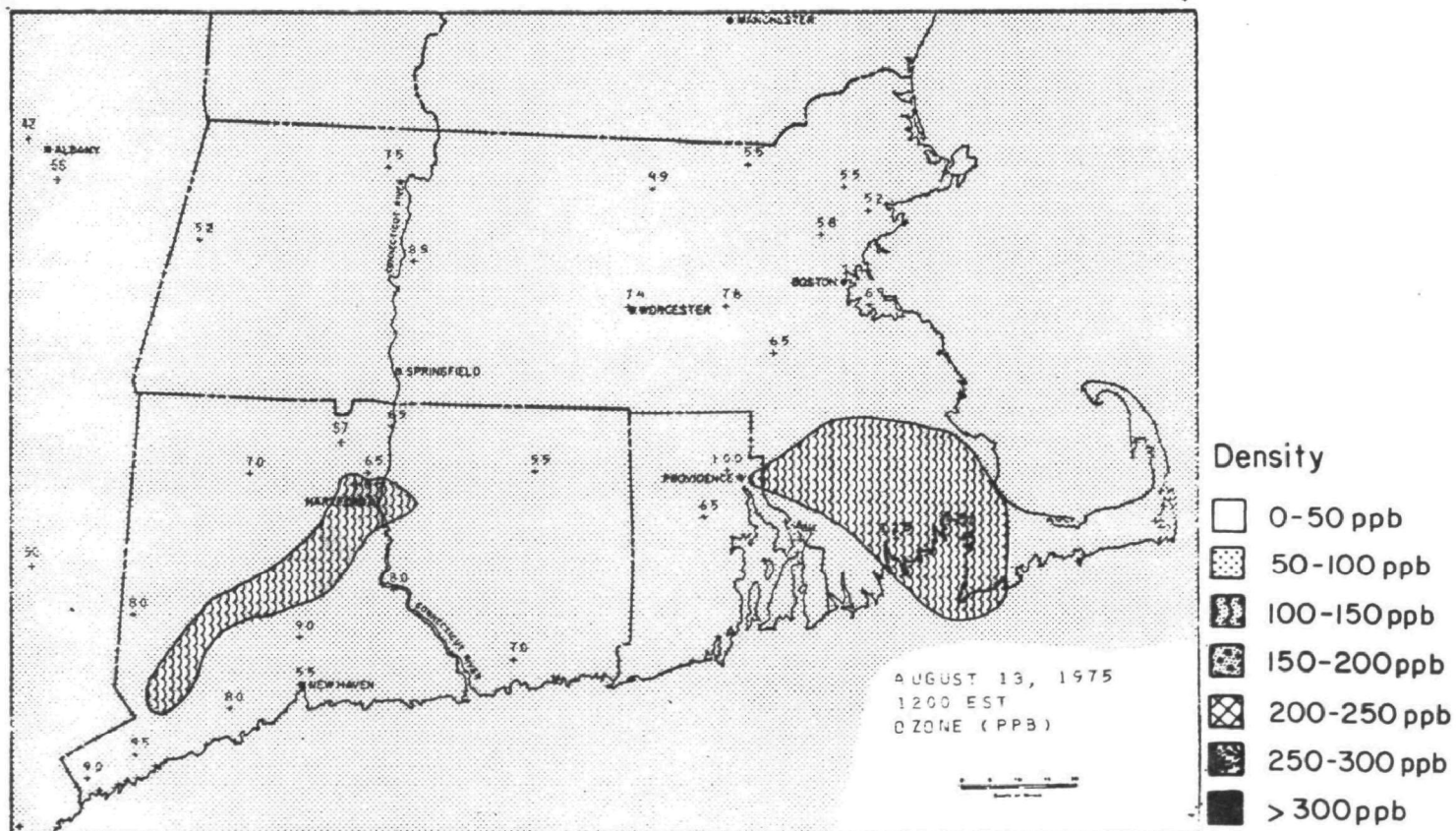
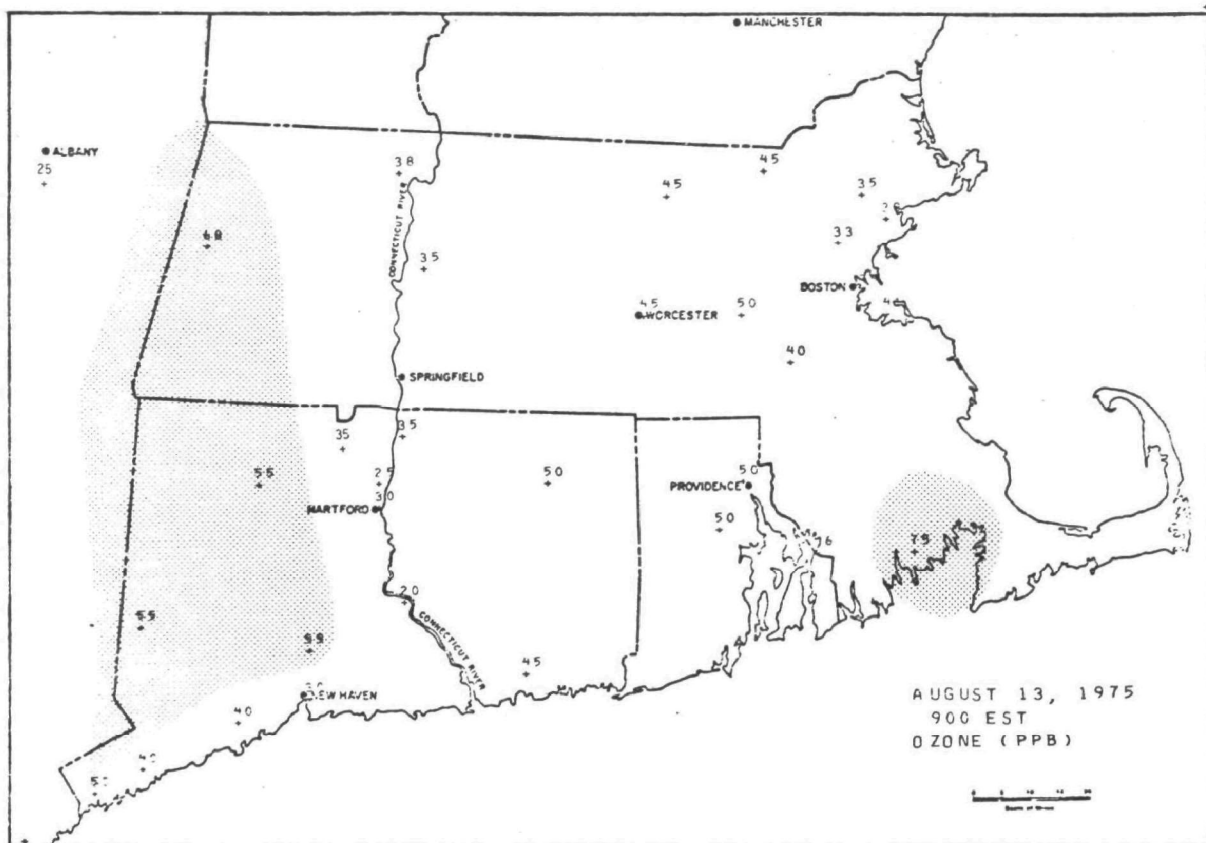


Figure 18a. Ozone distribution in southern New England on August 13, 1975.

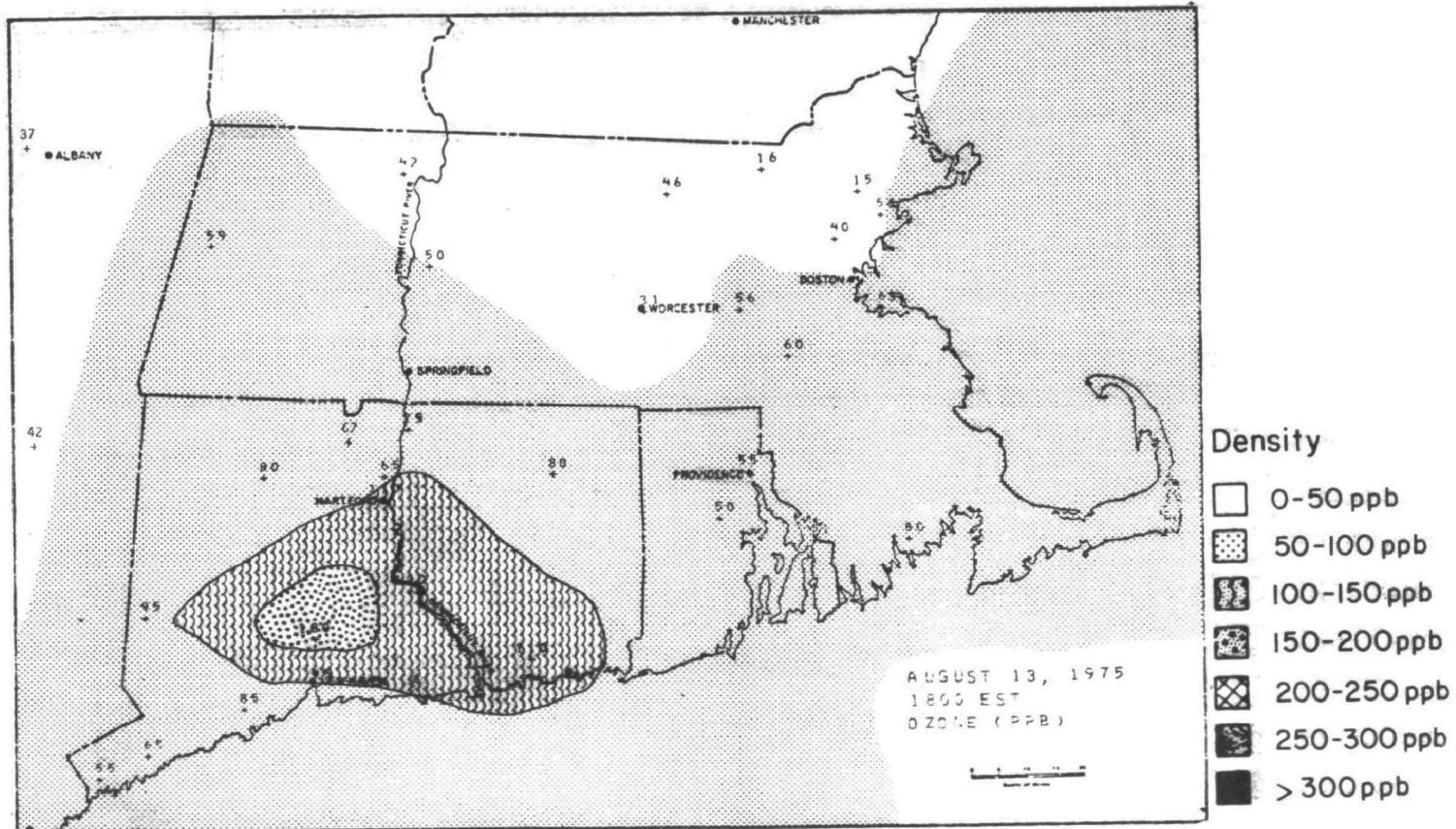
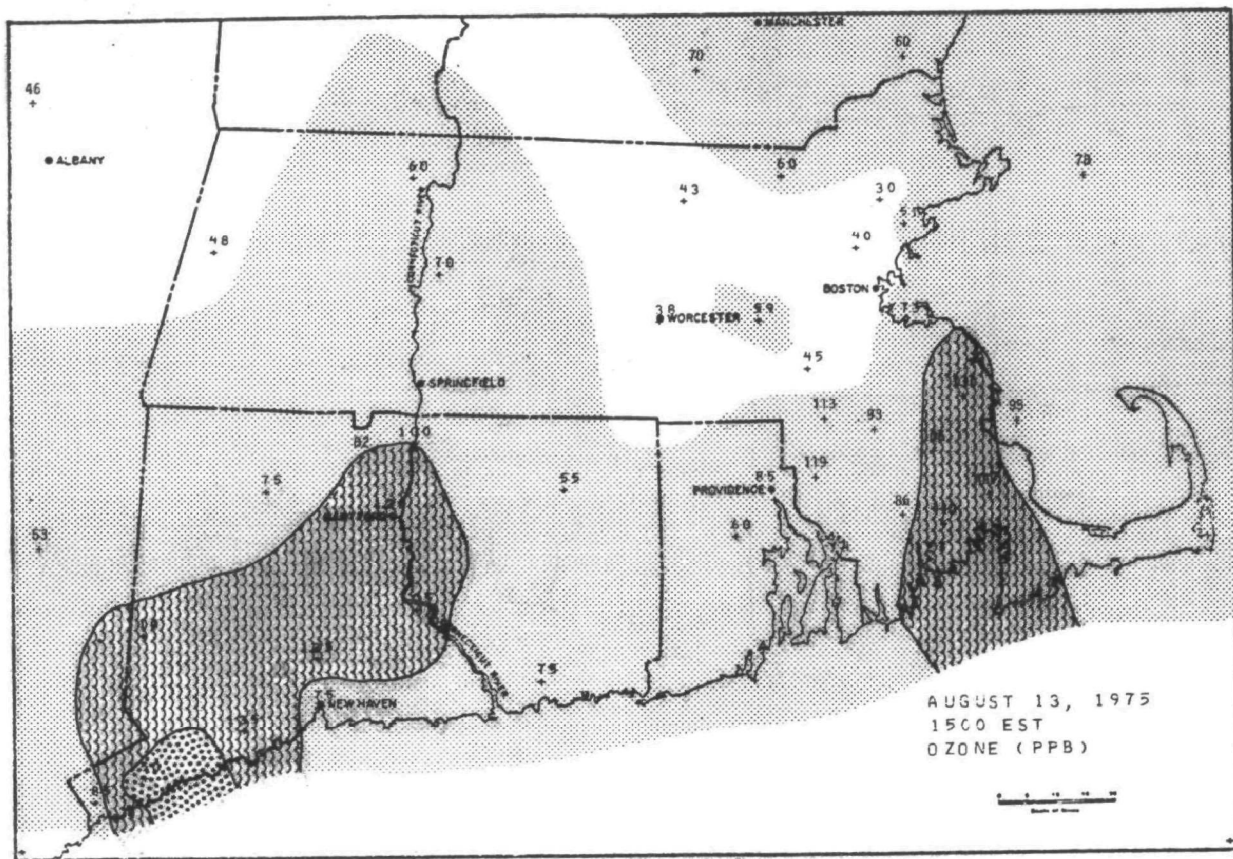


Figure 18b. Ozone distribution in southern New England on August 13, 1975.

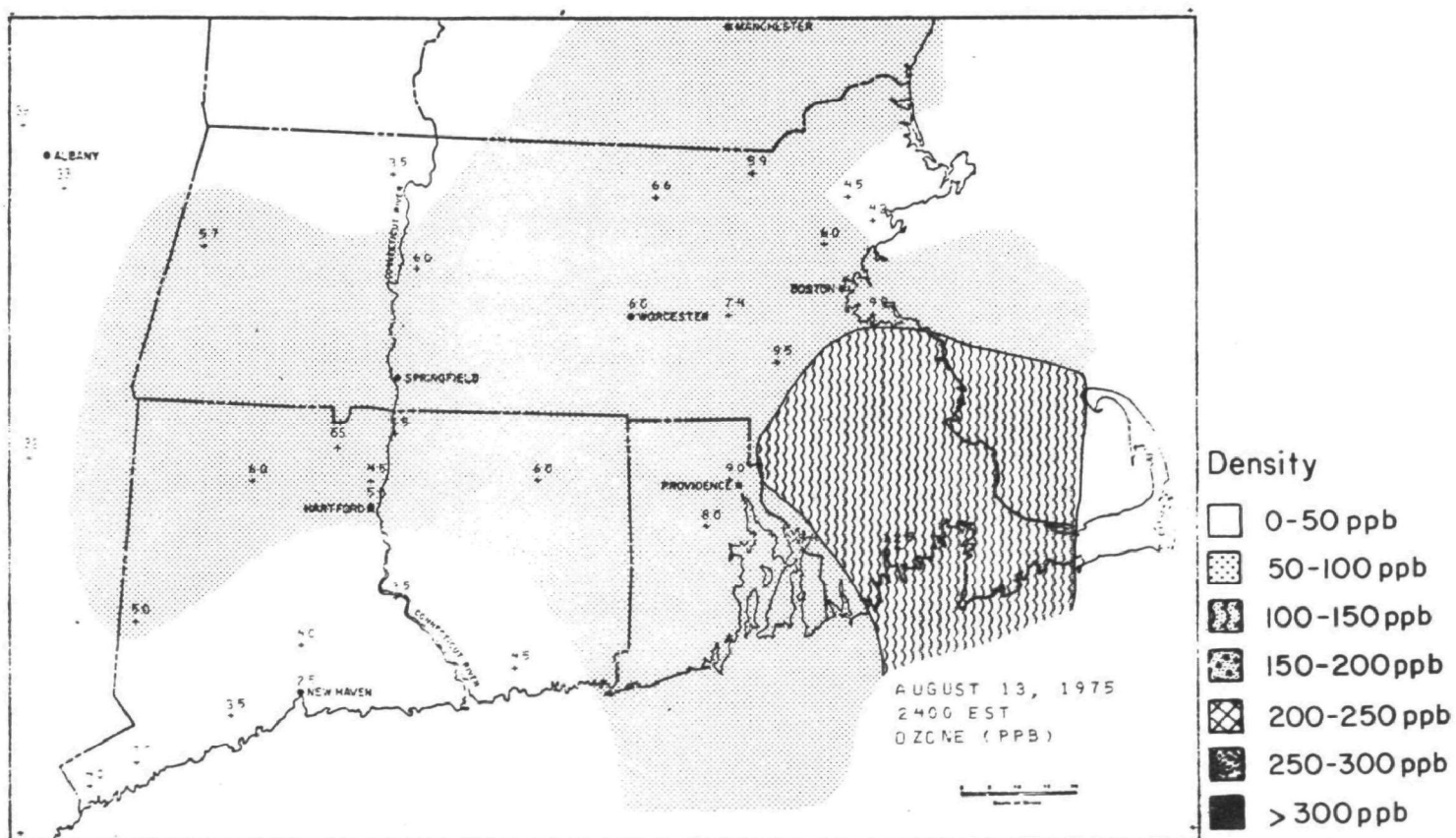
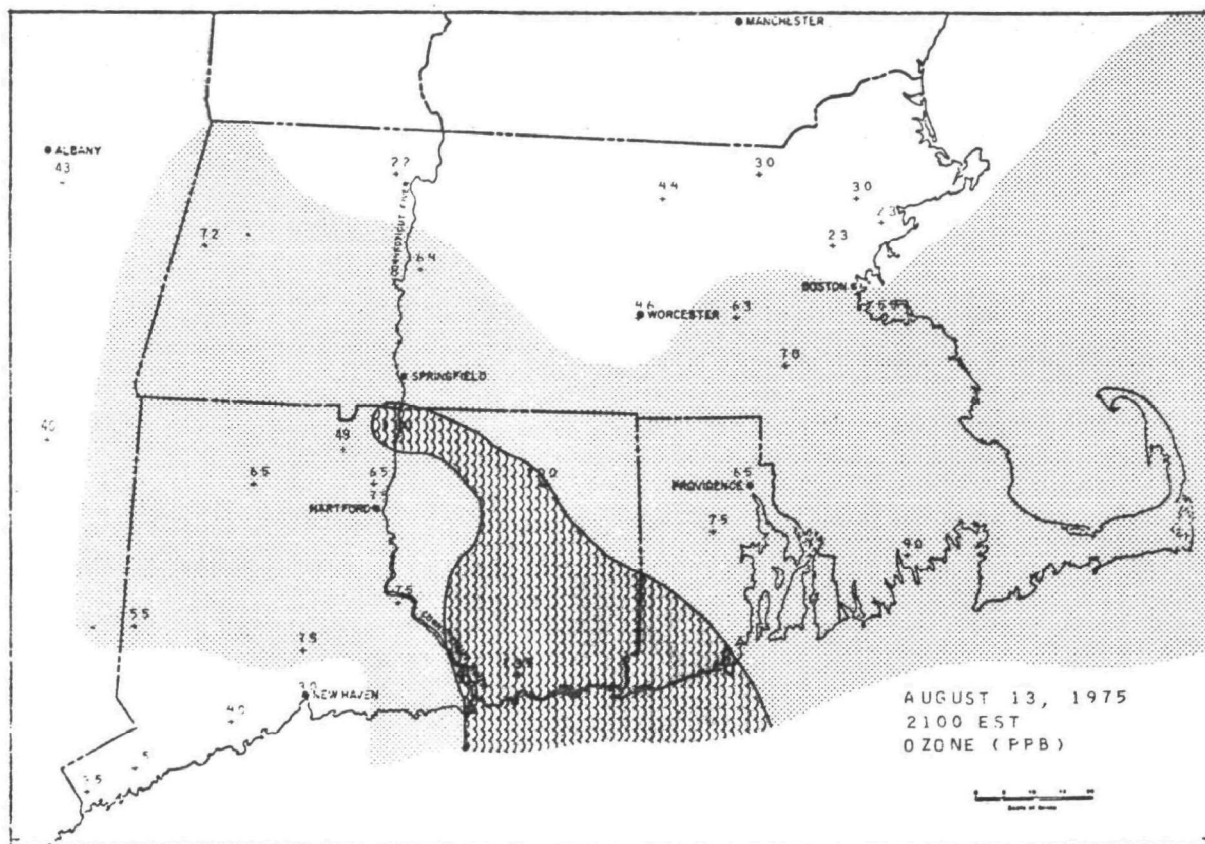


Figure 18c. Ozone distribution in southern New England on August 13, 1975.

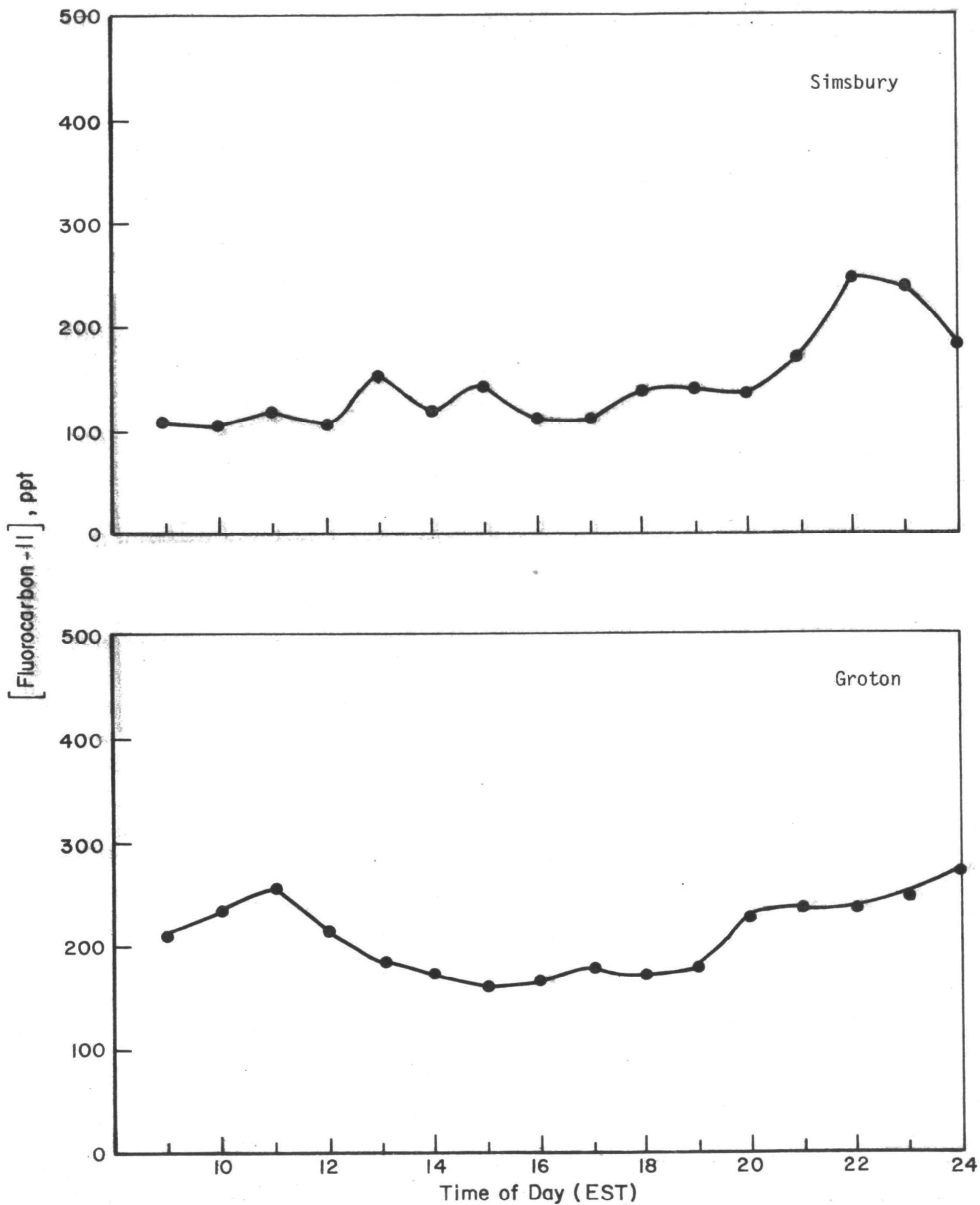


Figure 19. Fluorocarbon-11 profiles for August 13, 1975.



at about the time when the  $O_3$  distribution maps showed  $O_3$  moving through the Groton area. The F-11 concentration is still high at midnight, indicating that urban air is still moving into Groton. The  $O_3$  level has decreased by this time, no doubt due to the lack of sunlight to initiate reactions in the air mass leaving the urban source area after sundown.

As has been found on other case study days, the origin of high  $O_3$  in the Connecticut River Valley is in the emissions of upwind urban areas, with New Jersey, New York, and southwestern Connecticut all contributing to the ultimate  $O_3$ /precursor burden of the air crossing the valley under southwesterly winds.

#### AUGUST 21, 1975

August 21, 1975, was cool, clear and sunny in the Connecticut River Valley, as the entire region was dominated by a strong high pressure system. The wind data in Table 8 indicate moderate morning winds from the northwest with stronger afternoon and evening winds from the southwest. The trajectories in Figures A-10 and A-11 in the Appendix show air arriving at both Simsbury and Groton from the northwest until early afternoon, at which point the southwesterly flow sets in. The air arriving in Simsbury from the northwest originated in Canada north of Lake Ontario and crossed some rather remote stretches of New York State; it should be rather clean. Morning air in Groton may have crossed Hartford and may not be so clean. The fluorocarbon-11 profiles in Figure 20 also suggest this possibility.

TABLE 8. WINDS AT 1000 FEET ON AUGUST 21, 1975

Time	Location	Speed, mph	Direction, degrees
0700	Chatham, Mass.	10	295
0800	Springfield, Mass.	13	320
0800	Putnam, Conn.	10	314
1300	Chatham, Mass.	12	230
1400	Springfield, Mass.	16	219
1400	Putnam, Mass.	20	254
1900	Chatham, Mass.	30	235
1900	Albany, N.Y.	20	195

The ozone concentrations in southern New England throughout the day are shown in the distribution maps in Figure 21 a-c. The concentrations were low at 0900 and only moderate at most locations at noon. The one exception is

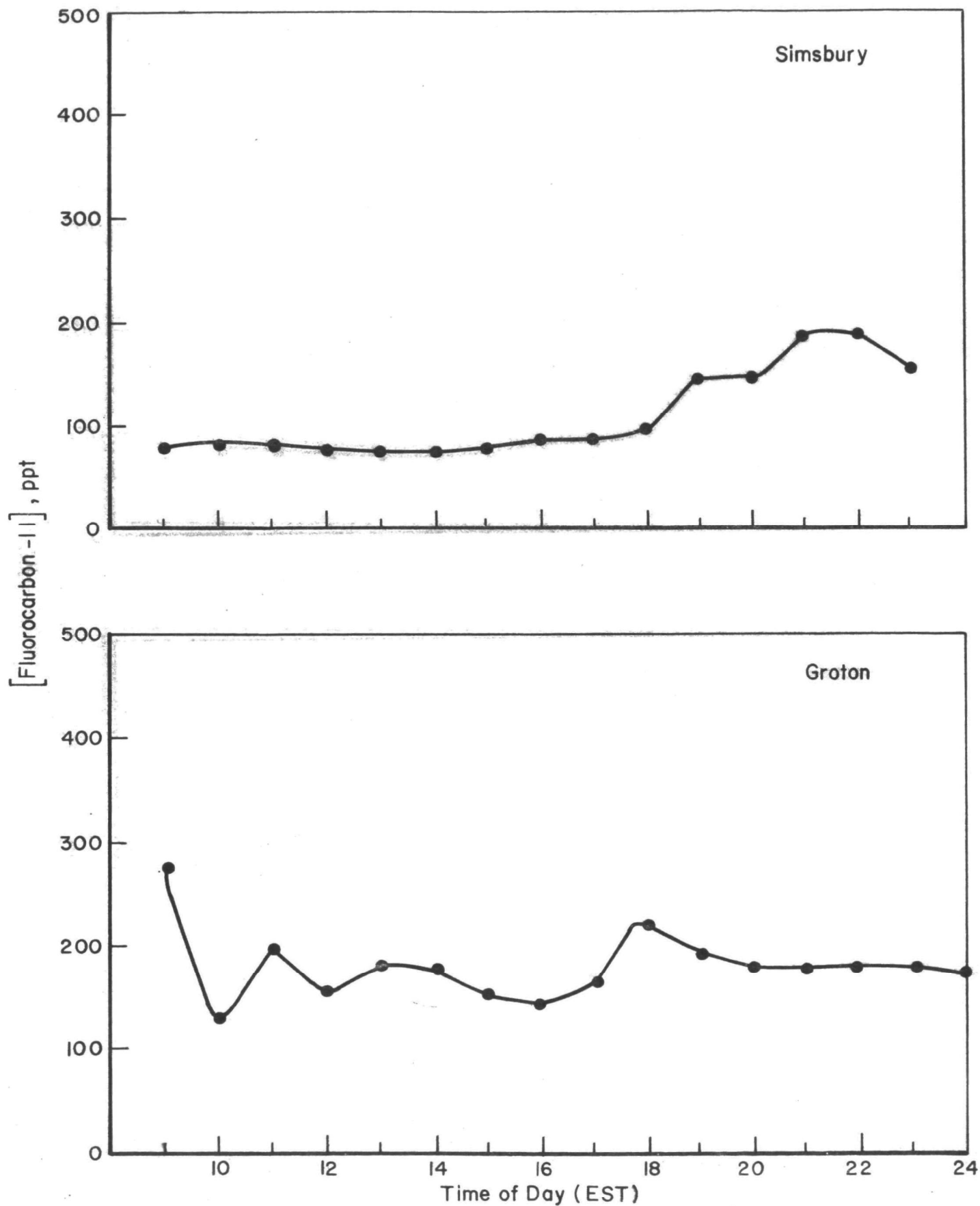


Figure 20. Fluorocarbon-11 profiles for August 21, 1975.

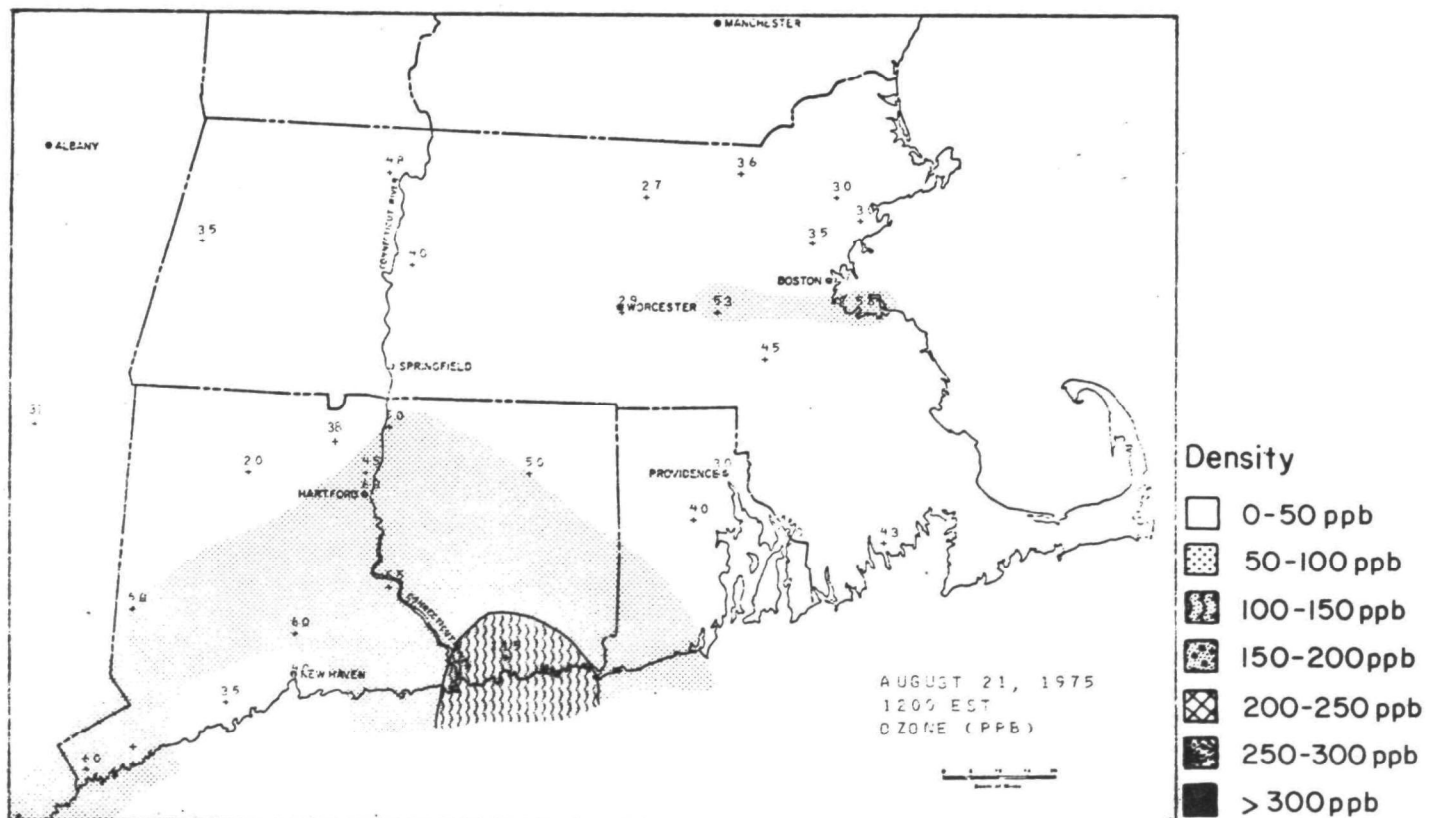
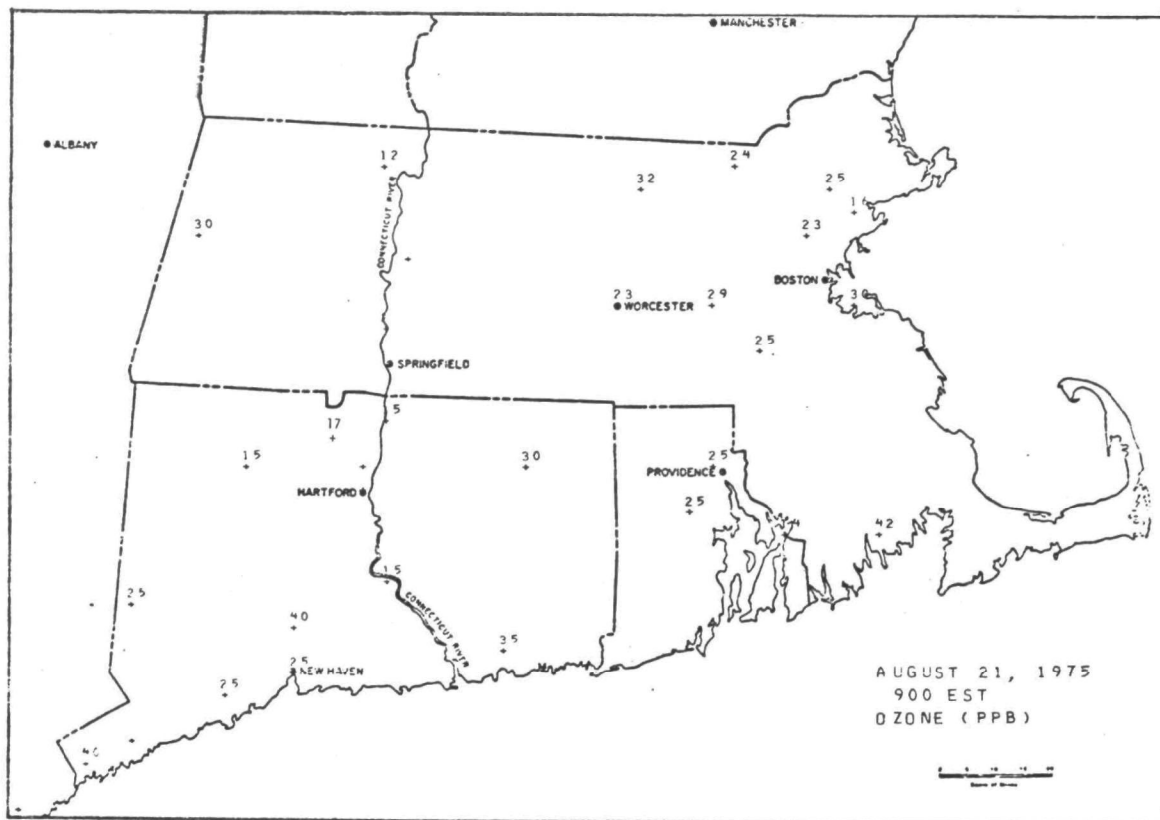


Figure 21a. Ozone distribution in southern New England on August 21, 1975.



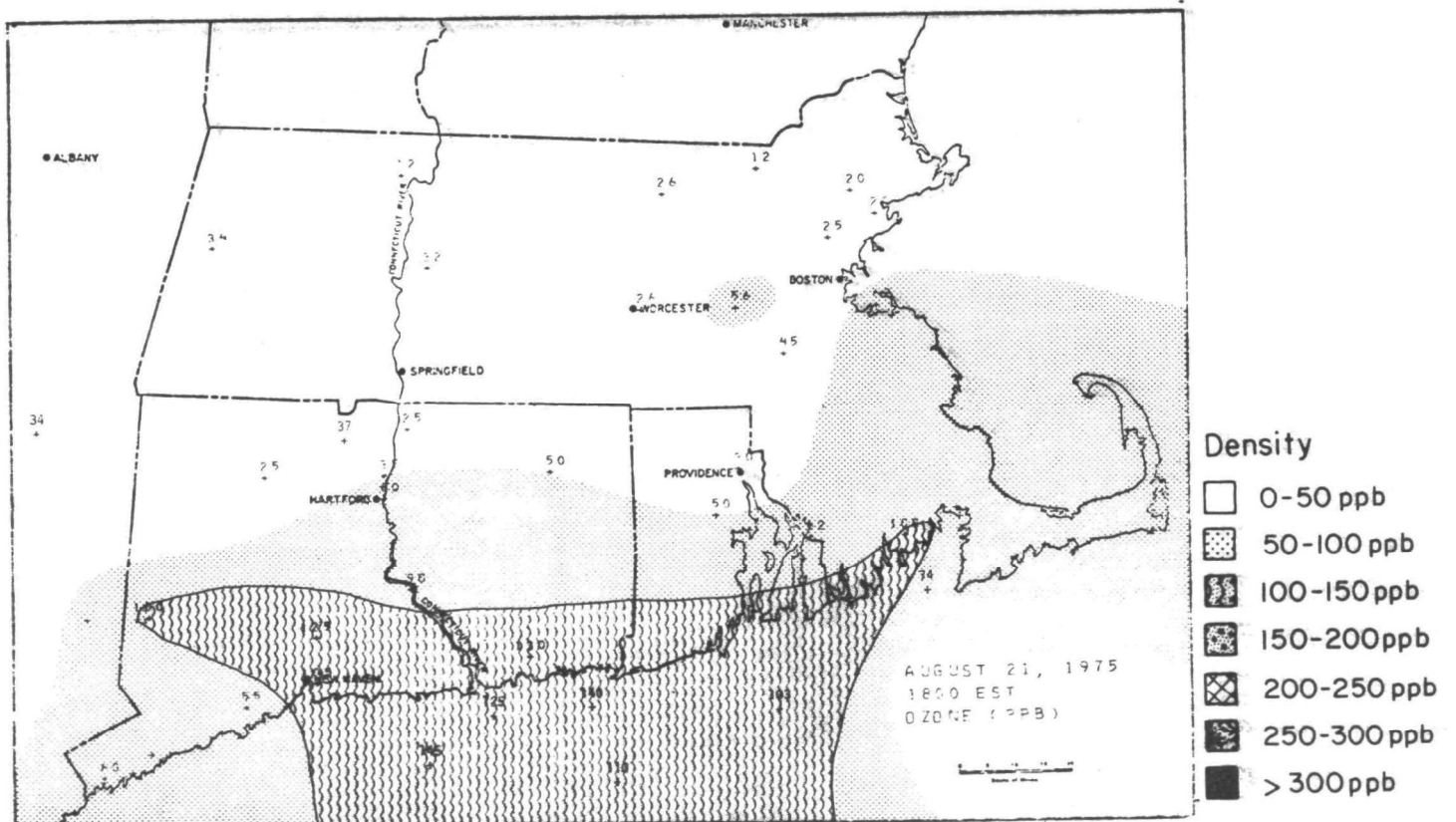
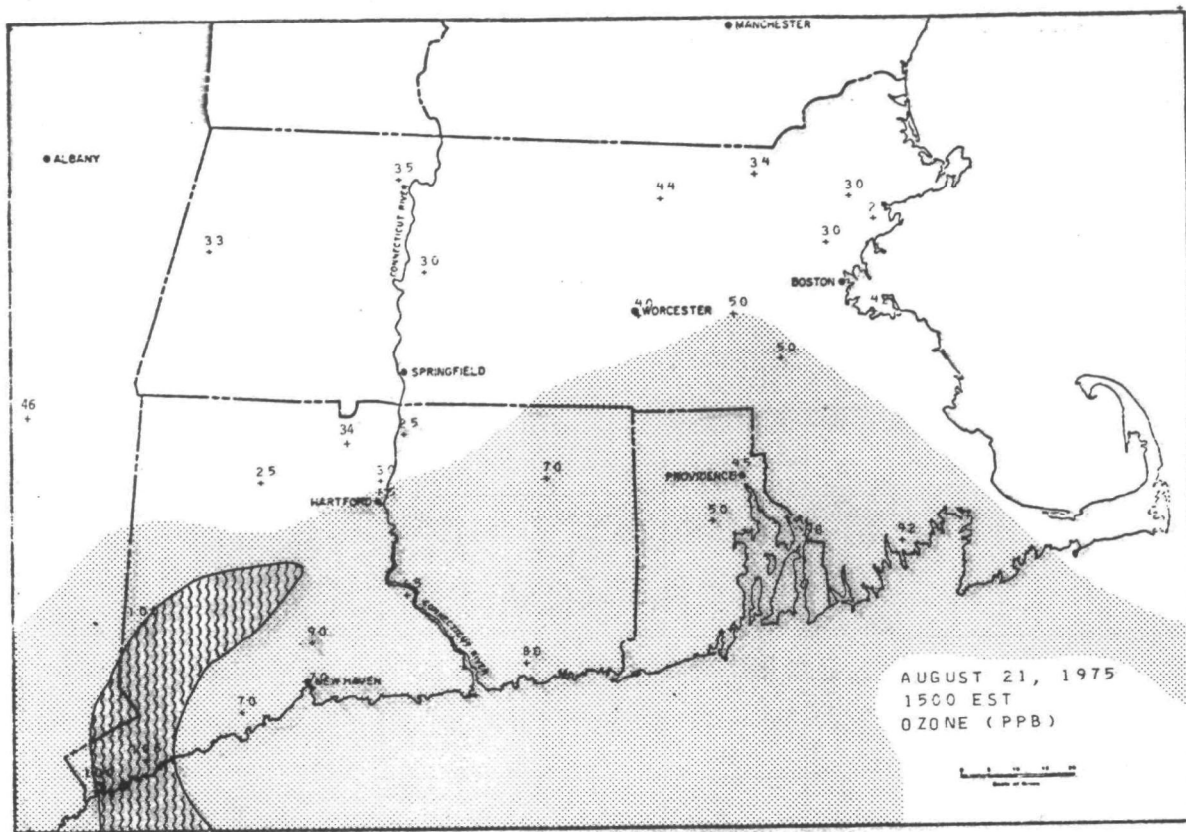


Figure 21b. Ozone distribution in southern New England on August 21, 1975.

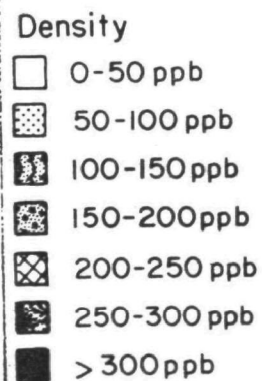
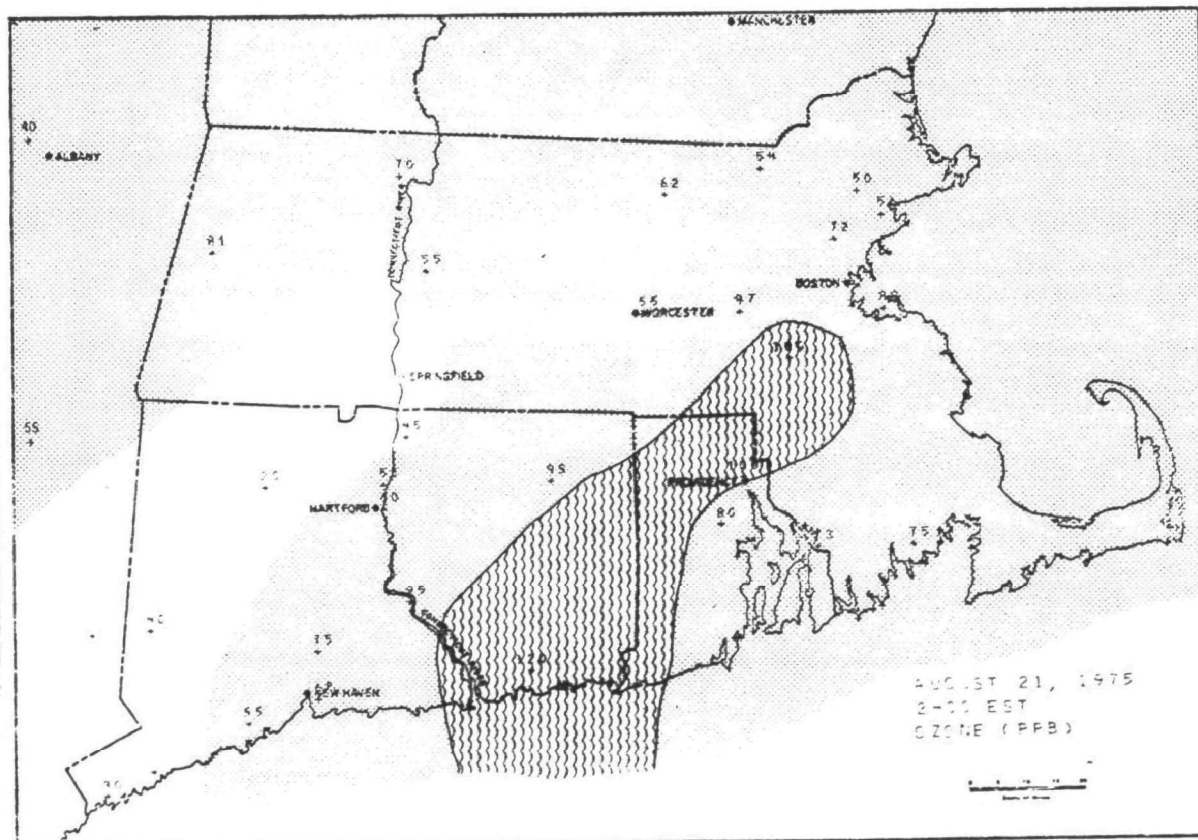
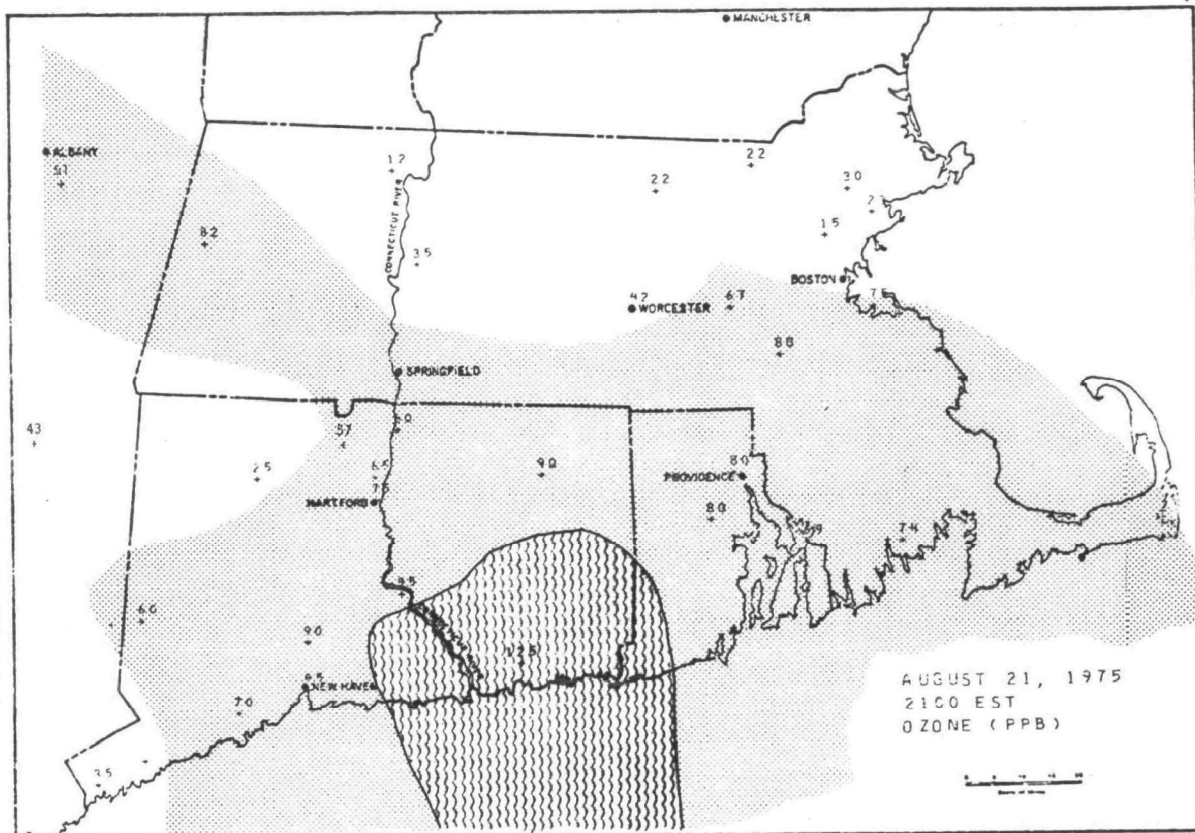


Figure 21c. Ozone distribution in southern New England on August 21, 1975.

Groton, which reached 115 ppb at noon. Both the fluorocarbon data and the trajectories imply that morning emissions in Hartford may be responsible.

Later in the afternoon a band of  $O_3$ -rich air was evident along the southern half of the region, with maximum values occurring in southern Connecticut and over Long Island Sound at 1800 EST. The dividing line between low  $O_3$  in the northern portion of the region and moderate to high  $O_3$  to the south is quite distinct. The trajectories shown earlier reveal the reason for the sharp separation; during the afternoon the air arriving at Groton and southern Connecticut has passed over or near several major urban centers, while Simsbury and more northerly locations experienced air which has passed through predominantly rural areas. Indeed the F-11 concentration in Simsbury was very close to the tropospheric background level during much of the day.

Since both the air mass trajectories and the Simsbury F-11 results demonstrate that the northerly portions of the region experienced clean rural air during much of the day, we should be able to derive some information on  $O_3$  formation in rural air using the data from these northerly locations. It is clear that the photochemical conditions for generating  $O_3$  exist on this day, as witnessed by the high levels observed in the southern portion of the region. The ozone concentrations found in the rural air of northern Connecticut and western Massachusetts should be the sum of tropospheric background  $O_3$  and any  $O_3$  synthesized from local or upwind rural emissions. The ozone distribution maps through 1800 EST demonstrate that these combined sources of  $O_3$  yield concentrations on the order of 25-40 ppb. After 1800 EST the F-11 concentration in Simsbury increased, indicating an influx of urban emissions. During this same period the  $O_3$  maps show that the band of  $O_3$ -enriched air to the south moved northward, so that by 2100 it encompassed Simsbury. The simultaneous increases in  $O_3$  and F-11 at night are strongly indicative of transport of urban air to this rural location.

The 25-40 ppb background rural ozone concentration derived above is a useful value to compare with  $O_3$  from other sources, such as urban plumes and regional blankets of  $O_3$  associated with high pressure systems. In the Connecticut River Valley, where ozone concentrations reached 200-300 ppb on some of our case study days, it is clear that this background  $O_3$  makes a relatively small contribution to the maximum  $O_3$  in the valley. As stated before, urban emissions transported into the valley from the southwest, superimposed on regional  $O_3$  concentrations, together create the high levels of  $O_3$  observed in the valley.

The high concentration of ozone observed over Long Island Sound and the lower half of southern New England on August 21 is clearly the result of transport of  $O_3$  and precursors into the area on southwest winds, judging from both the trajectories and the  $O_3$  distribution maps. The possibility of an overlap of urban plumes on this day is also suggested by the trajectories. This possibility has been discussed in a report by Wolff, et al.<sup>(20)</sup>, which should be consulted for further details.

#### THE RELATIONSHIP BETWEEN OZONE AND FLUOROCARBON-11 IN SOUTHERN NEW ENGLAND

Measurements of F-11 were made during the Northeast Oxidant Study to provide a means of distinguishing between urban and rural air. The sources of F-11 emissions are population oriented, so that air passing over urban areas has higher concentrations of F-11 than rural air. Since F-11 is essentially inert in the lower atmosphere, it can be used to trace the movement of urban air. In the case studies just discussed, we frequently referred to the F-11 data for this purpose.

Another possible use of the data, and the subject of this brief discussion, involves the derivation of information on background  $O_3$  using extrapolations of the F-11 results. This possibility was explored through the use of linear regression techniques on the F-11 and ozone data from Simsbury and Groton.

Regression equations were derived for three categories of data:

- (1) Hourly Averages
- (2) Daily Averages
- (3) Daily Maxima.

The results of these regressions are listed in Table 9.

The tabulated data show that the hourly averages are not well correlated, which is not surprising considering that both daytime and nighttime data were included. During the night  $O_3$  formation ceases and the concentration at the surface decays, while high levels of F-11 can persist. This alone would greatly reduce the correlation coefficient.

The daily average results are much more enlightening. The equations for Simsbury and Groton are

TABLE 9. LINEAR REGRESSION OF FLUOROCARBON-11 (PPT) ON  
OZONE (PPB) AT SIMSBURY AND GROTON  
([Ozone] = m[Fluorocarbon-11] + b)

		Slope	Intercept	Correlation Coefficient
Simsbury	Hourly Averages	0.02	29	0.03
	Daily Averages	0.21	0.75	0.68
	Daily Maxima	0.19	22	0.48
Groton	Hourly Averages	0.10	27	0.21
	Daily Averages	0.27	-7.7	0.65
	Daily Maxima	0.27	5.8	0.70

$$\text{Simsbury } [O_3]_{\text{Avg.}} = 0.21 [F-11]_{\text{Avg.}} + 0.75$$

$$\text{Groton } [O_3]_{\text{Avg.}} = 0.27 [F-11]_{\text{Avg.}} - 7.7.$$

A plot of the daily average Simsbury data is shown in Figure 22. If we make an assumption about the average F-11 concentration in clean tropospheric air, we can calculate an average  $O_3$  concentration for clean tropospheric air based on the above equations. Clean air concentrations of F-11 in 1975 in the northern hemisphere were reported<sup>(26)</sup> to vary between about 80-100 ppt, so that an assumed average of 90 ppt seems reasonable (the lowest daily average concentration in Simsbury was 92 ppt). Using this assumption, the average background tropospheric  $O_3$  concentration is calculated to be 20 ppb from the Simsbury data and 17 ppb from the Groton results.

We can compare these daily average background  $O_3$  values with the average ozone at Simsbury on August 21. This day was described earlier in the case studies as showing minimal urban emissions up to 1800 EST, based on the F-11 data. The average  $O_3$  concentration up to 1800 was 18 ppb, in very good agreement with the background value derived from the F-11 extrapolations.

The regressions based on the maximum daily value for  $O_3$  and F-11 will be useful in predicting maximum  $O_3$  and will be discussed further in the next section on predictive modelling.

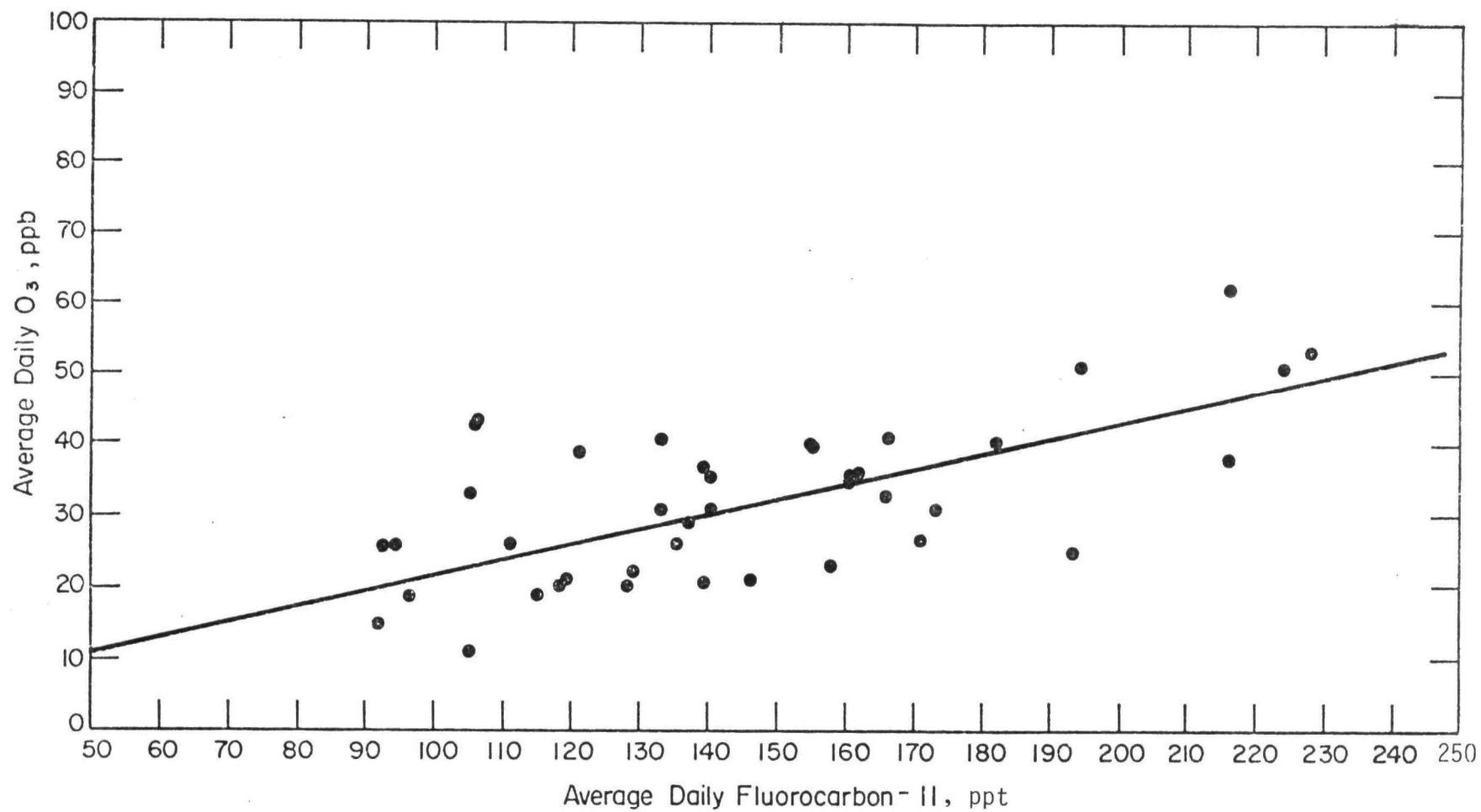


Figure 22. Average daily O<sub>3</sub> vs average daily F-11 at Simsbury.

### SECTION 3

#### STATISTICAL ANALYSIS OF OZONE IN SOUTHERN NEW ENGLAND

The objective of this section of the report is to develop a method for predicting the ozone levels that can be expected in Southern New England under various meteorological conditions. Data collected during the Northeast Oxidant Study at Simsbury and Groton, Connecticut, have been employed for these analyses, since these two sites provide a long and continuous record of diurnal pollutant and meteorological conditions.

#### PRELIMINARY ANALYSIS

In order to predict ozone levels likely to occur in southern New England under various meteorological conditions, a method of statistical analysis known as regression integral analysis was first attempted. This method can be used to predict a single value of a dependent variable from a sequence of values of an independent variable (it can also be used with multiple sequences of independent variable values), and has proven to be an appropriate tool for predicting an ozone level (such as the afternoon ozone maximum) from the distribution of precursor and meteorological variables during the morning hours<sup>(4)</sup>. The method proved fruitful only in a limited sense in this study, however. While developing regression integrals for various measures of afternoon ozone levels, it was noted that the only statistically significant components of fit were the zero order components of the polynomials describing the morning distributions of the independent variables. Since these zero order components are proportional to the means of the independent variables over the distribution period, these regression integrals proved to be equivalent to regressions with ozone level as dependent variable and morning averages of precursors and meteorological variables as independent variables.

In retrospect, one can see that the changes in average values of predictor variables dominate the relationship with ozone level. In order to fine tune this model and see what effect differences in distributions of predictor

variables have, one needs data with roughly the same average level of predictor variables but differing distributions over the time period under consideration. Under these conditions, one should be able to detect differences caused by distributional changes.

However, this discovery about regression integrals also has a positive aspect; namely, some rather good statistical relationships were discovered between ozone levels and some predictors even though significance was found only in the zero order relationship. Thus we decided to abandon the regression integral approach and to concentrate on simple regressions and multiple regressions between ozone levels and averages of precursor and meteorological variables taken over a suitable time period.

## REGRESSION ANALYSIS

Having decided to concentrate on regression analysis, consideration was now given to what measures of ozone level should be used, what should be the time period over which the precursor and meteorological variables would be averaged, and how wind speed and wind direction should be incorporated into this analysis. Based on some previous research<sup>(4)</sup> and on the preliminary regression integral analysis, we selected the 0600 through 1300 EST averages of the following variables (where available): NO, NO<sub>2</sub>, CO, nonmethane hydrocarbon, fluorocarbon-11, solar radiation, temperature, relative humidity, dew point, and ethylene/acetylene ratio. To incorporate wind speed and wind direction into the analysis, vector averages of the 0600 through 1300 EST wind speed—wind direction vectors were obtained. These average vectors were then classified by the following scheme into one of five categories:

- (Calm) - wind speed below 1 m/s (2.237 mi/h)
- (NE) - wind speed above 1 m/s and wind direction  
in the northeast quadrant
- (SE) - wind speed above 1 m/s and wind direction  
in the southeast quadrant
- (SW) - wind speed above 1 m/s and wind direction  
in the southwest quadrant
- (NW) - wind speed above 1 m/s and wind direction  
in the northwest quadrant.



By using dummy variables for categories NE, SE, SW, and NW, regressions made including these variables as predictors will be composed of five parallel hyperplanes, one hyperplane corresponding to each of the five categories. Formulated in this way, if the regression coefficient for any of the four directions is statistically significant, that indicates that the ozone level for this category is significantly different from the ozone level in the Calm category.

Finally, we decided to try three measures of ozone level. These were, respectively, average ozone (1300-1800 EST), mid-max ozone (maximum ozone in the time period 1300-1800 EST) and maximum ozone (1300-2400 EST). These measures were selected for the following reasons: the mid-max ozone was chosen as a measure of the maximum ozone photochemically generated from the morning precursors, the average ozone was chosen as a more stable measure of the ozone level generated by morning precursors, and the maximum was chosen in order to have a measure of late arriving transported ozone.

Two types of regression analyses were performed using these data and constructed variables. The first type consists of simple regressions of each of the measures of ozone level versus individual predictors, but incorporating the wind speed-wind direction categories. The second type is multiple regression of the measures of ozone level versus all combinations of predictors, including the wind speed-wind direction categories. These analyses were performed on the hourly ground station data collected at Groton from July 15, 1975, through August 22, 1975, and at Simsbury from July 15, 1975, through August 21, 1975.

## RESULTS OF REGRESSION ANALYSIS

Table 10 contains descriptive statistics of the variables included in the regression analysis. These are instructive as they show quite a difference in environmental conditions between Simsbury and Groton, the latter site having markedly higher levels of pollutants and a high proportion of days in the SW category of wind speed-wind direction.

Table 11 contains the regression analysis of the three ozone measures versus the wind speed-wind direction categories. Note that the Simsbury data show no days in the NE category and the Groton data contain no days in the SE category. There is only one observation in the Simsbury SE category and even that one observation is misleading since it occurred on July 18 when

TABLE 10. DESCRIPTIVE STATISTICS

Variable Name	Simsbury			Groton		
	Mean	Std. Dev.	No. of Cases	Mean	Std. Dev.	No. of Cases
Avg. O <sub>3</sub> , ppb	54.9	22.3	38	76.1	36.6	38
Mid-Max. O <sub>3</sub> , ppb	64.6	27.0	38	88.7	42.2	38
Max. O <sub>3</sub> , ppb	67.6	28.4	38	94.9	45.1	38
NO, ppb	3.0	1.8	38	10.0	3.4	35
NO <sub>2</sub> , ppb	3.5	2.4	38	17.5	8.7	36
CO, ppm	.19	.11	32	.69	.38	35
NMHC, ppmC	.40	.24	33	.23	.31	35
F-11, ppt	138.5	38.6	37	218.7	64.3	38
SOL R*	2.98	1.16	38	.66	.23	38
Temp, °C	23.8	3.4	38	23.6	2.3	38
Rel. Hum., %	68.0	13.7	38	—	—	—
Dew Pt., °C	—	—	—	18.1	3.3	38
NE	—	—	0	—	—	5
SE	—	—	1	—	—	0
SW	—	—	11	—	—	27
NW	—	—	11	—	—	1
Calm	—	—	15	—	—	5
Eth/Acy	.63	.99	14	—	—	—

\*Different instruments were used to monitor solar radiation at the two sites.

TABLE 11. REGRESSION ANALYSES-MEASURES OF OZONE VERSUS WIND DIRECTION

Site	Regression Coefficients					R	R <sup>2</sup>	Residual Std. Dev.	Significance Level
	NE	SE	SW	NW	Const.				
<u>Dependent Variable = Average Ozone (1300-1800 EST)</u>									
Simsbury	—	22.9	16.2	-13.4	53.4	.54	.29	19.63	.008
Groton	-6.5	—	33.6	39.9	52.1	.46	.21	34.02	.046
<u>Dependent Variable = Maximum Ozone (1300-1800 EST)</u>									
Simsbury	—	25.7	23.6	-14.4	61.3	.57	.32	23.18	.004
Groton	-5.8	—	42.1	58.0	58.0	.49	.24	38.48	.025
<u>Dependent Variable = Maximum Ozone (1300-2400 EST)</u>									
Simsbury	—	68.7	23.3	-16.1	63.7	.66	.43	22.26	.000
Groton	-8.4	—	42.4	51.4	64.6	.47	.22	41.58	.036

the air flow throughout the region was from the southwest. The SE category at Simsbury will therefore be ignored in the remaining discussion. There is also only one observation in the Groton NW category. Hence in these and ensuing regressions we will be primarily concerned with the Simsbury NW and SW categories as opposed to the Calm category, and the Groton NE and SW as opposed to Calm. In this regression table and in following ones it is generally true that wind speed-wind direction is more of a factor at the Simsbury site, and that the greatest impact of wind speed-wind direction as a predictor is on the maximum ozone variable.

As an example of the use of the results in Table 11, one equation will be analyzed further. We will choose the Simsbury site with maximum ozone as dependent variable, since this is the strongest result in the table (43 percent of the variance in maximum ozone is explained by wind speed-wind direction alone as indicated by an  $R^2$  of 0.43). The significance level of this regression is zero to three places. The constant of 63.7 indicates that the average maximum ozone in the Calm category is 63.7 ppb. A value of -16.1 for NW indicates that the average maximum ozone in the NW category is 47.6 ppb ( $63.7 - 16.1$ ). Similarly the average maximum ozone in the SW category is 87 ppb. These ozone levels are all different from the Calm level at the .1 level of significance. As stated earlier, the results in the Simsbury SE category are misleading and should be ignored.

Table 12 through 20 show the results of regression analyses of ozone levels against individual predictors, including wind speed-wind direction categories. The results of these regressions can be interpreted similarly to those in Table 11. For example, consider the regression of maximum ozone vs fluorocarbon-11 at Simsbury (Table 16). Since the average value of fluorocarbon-11 during the study was 138.5 ppt, the prediction of the maximum ozone level for this level of fluorocarbon-11 if the wind is calm would be

$$(.48)(138.5) + 4.0 = 70.5 \text{ ppb.}$$

Similarly, if the wind is from the SW, this equation predicts 73.9 for the maximum ozone level. Note that this simple regression explains 74 percent of the variation in maximum ozone. Note also the consistent values of the slopes of the predictor variable at the Simsbury and Groton sites.

One might get the impression from the above discussion that this regression equation predicts only about 3-4 ppb difference in  $O_3$  between calm winds

TABLE 12. REGRESSION ANALYSES-MEASURES OF OZONE VERSUS INDIVIDUAL PREDICTORS AND WIND DIRECTION  
PREDICTOR VARIABLE NAME = NO

Site	Predictor	Regression Coefficients					R	R <sup>2</sup>	Residual Std. Dev.	Significance Level
		NE	SE	SW	NW	Const.				
<u>Dependent Variable = Average Ozone (1300-1800 EST)</u>										
Simsbury	.87	—	22.2	16.8	-13.4	50.7	.54	.30	19.86	.018
Groton	.84	3.6	—	38.3	40.2	43.6	.50	.25	31.18	.06
<u>Dependent Variable = Maximum Ozone (1300-1800 EST)</u>										
Simsbury	2.4	—	21.2	25.3	-14.3	53.8	.59	.34	23.14	.006
Groton	1.6	6.9	—	47.2	58.4	42.5	.54	.30	35.06	.028
<u>Dependent Variable = Maximum Ozone (1300-2400 EST)</u>										
Simsbury	2.2	—	63.5	25.0	-16.0	55.9	.67	.46	22.15	.000
Groton	1.0	3.4	—	48.2	51.7	54.5	.52	.27	38.10	.047

TABLE 13. REGRESSION ANALYSES-MEASURES OF OZONE VERSUS INDIVIDUAL PREDICTORS AND WIND DIRECTION  
PREDICTOR VARIABLE NAME = NO<sub>2</sub>

Site	Predictor	Regression Coefficients					R	R <sup>2</sup>	Residual Std. Dev.	Significance Level
		NE	SE	SW	NW	Const.				
<u>Dependent Variable = Average Ozone (1300-1800 EST)</u>										
Simsbury	-.15	—	24.3	16.5	-13.5	54.9	.54	.29	19.92	.020
Groton	2.0	4.3	—	28.0	23.5	4.3	.69	.48	27.00	.000
<u>Dependent Variable = Maximum Ozone (1300-1800 EST)</u>										
Simsbury	-1.1	—	29.2	25.9	-15.1	64.7	.57	.33	23.39	.009
Groton	2.2	6.5	—	37.5	39.4	25.9	.71	.51	30.53	.000
<u>Dependent Variable = Maximum Ozone (1300-2400 EST)</u>										
Simsbury	-.13	—	68.7	23.5	-16.2	64.1	.66	.43	22.59	.001
Groton	2.0	2.3	—	38.1	35.1	36.5	.66	.43	34.85	.001

TABLE 14. REGRESSION ANALYSES-MEASURES OF OZONE VERSUS INDIVIDUAL PREDICTORS AND WIND DIRECTION  
PREDICTOR VARIABLE NAME = CO

Site	Predictor	Regression Coefficients					R	R <sup>2</sup>	Residual Std. Dev.	Significance Level
		NE	SE	SW	NW	Const.				
<u>Dependent Variable = Average Ozone (1300-1800 EST)</u>										
Simsbury	73.4	—	—	18.2	-9.7	38.4	.63	.39	19.07	.003
Groton	38.1	-6.9	—	27.7	30.5	31.0	.59	.34	32.85	.011
<u>Dependent Variable = Maximum Ozone (1300-1800 EST)</u>										
Simsbury	70.7	—	—	24.1	-9.6	45.6	.63	.39	21.21	.003
Groton	40.1	-6.05	—	35.6	48.2	35.7	.59	.35	37.66	.011
<u>Dependent Variable = Maximum Ozone (1300-2400 EST)</u>										
Simsbury	84.6	—	—	24.2	-11.0	45.6	.69	.48	19.40	.000
Groton	39.4	-10.3	—	35.0	40.2	44.3	.56	.31	41.22	.021

TABLE 15. REGRESSION ANALYSES-MEASURES OF OZONE VERSUS INDIVIDUAL PREDICTORS AND WIND DIRECTION  
PREDICTOR VARIABLE NAME = NMHC

Site	Predictor	Regression Coefficients					R	R <sup>2</sup>	Residual Std. Dev.	Significance Level
		NE	SE	SW	NW	Const.				
<u>Dependent Variable = Average Ozone (1300-1800 EST)</u>										
Simsbury	45.4	—	13.0	10.4	-12.0	37.1	.70	.49	16.83	.001
Groton	12.5	-5.2	—	34.1	41.5	49.2	.47	.22	35.81	.107
<u>Dependent Variable = Maximum Ozone (1300-1800 EST)</u>										
Simsbury	51.8	—	13.3	14.1	-13.5	42.7	.71	.50	19.04	.000
Groton	13.3	-4.3	—	42.3	59.8	54.8	.49	.24	40.54	.073
<u>Dependent Variable = Maximum Ozone (1300-2400 EST)</u>										
Simsbury	48.1	—	56.7	13.4	-15.1	46.4	.78	.61	17.75	.000
Groton	10.2	-8.6	—	41.9	51.5	63.5	.47	.22	43.86	.104



TABLE 16. REGRESSION ANALYSES-MEASURES OF OZONE VERSUS INDIVIDUAL PREDICTORS AND WIND DIRECTION  
PREDICTOR VARIABLE NAME = F-11

Site	Predictor	Regression Coefficients					R	R <sup>2</sup>	Residual Std. Dev.	Significance Level
		NE	SE	SW	NW	Const.				
<u>Dependent Variable = Average Ozone (1300-1800 EST)</u>										
Simsbury	.39	—	5.1	-.04	-12.8	5.2	.78	.61	15.05	.000
Groton	.41	-3.5	—	13.7	14.4	-22.2	.80	.64	23.15	.000
<u>Dependent Variable = Maximum Ozone (1300-1800 EST)</u>										
Simsbury	.46	—	3.4	4.4	-13.5	3.9	.79	.63	17.58	.000
Groton	.46	-2.4	—	19.5	29.1	-26.2	.81	.66	26.12	.000
<u>Dependent Variable = Maximum Ozone (1300-2400 EST)</u>										
Simsbury	.48	—	45.1	3.4	-15.3	4.0	.86	.74	15.53	.000
Groton	.47	-4.9	—	19.1	21.6	-22.3	.78	.61	29.72	.000

TABLE 17. REGRESSION ANALYSES-MEASURES OF OZONE VERSUS INDIVIDUAL PREDICTORS AND WIND DIRECTION  
PREDICTOR VARIABLE NAME = SOL R

Site	Predictor	Regression Coefficients					R	R <sup>2</sup>	Residual Std. Dev.	Significance Level
		NE	SE	SW	NW	Const.				
<u>Dependent Variable = Average Ozone (1300-1800 EST)</u>										
Simsbury	6.4	—	22.5	16.2	-13.3	34.4	.63	.40	18.32	.002
Groton	71.9	24.7	—	39.0	51.7	-3.6	.59	.34	31.40	.006
<u>Dependent Variable = Maximum Ozone (1300-1800 EST)</u>										
Simsbury	6.8	—	24.3	23.6	-14.2	41.1	.64	.41	22.00	.001
Groton	82.9	30.1	—	48.3	71.6	-6.2	.61	.37	35.37	.003
<u>Dependent Variable = Maximum Ozone (1300-2400 EST)</u>										
Simsbury	5.9	—	67.0	23.3	-15.9	46.2	.70	.49	21.41	.000
Groton	92.1	31.5	—	49.3	66.5	-6.7	.61	.37	37.99	.004

TABLE 18. REGRESSION ANALYSES—MEASURES OF OZONE VERSUS INDIVIDUAL PREDICTORS AND WIND DIRECTION  
PREDICTOR VARIABLE NAME = -TEMP.

Site	Predictor	Regression Coefficients					R	R <sup>2</sup>	Residual Std. Dev.	Significance Level
		NE	SE	SW	NW	Const.				
<u>Dependent Variable = Average Ozone (1300-1800 EST)</u>										
Simsbury	3.1	—	8.7	10.5	-11.8	-17.2	.69	.48	17.12	.000
Groton	5.8	-6.2	—	20.5	22.9	-76.2	.56	.32	32.07	.012
<u>Dependent Variable = Maximum Ozone (1300-1800 EST)</u>										
Simsbury	3.7	—	7.3	16.7	-12.3	-24.3	.71	.51	20.02	.000
Groton	5.5	-5.5	—	29.8	42.0	-62.0	.56	.31	37.17	.014
<u>Dependent Variable = Maximum Ozone (1300-2400 EST)</u>										
Simsbury	3.5	—	50.8	16.7	-14.2	-17.4	.77	.59	19.32	.000
Groton	6.3	-8.1	—	28.1	32.9	-74.6	.55	.30	39.85	.015

TABLE 19. REGRESSION ANALYSES—MEASURES OF OZONE VERSUS INDIVIDUAL PREDICTORS AND WIND DIRECTION

PREDICTOR VARIABLE NAME = REL. HUM. (SIMSBURY)  
DEW PT. (GROTON)

Site	Predictor	Regression Coefficients					R	R <sup>2</sup>	Residual Std. Dev.	Significance Level
		NE	SE	SW	NW	Const.				
<u>Dependent Variable = Average Ozone (1300-1800 EST)</u>										
Simsbury	-.60	—	27.2	21.3	-13.2	92.4	.64	.41	18.10	.001
Groton	.94	-9.2	—	29.1	35.0	38.8	.46	.21	34.42	.088
<u>Dependent Variable = Maximum Ozone (1300-1800 EST)</u>										
Simsbury	-.64	—	29.3	29.1	-14.1	102.9	.65	.42	21.77	.001
Groton	.65	-9.6	—	39.0	54.5	48.8	.49	.24	39.01	.055
<u>Dependent Variable = Maximum Ozone (1300-2400 EST)</u>										
Simsbury	-.57	—	71.4	28.1	-15.9	101.10	.71	.50	21.14	.000
Groton	-.13	-8.0	—	43.0	52.1	66.4	.47	.22	42.20	.078

TABLE 20. REGRESSION ANALYSES-MEASURES OF OZONE VERSUS INDIVIDUAL PREDICTORS AND WIND DIRECTION  
PREDICTOR VARIABLE NAME = ETH/ACY

Site	Predictor	Regression Coefficients					R	R <sup>2</sup>	Residual Std. Dev.	Significance Level
		NE	SE	SW	NW	Const.				
<u>Dependent Variable = Average Ozone (1300-1800 EST)</u>										
Simsbury	-3.7	-	-	22.5	-16.4	54.6	.62	.38	16.7	.173
Groton	-	-	-	-	-	-	-	-	-	-
<u>Dependent Variable = Maximum Ozone (1300-1800 EST)</u>										
Simsbury	-5.7	-	-	29.3	-16.4	63.0	.66	.43	17.56	.118
Groton	-	-	-	-	-	-	-	-	-	-
<u>Dependent Variable = Maximum Ozone (1300-2400 EST)</u>										
Simsbury	-6.4	-	-	27.3	-17.6	65.2	.68	.46	16.91	.094
Groton	-	-	-	-	-	-	-	-	-	-

and winds from the SW quadrant. This is true if the value of fluorocarbon-11 is the same for each of these categories (i.e., no or constant input of urban emissions). However, it is likely that the average fluorocarbon-11 is higher in the SW quadrant due to urban emissions, making a comparison at the same fluorocarbon-11 concentration of less value. The use of actual morning average F-11 values when making predictions should be much more informative.

These regressions provide a basis for predicting ozone levels based on an average morning concentration of a given predictor variable, and the category to which the morning wind speed-wind direction belongs. Some of these variables, such as fluorocarbon-11, provide a rather good base for predicting ozone levels. These predictions can be strengthened somewhat by adding combinations of variables in the regression analyses. However, since correlations among predictors make the resulting regression coefficients more uncertain and also mask any causal or correlative significance of these coefficients, the effectiveness of these multiple regression equations as predictors of ozone level may be limited. With these cautionary notes, Table 21 contains multiple regression analyses of ozone levels versus all predictors. Since these equations are based on the numbers of observations in common to all variables, they have fewer observations than many of the simple regressions, and hence their effectiveness cannot be directly compared by, for example, considering the values of  $R^2$  in individual regressions as compared to  $R^2$  in the multiple regressions.

It should be noted that the use of the multiple regression results in Table 21 for predicting ozone should only be attempted when values for all of the predictor variables are available. If one or more predictor variables are missing, the effectiveness of the multiple regression equation is greatly reduced and it may even yield misleading results. Since data on all the predictors used in Table 21 will rarely be available except during special studies, the utility of the multiple regressions in Table 21 for routine predictions is marginal. Indeed we cannot even cross-compare the multiple regression models at the two sites since one of the variables (solar radiation) is not directly comparable. For purposes of routine predictions then, the individual regressions in Tables 11-20 are much more useful. Our studies suggest that the regression of greatest utility for simple predictions based only on generally available meteorological data is the temperature regression shown in Table 18. We find very little gain in predictive capability when

TABLE 21. MULTIPLE REGRESSION ANALYSES—MEASURES OF OZONE VERSUS COMBINATIONS OF PREDICTORS AND WIND DIRECTION

Site	Regression Coefficients														R	R <sup>2</sup>	Residual Std. Dev.	Significance Level
	NO	NO <sub>2</sub>	CO	NMHC	F-11	So1 R	Temp	RH	DP	NE	SE	SW	NW	Const.				
<u>Dependent Variable = Average Ozone (1300-1800 EST)</u>																		
Simsbury	-1.9	-4.9	76.7	20.0	.23	-1.5	1.2	-.36	-	-	-	8.6	-11.5	23.4	.87	.76	13.6	.000
Groton	-2.5	-	6.5	-21.4	.39	57.9	-3.0	-	2.9	19.6	-	23.3	21.9	-21.9	.86	.74	21.7	.000
<u>Dependent Variable = Maximum Ozone (1300-1800 EST)</u>																		
Simsbury	-.93	-5.0	58.9	20.7	.32	-2.0	.97	-.42	-	-	-	14.3	-12.8	31.5	.86	.75	15.8	.001
Groton	-2.3	-.57	4.1	-25.1	.51	79.1	-6.0	-	5.0	27.5	-	31.5	43.0	14.1	.87	.76	24.6	.000
<u>Dependent Variable = Maximum Ozone (1300-2400 EST)</u>																		
Simsbury	-1.0	-4.0	61.5	17.7	.33	-2.4	.71	-.42	-	-	-	12.1	-13.7	37.9	.88	.77	14.36	.000
Groton	-2.8	-1.0	-10.2	-15.9	.59	43.6	.56	-	-2.1	22.4	-	46.7	47.3	-15.5	.86	.73	27.7	.001

other meteorological variables such as relative humidity and solar radiation are included, since temperature is highly correlated with such variables. Thus the simplest and most convenient predictions can be made using morning temperature and wind direction/speed vector data, along with the equations from Table 18. Increased accuracy is obtained by using the fluorocarbon-11 regression or the multiple regressions, but the necessary data are not generally available.

A comparison of ozone predictions based on the temperature and wind vector regression results (Table 18) for each site and across sites is given in Table 22. Predictions for calm and southwest winds are included; data are not sufficient in the other wind categories to permit cross-comparison. The average temperature over the entire study at each site was used for these predictions, rather than the average morning temperature. The table shows that the two equations make similar predictions when the winds are calm, although the Simsbury model predictions are slightly lower. Under southwest wind conditions the Groton model predicts considerably higher  $O_3$ . Predictions for rural southern New England areas similar to Simsbury should probably be made with the Simsbury model; predictions for less rural and/or coastal areas should employ the model derived from the Groton data. Obviously it would be useful to have many more data and data under a greater variety of conditions (e.g., greater variation in wind direction) in order to derive more meaningful predictive equations. The equations presented in this section can be used with the appropriate cautions to predict ozone, but the user must bear in mind the limited data base upon which the equations have been derived and the statistical nature of the predictions. The equations should help to characterize the "average" behavior of ozone based on a limited set of predictor variables; extreme values caused by unusual combinations of conditions or conditions which do not affect a predictor variable will not be accurately predicted.



TABLE 22. CROSS-COMPARISON OF OZONE PREDICTIONS BASED  
ON THE SIMSBURY AND GROTON EQUATIONS FROM  
TABLE 18 (TEMPERATURE REGRESSION - OZONE IN PPB)

	<u>Simsbury O<sub>3</sub> Predicted by Simsbury Model</u>		<u>Simsbury O<sub>3</sub> Predicted by Groton Model</u>	
	<u>Calm</u>	<u>SW</u>	<u>Calm</u>	<u>SW</u>
Avg. O <sub>3</sub>	57	68	62	82
Mid-Max. O <sub>3</sub>	64	81	69	99
Max. O <sub>3</sub>	66	83	75	103
	<u>Groton O<sub>3</sub> Predicted by Groton Model</u>		<u>Groton O<sub>3</sub> Predicted by Simsbury Model</u>	
	<u>Calm</u>	<u>SW</u>	<u>Calm</u>	<u>SW</u>
Avg. O <sub>3</sub>	61	81	56	66
Mid-Max. O <sub>3</sub>	68	98	63	80
Max. O <sub>3</sub>	74	102	65	82

## SECTION 4

### SUMMARY

The objective of this study has been to use data collected during the 1975 Northeast Oxidant Study to determine the cause of high ozone concentrations in the Connecticut River Valley and to develop a method for predicting ozone levels that can be expected in southern New England under various meteorological conditions.

The Connecticut River Valley situation has been investigated by first examining the meteorological data for special effects of the valley and then examining in detail selected days during the Northeast Study. Meteorological data, air mass trajectories, fluorocarbon-11 profiles and ozone distribution maps were all used to elucidate the Connecticut River Valley situation. The results of this investigation indicate that the cause of high ozone in the Connecticut Valley is rooted in the location of the valley. During the summer months, the prevailing southwesterly winds place the valley directly downwind of the New York/New Jersey/southwestern Connecticut urban complex (and on some days the Philadelphia and Washington/Baltimore areas). Typical winds speeds are in the ideal range to transport the strong morning urban emissions to the Connecticut Valley with a reaction time long enough to photochemically generate high concentrations of ozone yet short enough to avoid extensive dilution. The ozone formed from the urban emissions (i.e., the urban plume) was observed on many case study days to move into Connecticut from the southwest in early afternoon, cross the Connecticut River Valley, and continue into Massachusetts during the evening. In one case an  $O_3$ -rich air mass was tracked as far north as the coast of Maine. The dimensions of the urban plumes on several days were found to vary from 30-80 miles in width and 100-175 miles in length, seemingly depending on wind speed.

Urban plumes were occasionally observed aloft, and firm evidence was presented for the overnight survival of  $O_3$  aloft above the nocturnal inversion. Vertical mixing the following morning was shown to result in high surface ozone concentrations early in the morning before photochemical generation of  $O_3$  should be significant.

Overlapping of urban plumes appeared likely on some case study days and was discussed briefly. Regional ozone of 50-100 ppb, probably associated with high pressure systems, was observed on several days outside the urban plume. Concentrations generated within the urban plume are superimposed on regional and locally generated  $O_3$  and result in very high concentrations (>200 ppb) in southern New England. Fluorocarbon-11 results and air mass trajectories were used to define clean rural air conditions. Under these conditions on a photochemically active day, average "background" levels of  $O_3$  of about 20 ppb were observed. Daily maximum  $O_3$  under these clean conditions was 25-40 ppb. Extrapolation of F-11 vs  $O_3$  linear regressions at Simsbury and Groton to background tropospheric F-11 concentrations (i.e., no urban input) suggested an average tropospheric "background" ozone concentration of about 20 ppb.

Several methods of predicting ozone in southern New England were investigated including regression integrals, simple regressions and multiple regressions. Both simple and multiple regression equations were derived for predicting ozone based on a variety of chemical and meteorological predictor variables. Fluorocarbon-11, the tracer for urban air, has the greatest predictive capability of the single variables but F-11 data are not routinely available. The multiple regression equations should be the most comprehensive in that they incorporate the greatest number of predictor variables, but again the necessary input data are not generally available. The most generally useful predictive equations are probably those based on widely available meteorological data. We have suggested the use of the regression equations involving temperature and the wind vector categories. Since temperature is highly correlated with other meteorological variables such as relative humidity and solar intensity, the regressions involving temperature and wind vector categories should reflect the effects of these additional meteorological variables. Thus, the use of the temperature/wind vector regression results seems to provide the most widely useful means for simple predictions of expected ranges of ozone concentrations.

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## APPENDIX A\*

### 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 July 16 to August 31, 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 the 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 (1900 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.

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\* Courtesy of Stanford Research Institute.

18 JULY 1975

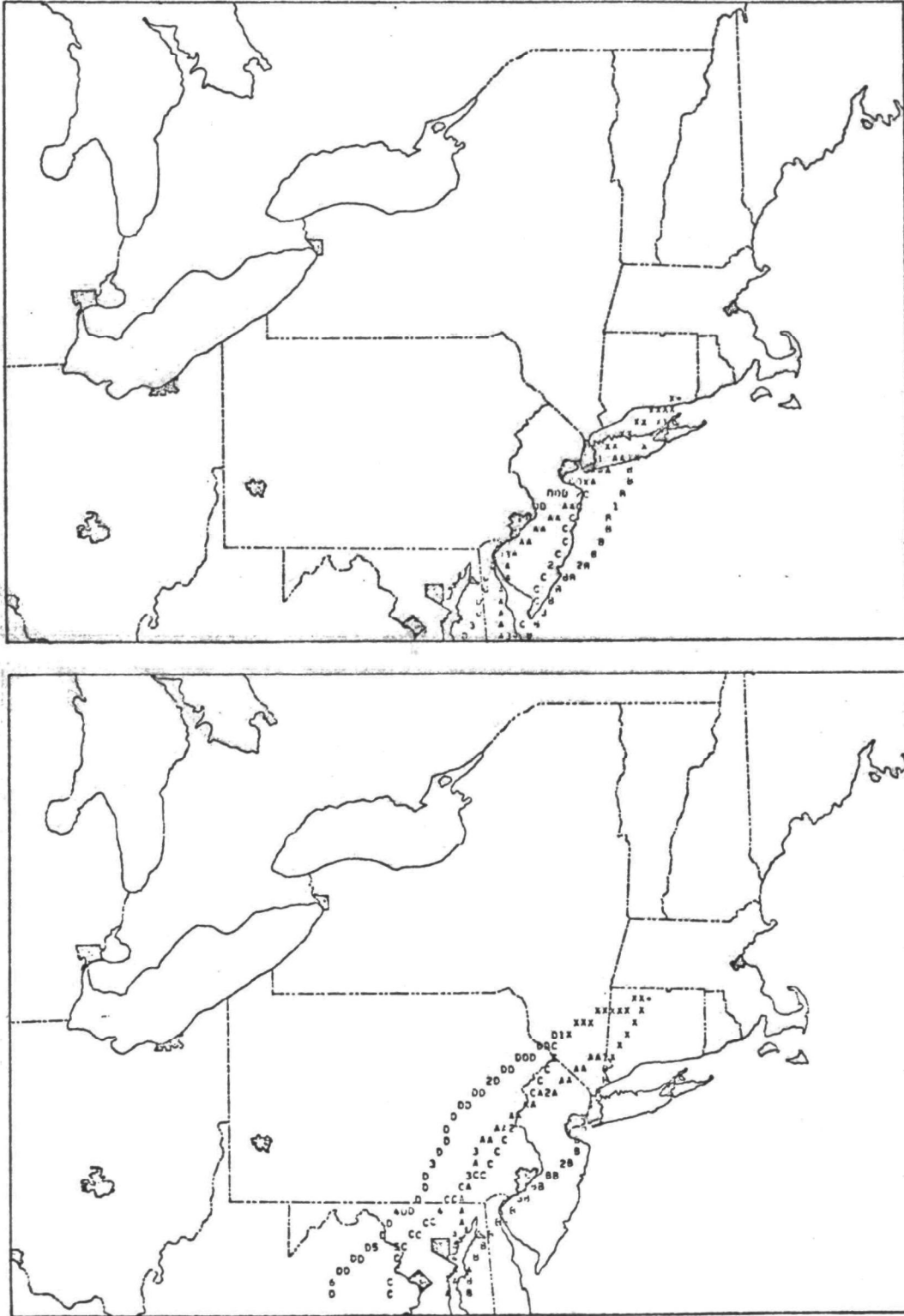


Figure A-1. Backward trajectories for Groton and Simsbury, Connecticut.

19 JULY 1975

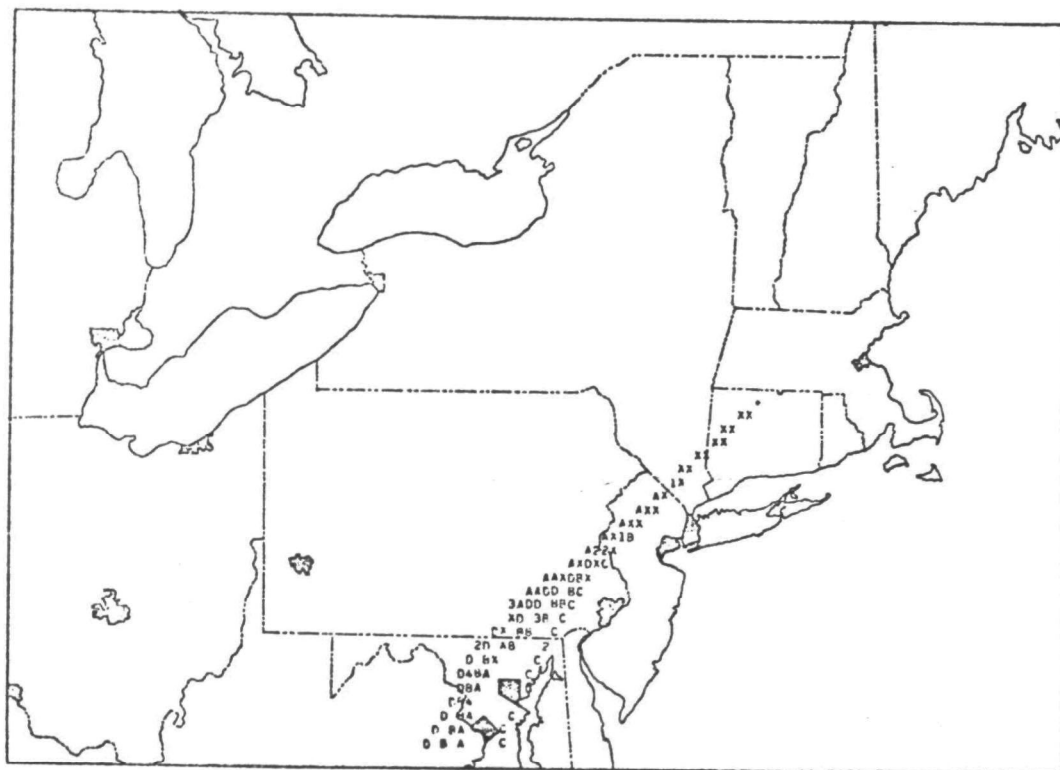
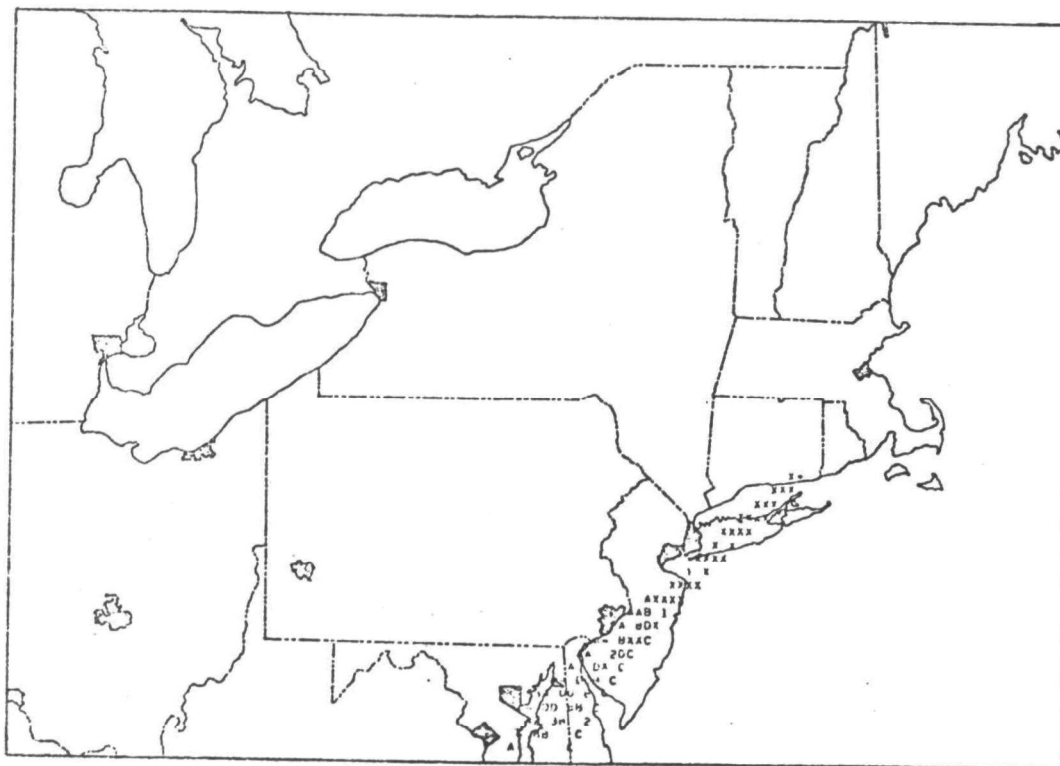
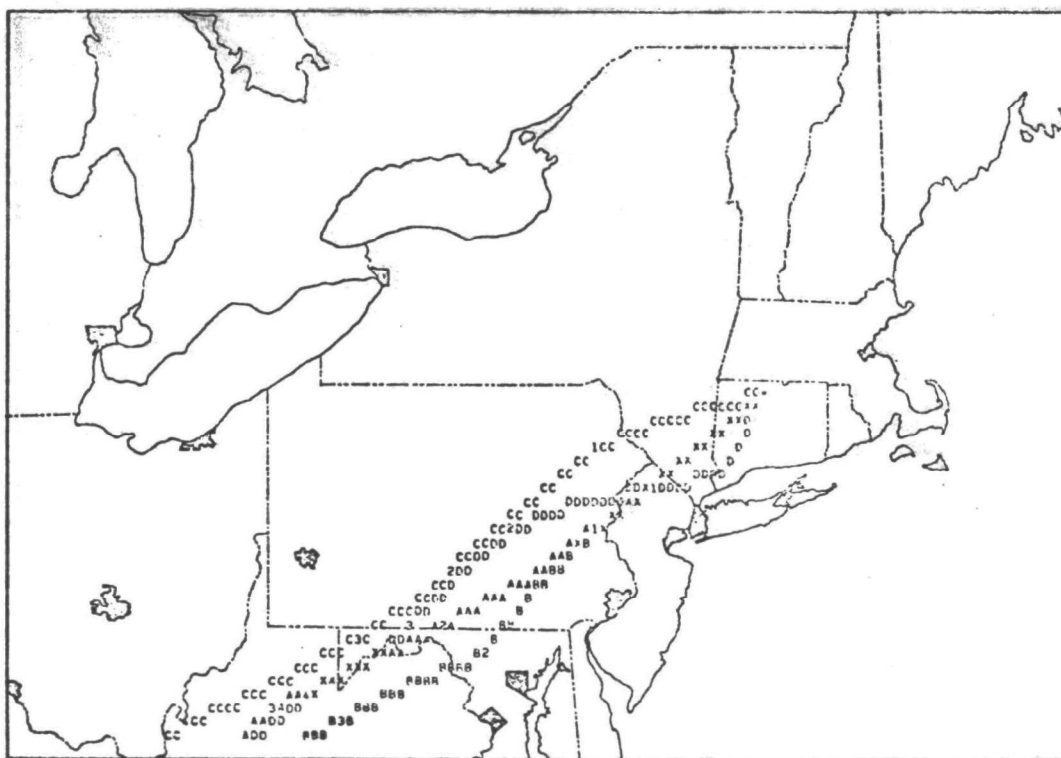


Figure A-2. Backward trajectories for Groton and Simsbury, Connecticut.





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23 JULY 1975

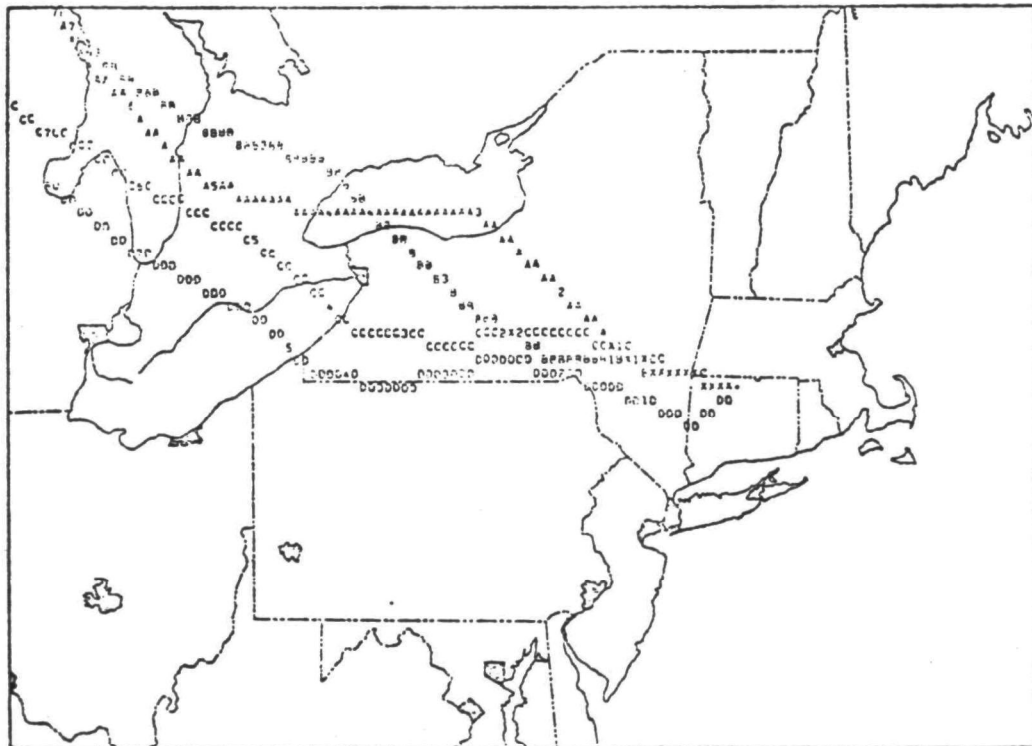
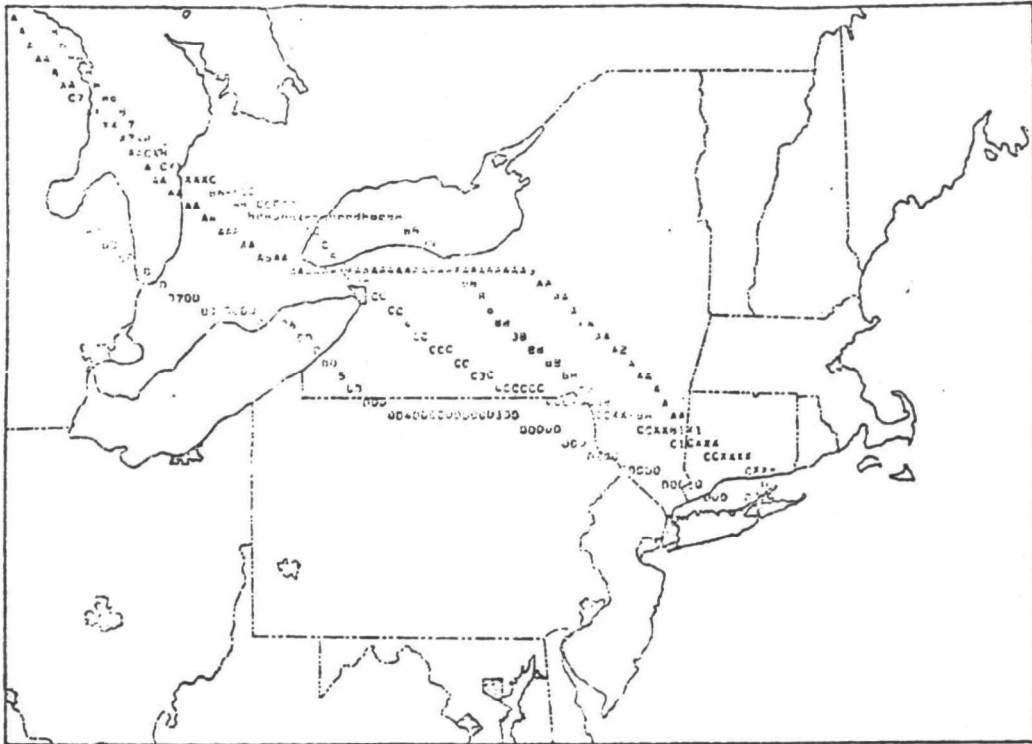


Figure A-4. Backward trajectories for Groton and Simsbury, Connecticut.

24 JULY 1975

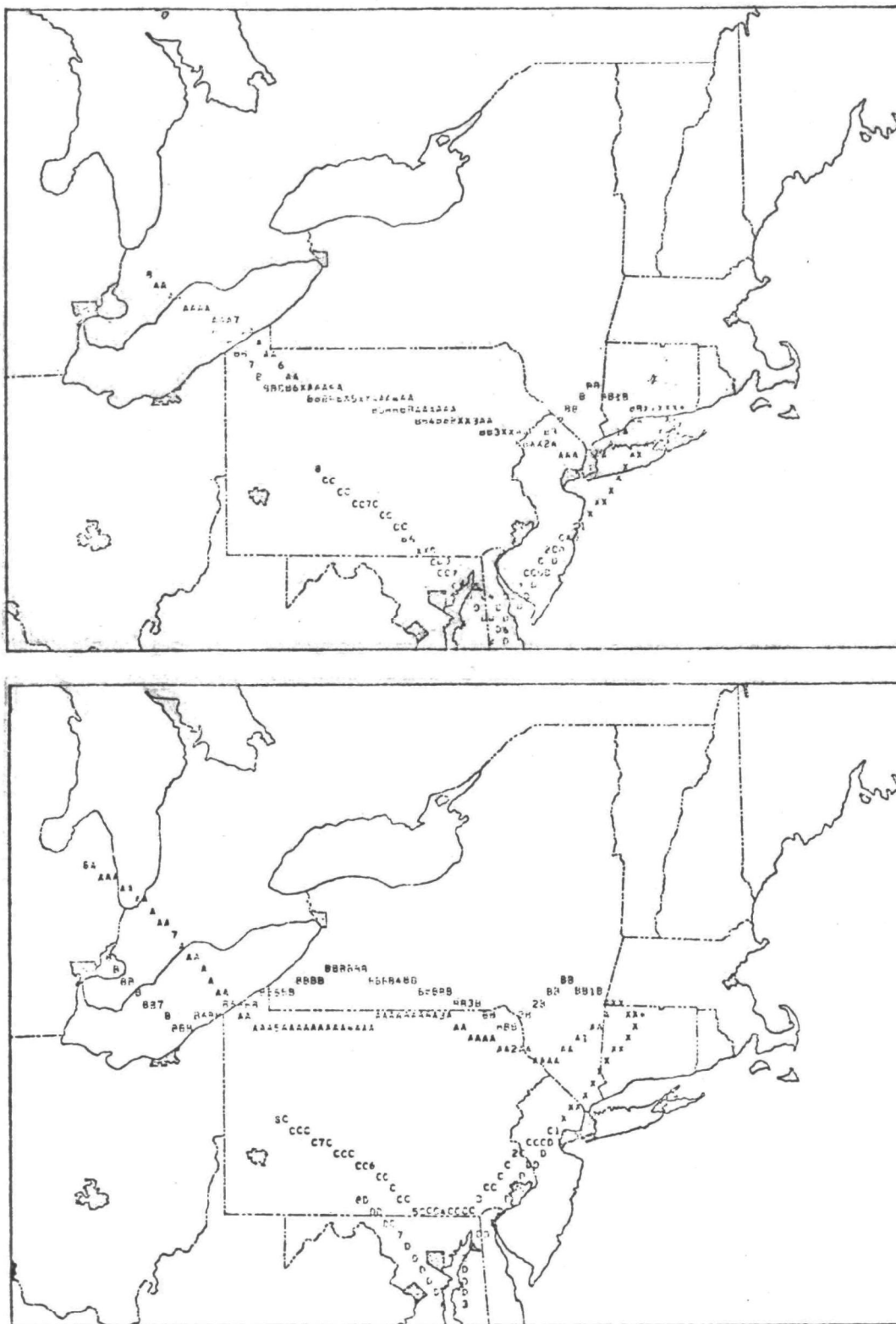


Figure A-5. Backward trajectories for Groton and Simsbury, Connecticut.

10 AUGUST 1975

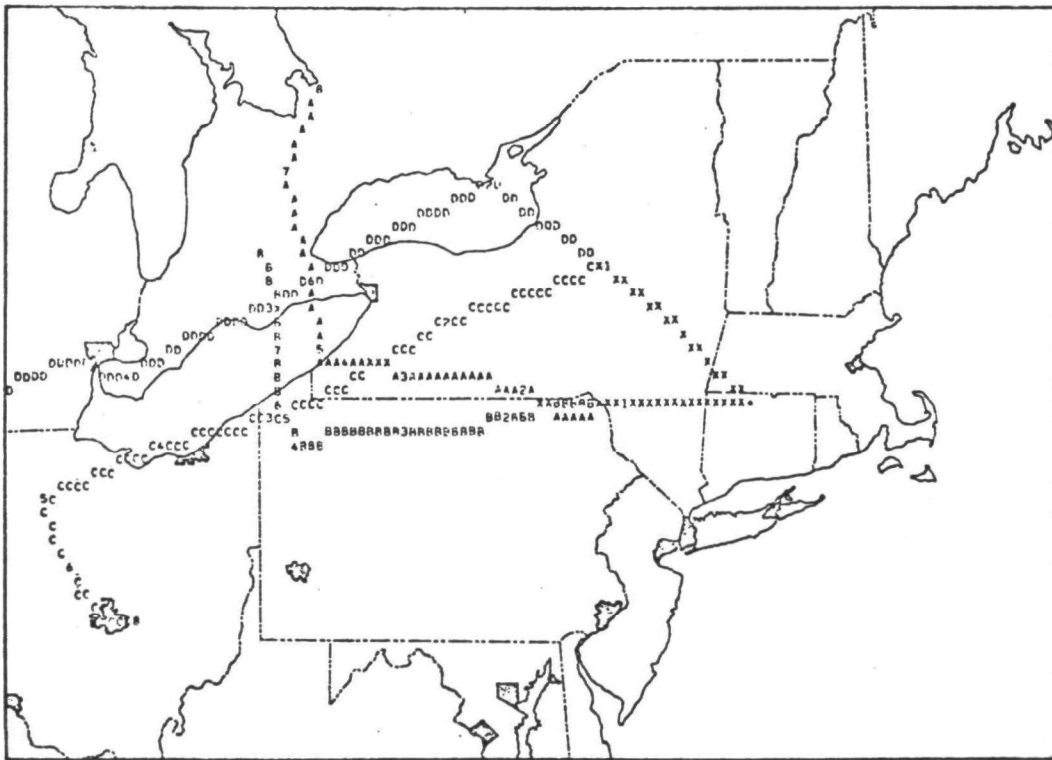
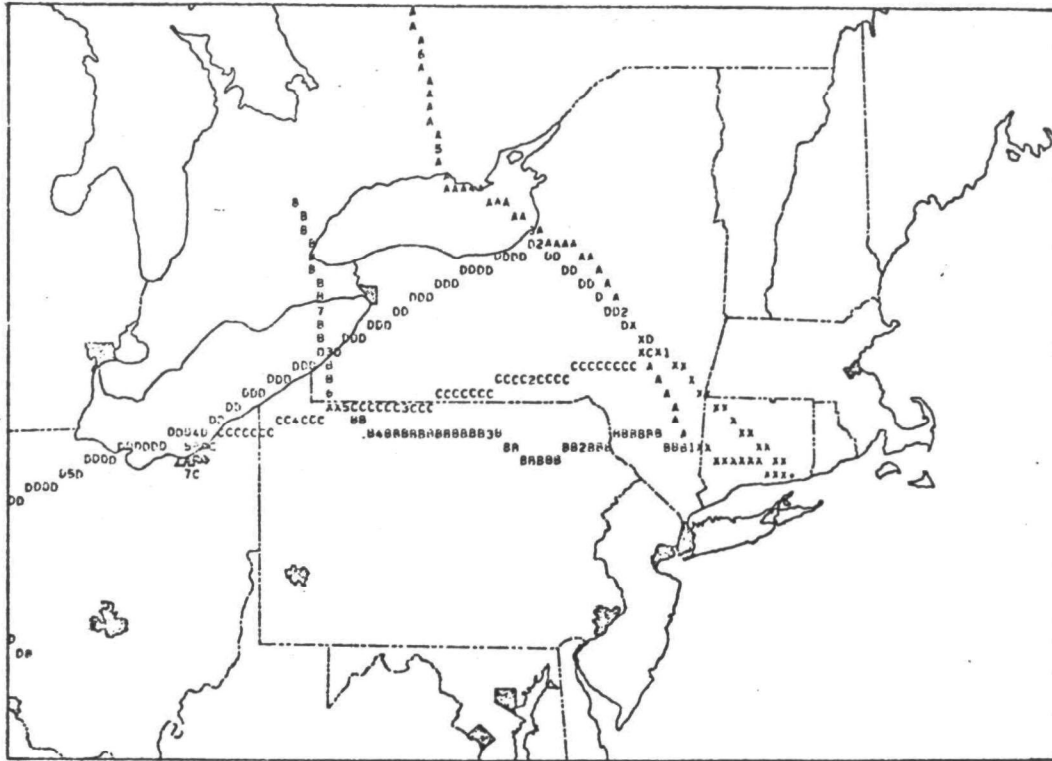


Figure A-6. Backward trajectories for Groton and Simsbury, Connecticut.

11 AUGUST 1975

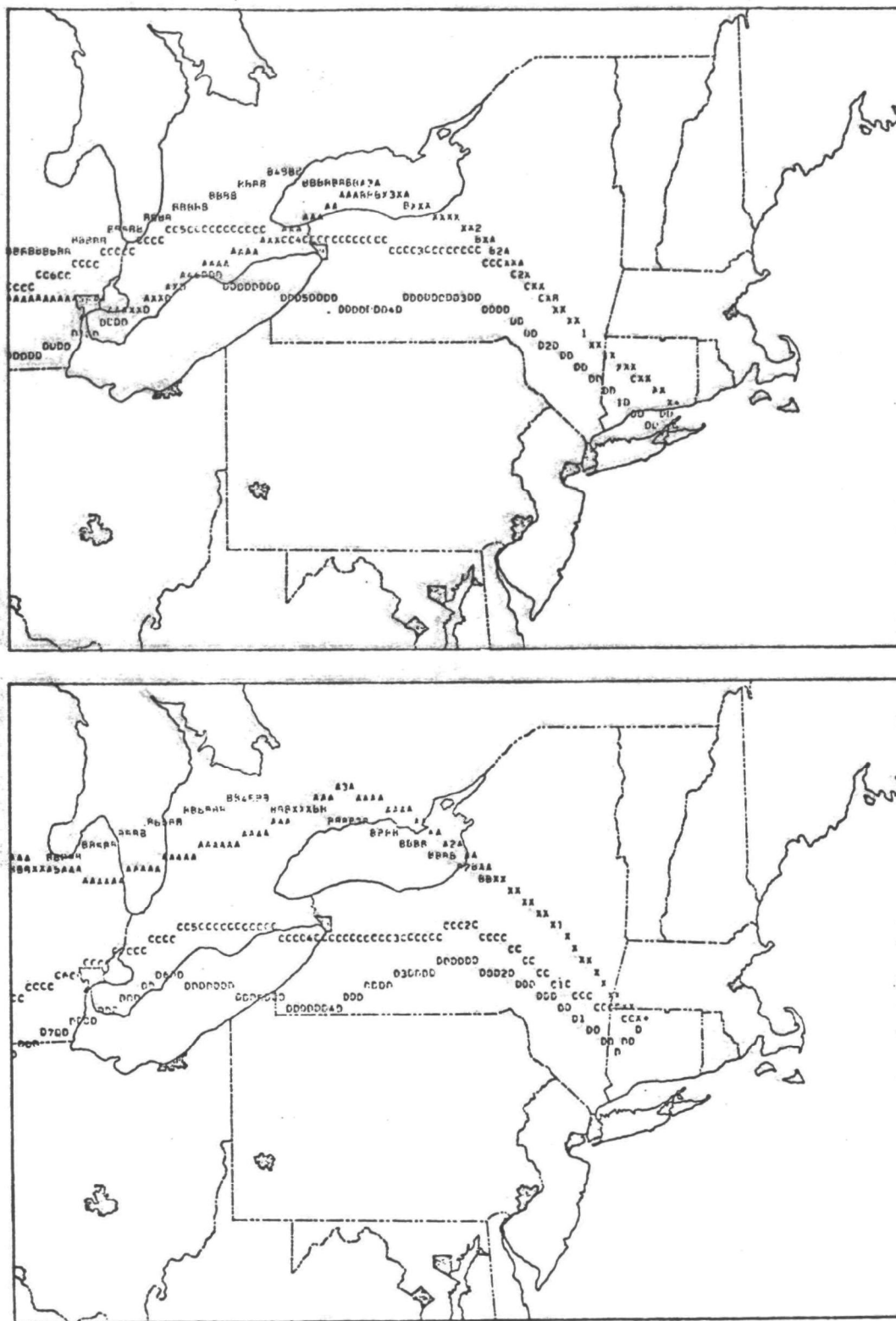


Figure A-7. Backward trajectories for Groton and Simsbury, Connecticut.

13 AUGUST 1975

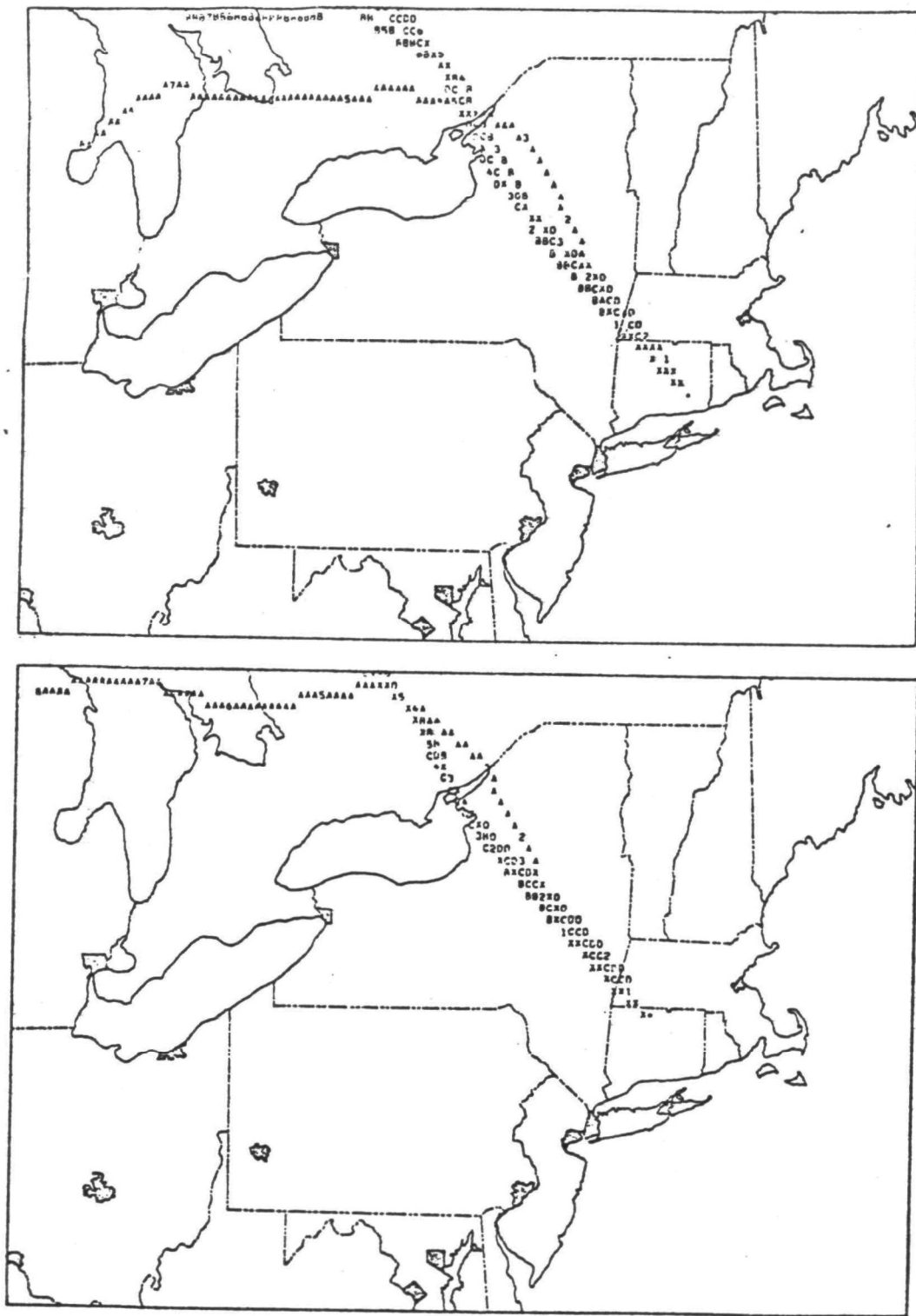


Figure A-8. Backward trajectories for Groton and Simsbury, Connecticut.

14 AUGUST 1975

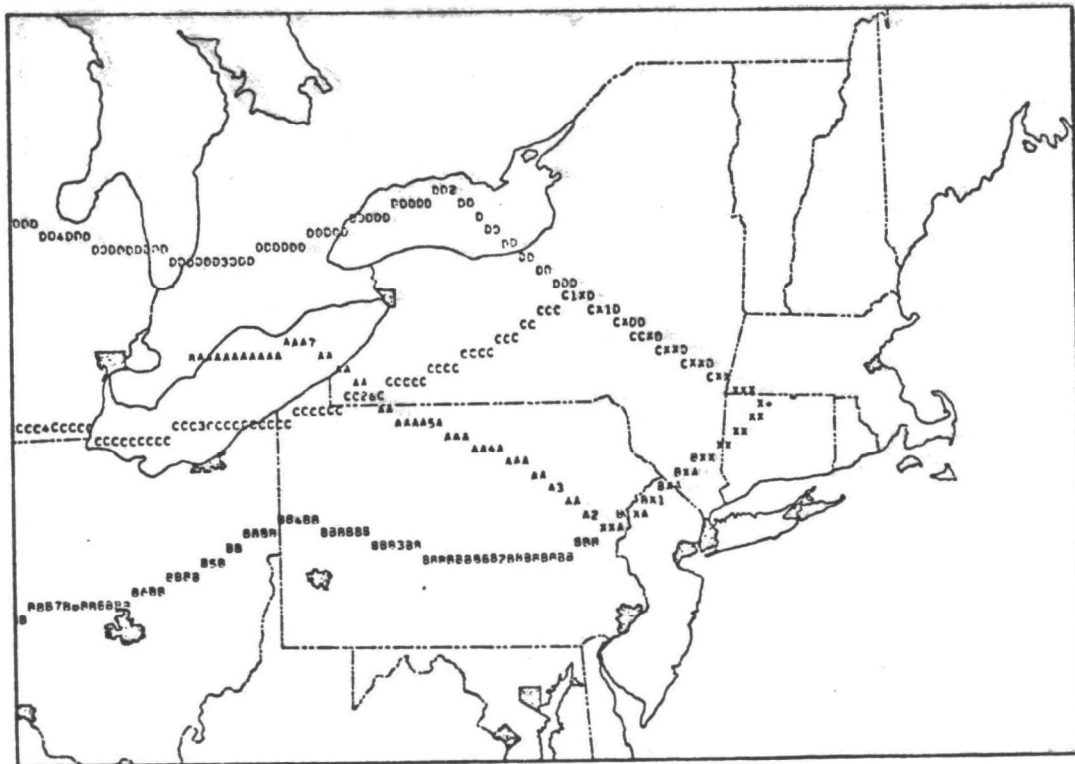
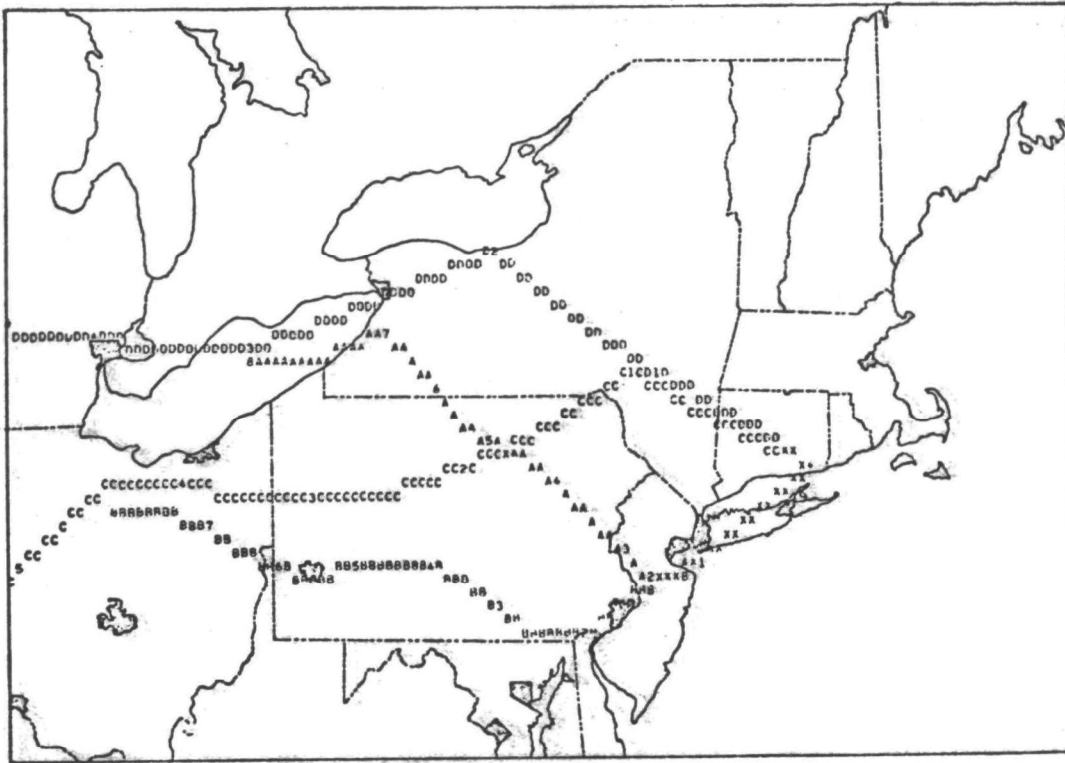
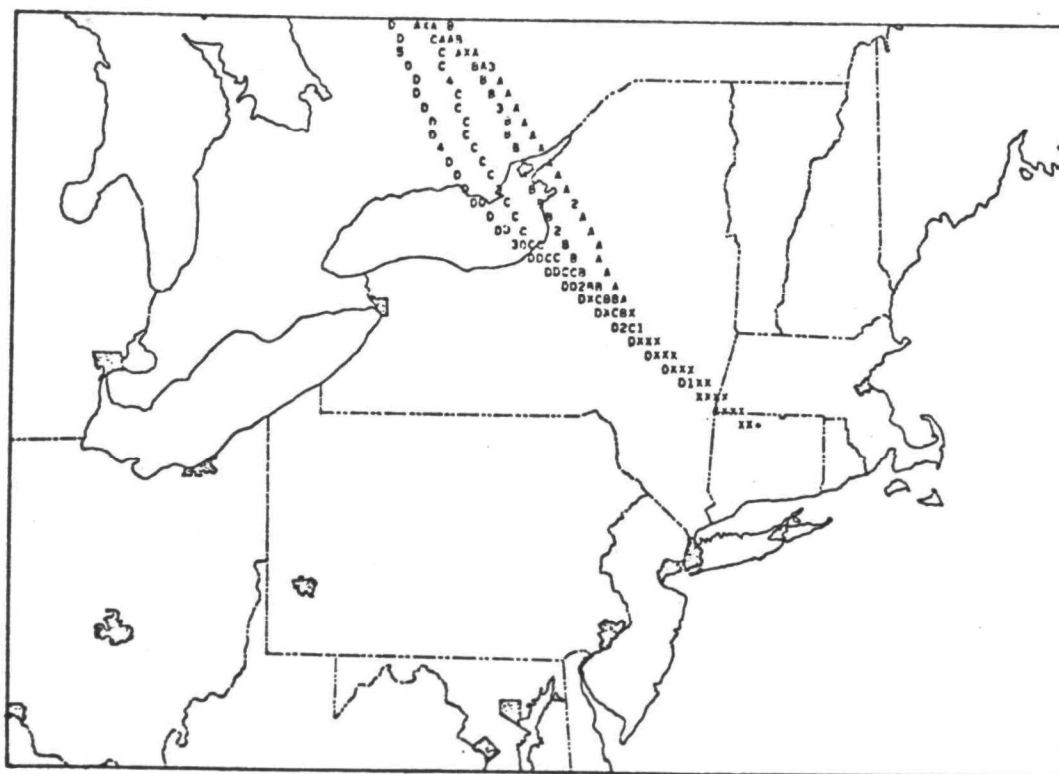
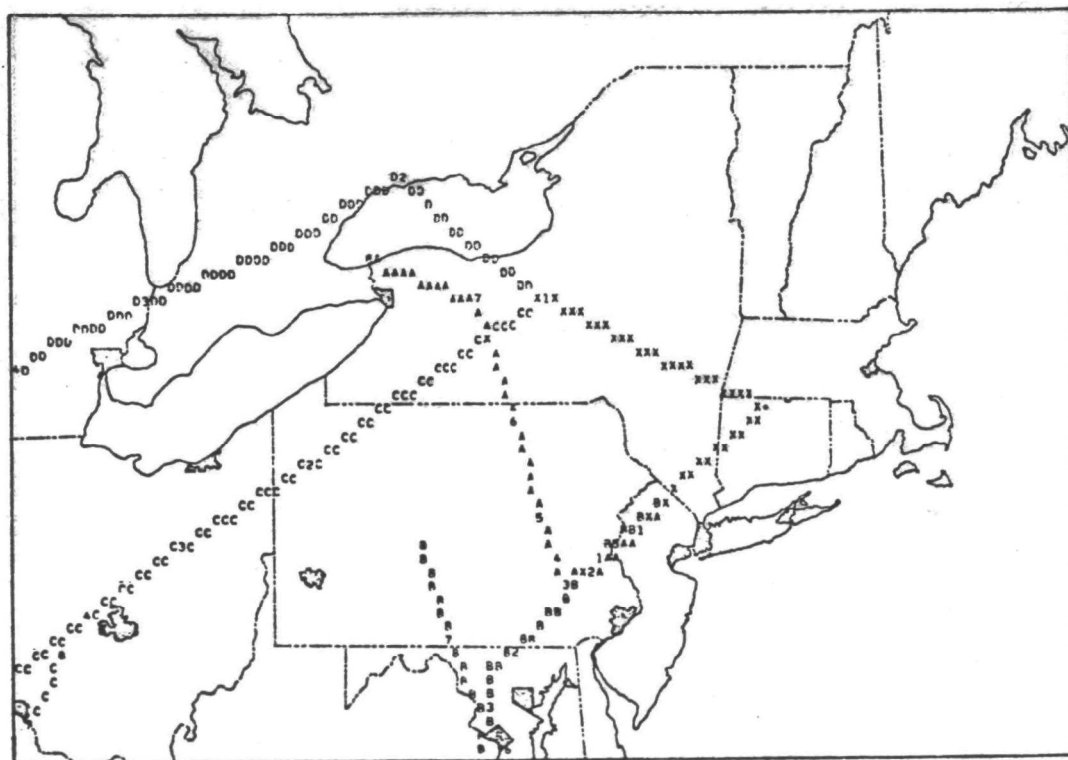


Figure A-9. Backward trajectories for Groton and Simsbury, Connecticut.

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[illegible]

102

<b>TECHNICAL REPORT DATA</b> <i>(Please read instructions on the reverse before completing)</i>		
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18 DISTRIBUTION STATEMENT  RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21 NO. OF PAGES 113
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