EPA 901/9-78-001

Final Report

September 1978

ATMOSPHERIC PROCESSES AFFECTING OZONE CONCENTRATIONS IN NORTHERN NEW ENGLAND

By:

F. L. Ludwig
Rosemary Maughan

Prepared For:

Environmental Protection Agency
Region 1
J.F. Kennedy Federal Office Building
Boston, Massachusetts

Contract No. 68-02-2548 (Requisition No. F74673)

SRI International Project 6908

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Approved By:

R.T.H. Collis, Director
Atmospheric Sciences Laboratory

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Advanced Developments Division

ABSTRACT

Readily available meteorological and air quality data were analyzed to determine the extent to which ozone concentrations in the Northern New England states of Maine, New Hampshire, and Vermont are influenced by causes external to those states. It is concluded on the basis of air trajectory and wind analysis that ozone generated from precursor emissions to the southwest or west is transported into the southern parts of Vermont, New Hampshire, and Maine. In the northern parts of New Hampshire and Vermont, violations of the ozone standard are more frequently associated with air that has come from the areas around Lakes Erie and Ontario. Although the Northern New England states are influenced by ozone transported from elsewhere, some control measures might still be required within the area even if the external sources were controlled and concentrations entering the region were reduced to levels near the tropospheric background.

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ACKNOWLEDGMENTS

Barbara Ikalainen, the EPA Project Officer, and Norman Beloin, also of EPA, have given indispensable assistance in providing data, background information, and guidance for which we are very grateful. We are indebted to Mr. David Dixon, Mrs. Norma Gordon and the staff of the Maine Bureau of Air Quality for the many suggestions that they made concerning this report. Mr. Dale Coventry of EPA provided valuable assistance. In the preparation of this report we have received much help from Linda Jones, Josette Louvigny, Joyce Kealoha, and Grace Tsai of SRI International.

I INTRODUCTION

Observations in the Northern New England States of Maine, New Hampshire, and Vermont have shown that the National Ambient Air Quality Standard (NAAQS) for ozone of 80 ppb is violated on occasion. National policy requires states and local agencies to take corrective action to prevent such violations of the standard in the future. The intelligent planning of corrective measures requires that the causes of the violations be understood. It is this fact that has motivated the research described in this report. We have attempted to identify, understand, and quantify, where possible, the causes of the oxidant problems in Northern New England. Understanding the oxidant problem is an intermediate goal; the ultimate goal has been to determine if an oxidant control strategy is actually required for the Northern New England states.

At first it seems paradoxical to question the need for a strategy to control the problem when the existence of the problem has already been admitted. However, in the case of atmospheric oxidants the causes may not be fully under the control of persons or organizations in the areas where the problems are known to occur. If the ingredients of the problem are generated locally, then the problem is controllable locally, but if they are brought in from elsewhere or if the ozone is the result of natural causes, then control strategies imposed only in the problem areas will be futile.

There have been a few constraints to this study. The most important of these is that only readily available data have been used. In general, this has not been a particularly severe problem, but there are instances where we have used the results of studies from other areas as basis for estimating Northern New England effects by analogy. Otherwise, the approach to the research has been quite straightforward. The severity of the problem was first defined by analysis of existing monitoring data. The possible causes, both natural and anthropogenic, were next examined. It was then possible to use the existing data and past studies to try to find evidence for the different processes thought to be operating to produce the ozone problem in Northern New England.

In general, the evidence that was sought for the possible origins of the Northern New England ozone was related to natural versus anthropogenic causes, and to transport into the area from outside versus local origin. The search for the evidence has led to the examination of some specific phenomena--e.g., the effects of sea breeze circulations and the differences between weekdays and weekends, but in each case the central problem has been the origin of the ozone, especially remote versus local. Finally, the methods used in this study have been chosen to match available data and the questions being addressed.

This report is organized along the same lines as the research. It begins with the statement of the problem. This is followed by discussion of the evidence that is available, and that discussion is followed in turn by analysis of the evidence. The report concludes with a section that summarizes the known facts regarding the origins of high concentrations of ozone in the Northern New England states. Most importantly, this final section relates those known facts to possible corrective measures that might be taken to avoid future violations of the NAAQS for oxidant in the Northern New England area.

II DATA

A. *General*

The work reported here has been confined to the analysis and interpretation of readily available data. No field measurement programs were mounted to collect new data. While the use of the data collected for other purposes does restrict the study somewhat, it is still possible to extract considerable information of use in this study.

Data obtained by routine monitoring of air quality at several sites in the Northern New England states have provided a valuable source of information. Other sources of routinely collected data are the numerous weather stations. The meteorological data have proven very valuable to the interpretation of the air quality data. Finally, some special studies have been conducted in New England in the past. The reports from those studies have also provided information valuable to the project. In the following sections, these data sources are discussed in more detail.

B. *Regular Surface Observations*

1. *Pollution Data*

Hourly ozone concentrations for a number of sites in New England were obtained from the EPA SAROAD data base. The data for sites in Vermont, Maine, and New Hampshire are of principal interest in this report. Figure 1 shows the location of these sites. The periods for which ozone data were available at each site in the three Northern New England states during the period January 1976 to June 1977 are listed in Table 1. Only Nashua and Manchester in New Hampshire have complete data sets; Burlington and Berlin each have only one month missing. The disparity among the data periods of the other sites has made spatial variation analysis difficult.

The EPA reviewed the sites and the monitoring of ozone, NO_2 and HC in New England between April and August 1977. Their comments on the sites in Vermont, Maine, and New Hampshire are included in Appendix A of this report. While all sites are described as adequate, and most are thought likely to experience some ozone depression due to urban locations, it should be noted that Manchester and Nashua in New Hampshire would "experience significant ozone depression" due to downtown locations. This, of course, has implications in the assessment of violations of the NAAQS for oxidant; the severity of the problem in such areas may well be greater than the measured concentrations would indicate.

2. *Meteorological Data*

Extensive use has been made of routinely collected National Weather Service data. Surface weather maps at 3-hour intervals and twice-daily upper air maps were referenced from microfilm data sets acquired from the National Climatic Center. The Daily Weather Map Series, produced by the National Oceanic and Atmospheric Administration (NOAA), showing surface station information and pressure patterns for the whole United States at 0700 EST (0800 EDT), were also used. Examples of these data sources are shown in Figures 2 and 3. More detailed meteorological data were taken from copies of National Weather Service WBAN form 10A, listing hourly data for sky cover, visibility, temperature, humidity, wind speed, and direction. Three-hourly data listings were also used. Data from Burlington, Vermont; Concord,

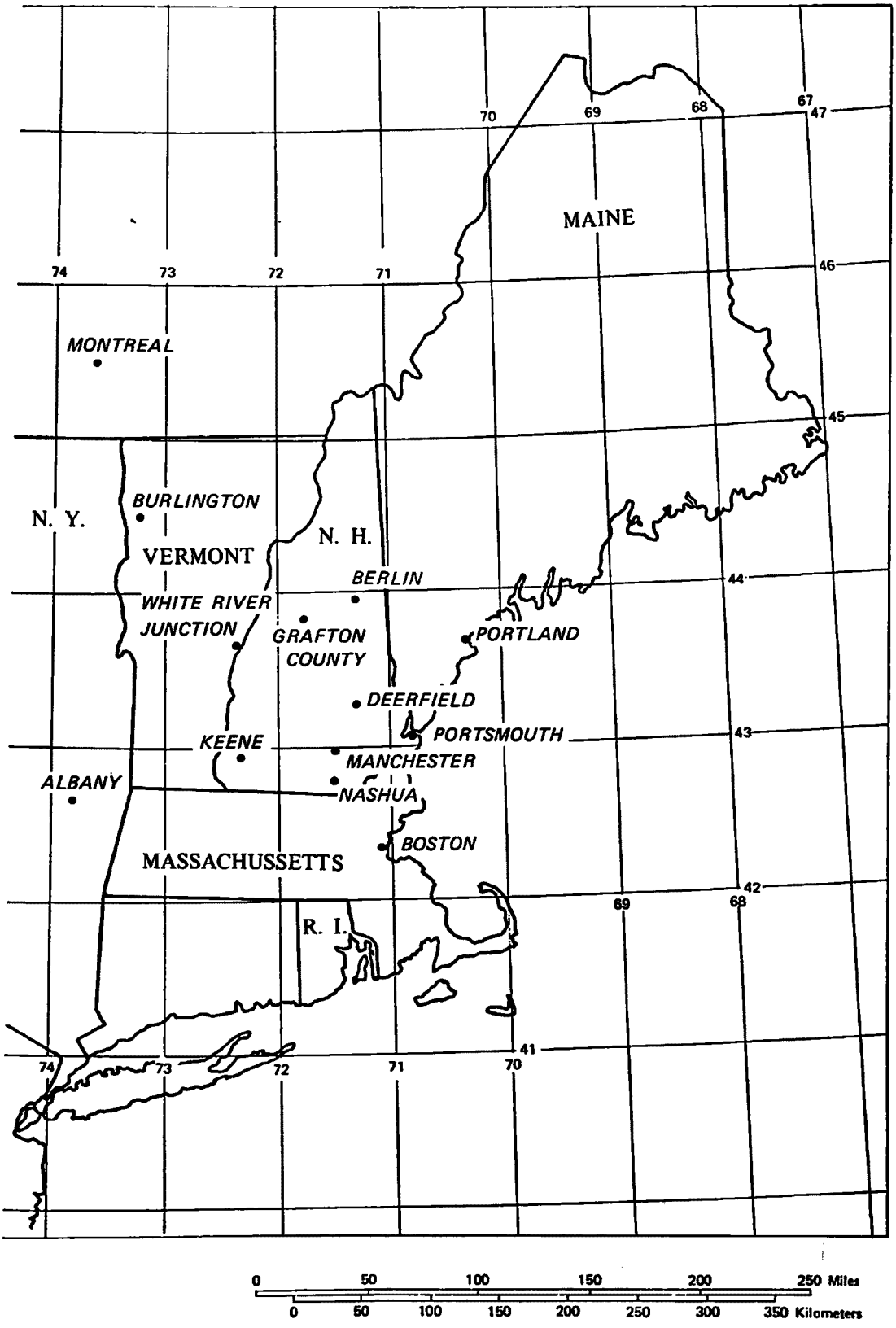


FIGURE 1 LOCATION OF SAROAD OZONE MONITORING SITES IN NEW ENGLAND

TABLE 1

Months for Which Ozone Data Were Available

For Sites in Vermont, Maine, and New Hampshire During 1976 and 1977

State	Site	1976												1977					
		J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J
Maine	Portland			X	X	X	X	X	X	X	X	X							
Vermont	Burlington	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X
	White River Junction													X	X	X	X	X	X
New Hampshire	Berlin	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X
	Deerfield							X	X										
	Grafton Country					X	X	X	X	X									
	Keene																X	X	X
	Manchester	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	Nashua	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	Portsmouth															X	X	X	X

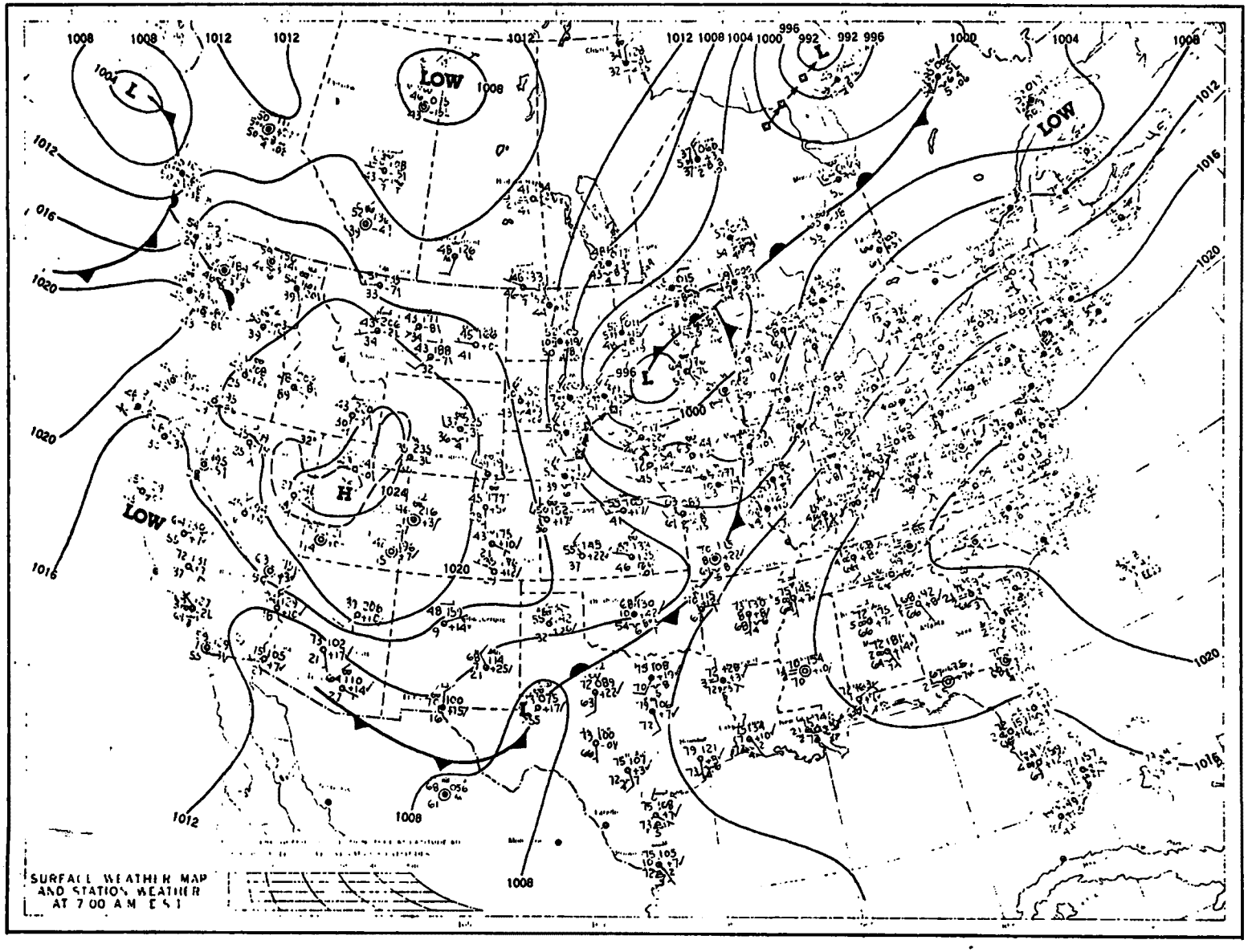


FIGURE 2 EXAMPLE OF SURFACE WEATHER MAP

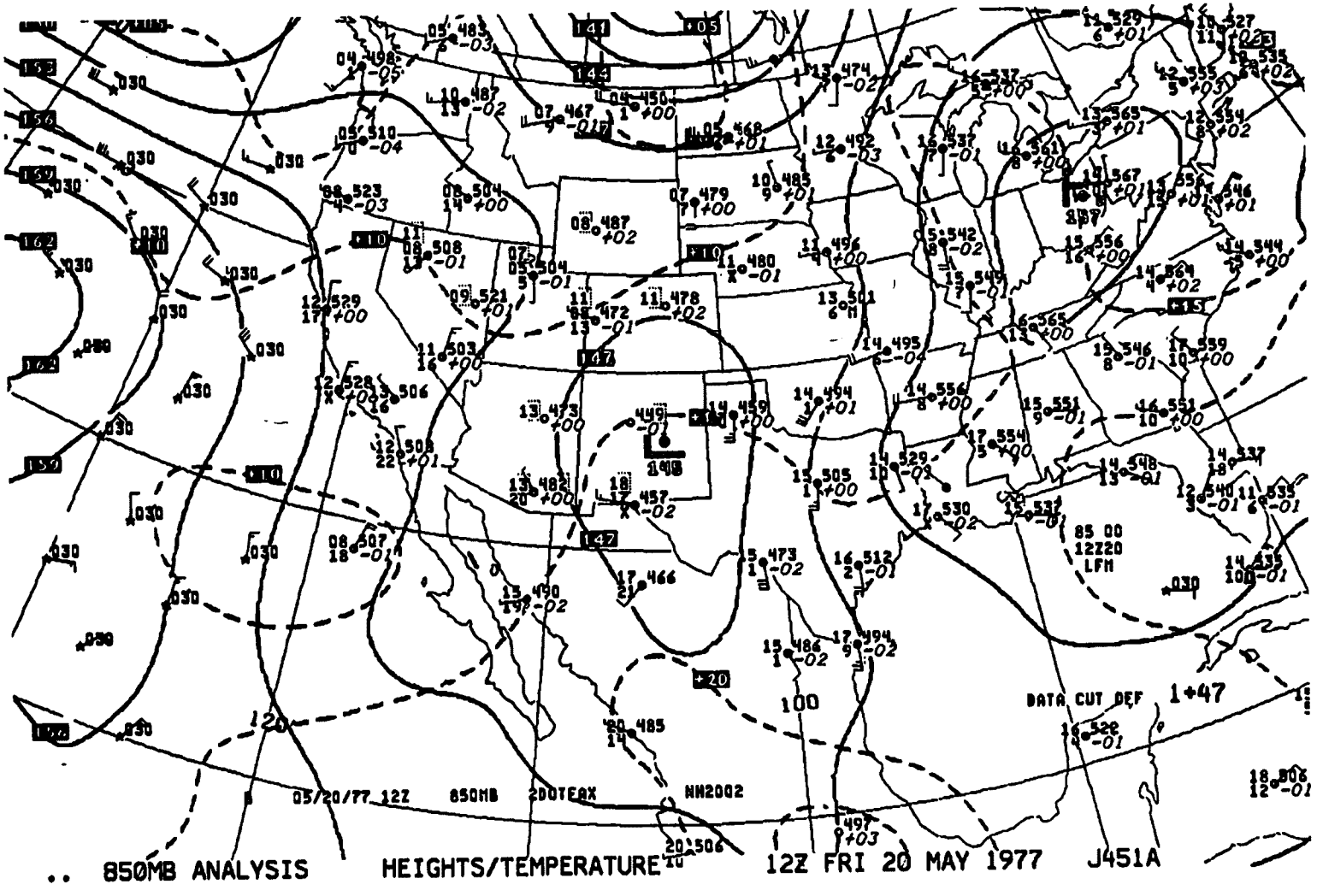


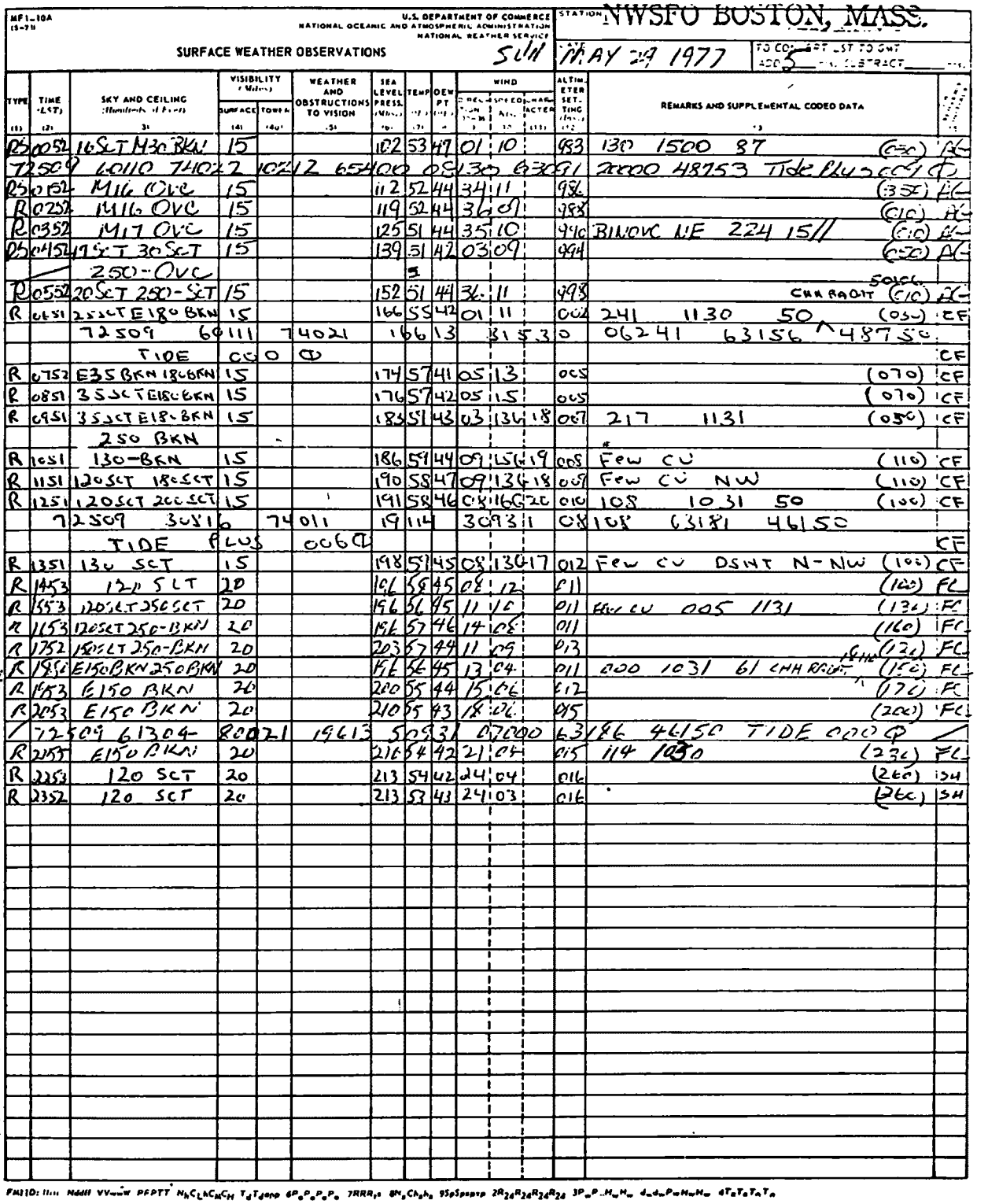
FIGURE 3 EXAMPLE OF UPPER AIR CHART (850 mb)

New Hampshire; Portland, Maine; Boston, Massachusetts; and Albany, New York were used in the study of selected high ozone periods. An example of National Weather Service Records is shown in Figure 4.

C. *Special Studies*

Very few special studies of photochemical pollutants were identified for the Northern New England States. One such study involved the measurement of hydrocarbons, oxides of nitrogen, ozone and meteorological parameters at three locations in the vicinity of Portland, Maine during the summer of 1974 (Londergan and Polgar, 1975). The report of this study also included a limited discussion of ozone measurements made aloft from an aircraft.

Other special studies that made use of aircraft were centered over the Southern New England States (see, e.g. Ludwig and Shelar, 1977), and contributed little to the understanding of conditions in Northern New England. An exception was a report by Spicer, Gemma, and Sticksel (1977) that contained some analyses extending to the offshore areas of Maine and New Hampshire. Finally, most analyses of existing data (e.g., Wishinki, 1977) were generally based on fewer data than the study reported here.



MF1-10A (5-71)

U.S. DEPARTMENT OF COMMERCE
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
NATIONAL WEATHER SERVICE

SURFACE WEATHER OBSERVATIONS

STATION NWSFO BOSTON, MASS.

DATE MAY 29 1977

TO CONVERT EST TO GMT ADD 5 — IN SUBTRACT

TYPE (1)	TIME (LST) (2)	SKY AND CEILING (Hundreds of Feet) (3)	VISIBILITY (Miles) SURFACE (4a)	VISIBILITY (Miles) TOWER (4b)	WEATHER AND OBSTRUCTIONS TO VISION (5)	SEA LEVEL PRESS. (Mbs) (6)	TEMP °F (7)	DEW PT °F (8)	WIND DIR. (9)	WIND SPEED (10)	WIND CHARACTER (11)	ALTIMETER SETTING (Inches) (12)	REMARKS AND SUPPLEMENTAL CODED DATA (13)	
RS	0052	16 SCT M30 BKN	15			102	53	49	01	10		983	130 1500 87 (050)	AC
	72509	60110 74022	10Z	42	65400	08	130	63091					20000 48753 TIDE PLUS 0004	CF
RS	0152	M16 OVC	15			112	52	44	34	11		98	(350)	AC
R	0252	M16 OVC	15			119	52	44	36	09		988	(310)	AC
R	0352	M17 OVC	15			125	51	44	35	10		990	BINOVC NE 224 15// (310)	AC
RS	0452	9 SCT 30 SCT	15			139	51	42	03	09		994	(320)	AC
		250-OVC					5						50 1616	
R	0552	20 SCT 250-SCT	15			152	51	44	36	11		998	CHN RAGIT (310)	AC
R	0651	25 SCT E180 BKN	15			166	55	42	01	11		002	241 1130 50 (030)	CF
		72509 60111		74021		166	13		31	53	0		06241 63156 48750	
		TIDE	000		0060									CF
R	0752	E35 BKN 180 BKN	15			174	57	41	05	13		005	(070)	CF
R	0851	35 SCT E180 BKN	15			176	57	42	05	15		005	(070)	CF
R	0951	35 SCT E180 BKN	15			183	51	43	03	13	18	007	217 1131 (050)	CF
		250 BKN												
R	1051	130-BKN	15			186	51	44	09	15	19	008	Few CU (110)	CF
R	1151	120 SCT 180 SCT	15			190	58	47	09	13	18	009	Few CU NW (110)	CF
R	1251	120 SCT 200 SCT	15			191	58	46	08	16	20	010	108 1031 50 (100)	CF
		72509 30816		74011		19	114		30	93	1	008	108 63181 46150	
		TIDE PLUS		0060										CF
R	1351	130 SCT	15			198	51	45	08	13	17	012	Few CU DSNT N-NW (100)	CF
R	1453	120 SLT	20			196	58	45	08	12		011	(100)	FC
R	1553	120 SLT 250 SCT	20			196	56	45	11	10		011	Few CU 005 1131 (130)	FC
R	1653	120 SCT 250-BKN	20			196	57	46	14	08		011	(160)	FC
R	1752	150 SLT 250-BKN	20			203	57	44	11	09		013	(120)	FC
R	1852	E150 BKN 250 BKN	20			196	56	45	13	04		011	000 1031 61 CHN RAGIT (150)	FC
R	1953	E150 BKN	20			200	55	44	15	06		012	(170)	FC
R	2053	E150 BKN	20			210	55	43	18	06		015	(200)	FC
		72509 61304	200	21	19613	50	931		07	000		63186	46150 TIDE 0000	
R	2153	E150 BKN	20			216	54	42	21	04		015	114 1030 (230)	FC
R	2253	120 SCT	20			213	54	42	24	04		016	(260)	SH
R	2352	120 SCT	20			213	53	43	24	03		016	(260)	SH

A synoptic observation, in WMO code format FM12D, is entered on line following regular observation.

FM12D: IIiii Nddff VVwwNw PPPTT $N_hC_LhC_MC_H$ T_dT_dnnn $6P_oP_oP_oP_o$ $7RRR_{ss}$ $8N_sC_hh_sh_s$ $9SpSpspsp$ $2R_{24}R_{24}R_{24}R_{24}$ $3P_oP_oH_wH_w$ $4d_wd_wP_wH_wH_w$ $4T_oT_oT_oT_o$

*U S GOVERNMENT PRINTING OFFICE 1973—762-255

FIGURE 4 EXAMPLE OF NATIONAL WEATHER SERVICE HOURLY WEATHER OBSERVATIONAL RECORDS

III BACKGROUND

A. *The Nature of the Problem*

The NAAQS for oxidant states that an hourly average of 80 ppb should not be exceeded more than once in any year. With the exception of Berlin, New Hampshire, no single site measuring oxidant in Maine, New Hampshire, or Vermont came close to meeting that standard in either 1976 or 1977. The greatest numbers of times when the concentrations equaled or exceeded the NAAQS were experienced at Nashua in both years (168 hours in 1976, and 190 hours in 1977) while both Portsmouth and Manchester showed well over 100 such hours in 1977 (150 and 112, hours respectively). Even Burlington and White River Junction in Vermont, seemingly remote from possible anthropogenic sources of oxidant from major urban areas to the south and west, both experienced nearly 100 hours of 80 ppb or more in the first six months of 1977.

Figure 5 shows that the frequencies of high concentrations exhibited marked seasonal cycles, tending to be above the standard for the greatest number of hours in May, June, July, and August. There were no violations between October and February. Differences in meteorology from year to year can cause substantial differences in the frequency of standards violations, especially in the months at the beginning and end of the photochemical "season". For example, one major difference between the two years studied was the greater number of violations in March, April and May 1977 than during the same months in 1976. This, together with the large number of hours at all sites in May 1977 when the standard was equaled or violated, meant that there were a greater number of such cases in the three states during the first six months of 1977 that were available for analysis than there were during the whole of the year 1976.

The duration of periods when concentrations were 80 ppb or more is shown in Table 2. At most sites, 50% of these periods persisted for up to 4 hours, and 10% up to 6 hours. There were two periods, 17-18 May 1977 and 28-29 June 1977 that persisted for 16 to 22 hours. The most prolonged period of high ozone concentrations occurred at Nashua, on 26-27 May 1977, where levels equaled or exceeded 80 ppb for 25 hours without interuption. If one ignores the single hour recording 75 ppb, linking two periods, the full extent was 37 hours.

The observed seasonal patterns confirm what is known of the seasonal variations in both natural and anthropogenic sources of ozone. Although large amounts of ozone are produced in the stratosphere, the contribution to ground level ozone concentrations is generally small (see Section III-B-1-b). However, there are occasions during the late winter and spring when much higher concentraions of stratospheric ozone can be mixed well down in the troposphere. This, together with the start of photochemical activity and subsequent anthropogenic production of ozone, mean that the spring months are likely to mark the onset of relatively high levels of oxidant, and of consequent violations of the standard. As the year progresses, violations are more likely to reflect photochemical activity alone. As this ceases in the fall, oxidant levels, reflecting the lower autumn background concentrations and decreasing photochemical activity, are less likely to violate the standard.

The diurnal variations in the frequency of occurrence of ozone concentrations of 80 ppb or more that are displayed in Figure 6 show a general pattern that is clear and common to all sites: A maximum number of violations occurred during daylight hours, peaking in the main between 1400 and 1600 hours EDT, but significant frequencies were observed at some sites, e.g. Portland, into early evening. There were also secondary peaks occurring during night

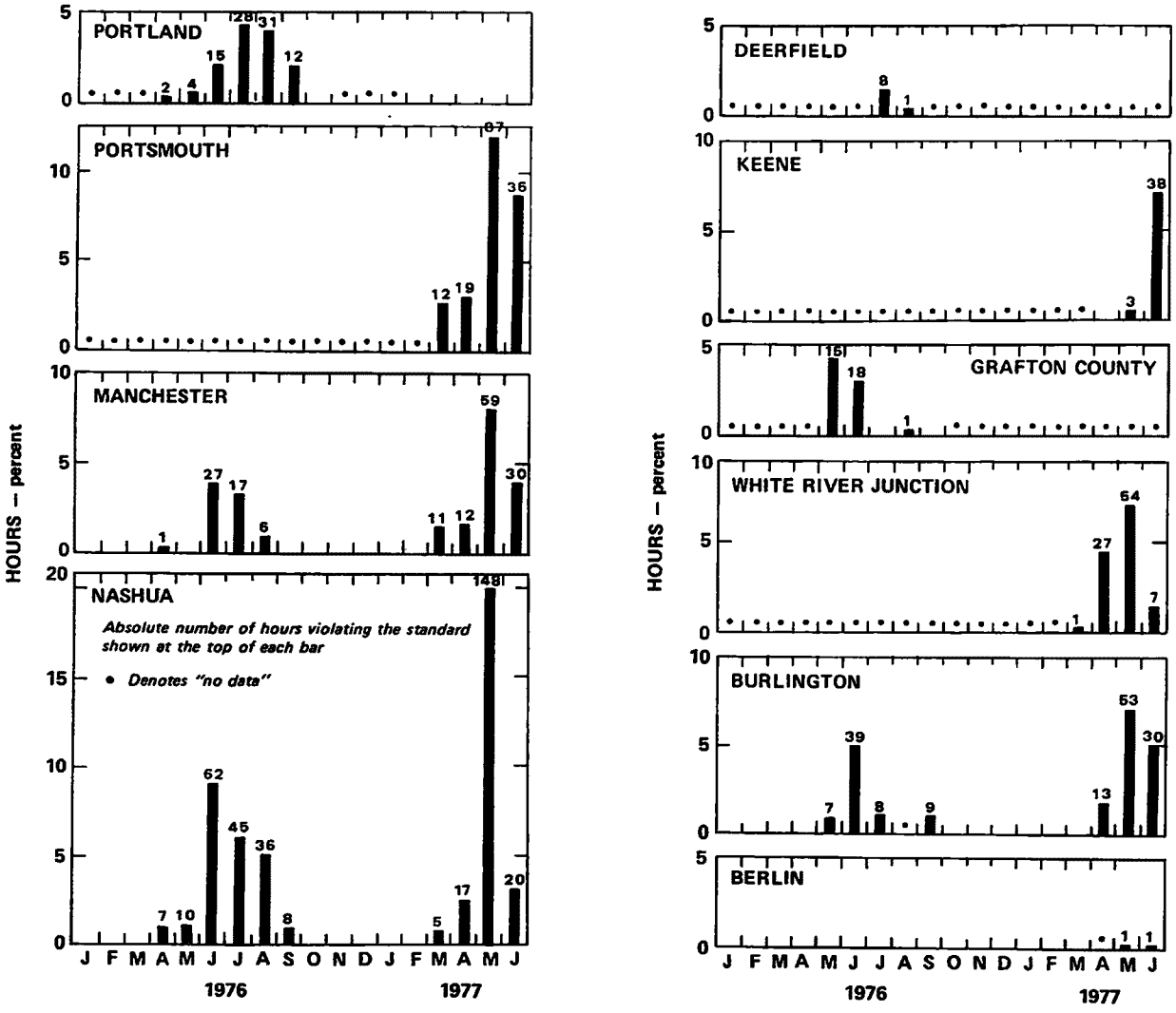


FIGURE 5 PERCENTAGE OF HOURS WHEN OZONE CONCENTRATIONS EQUALLED OR EXCEEDED NAAQS

Table 2

FREQUENCY OF OZONE CONCENTRATIONS OF 80 ppb
OR GREATER FOR VARYING PERIODS OF TIME
(Number of Cases)

Consecutive Hours / Station / Duration	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Berlin	2																								
Deerfield	4	3	1	1																					
Grafton Co.	8	6	4	4	3	1	1	1	1	1	1	1	1	1	1										
Keene	6	6	6	4	4	2	2	2	1	1	1	1	1	1	1	1									
Burlington	33	26	22	17	15	10	7	7	5	5	3	3	3	2	1	1	1	1	1	1					
White River Junction	21	14	13	12	10	7	3	3	2	1	1	1	1												
Portland	25	18	14	9	8	7	4	4	3																
Portsmouth	30	24	19	17	14	12	9	7	7	4	4	2	2	1	1	1									
Manchester	43	32	24	18	10	8	6	3	3	2	2	2	2	1	1	1	1	1	1						
Nashua	70	56	40	32	27	23	22	20	14	14	9	5	4	3	3	3	2	2	2	2	2	1	1	1	1

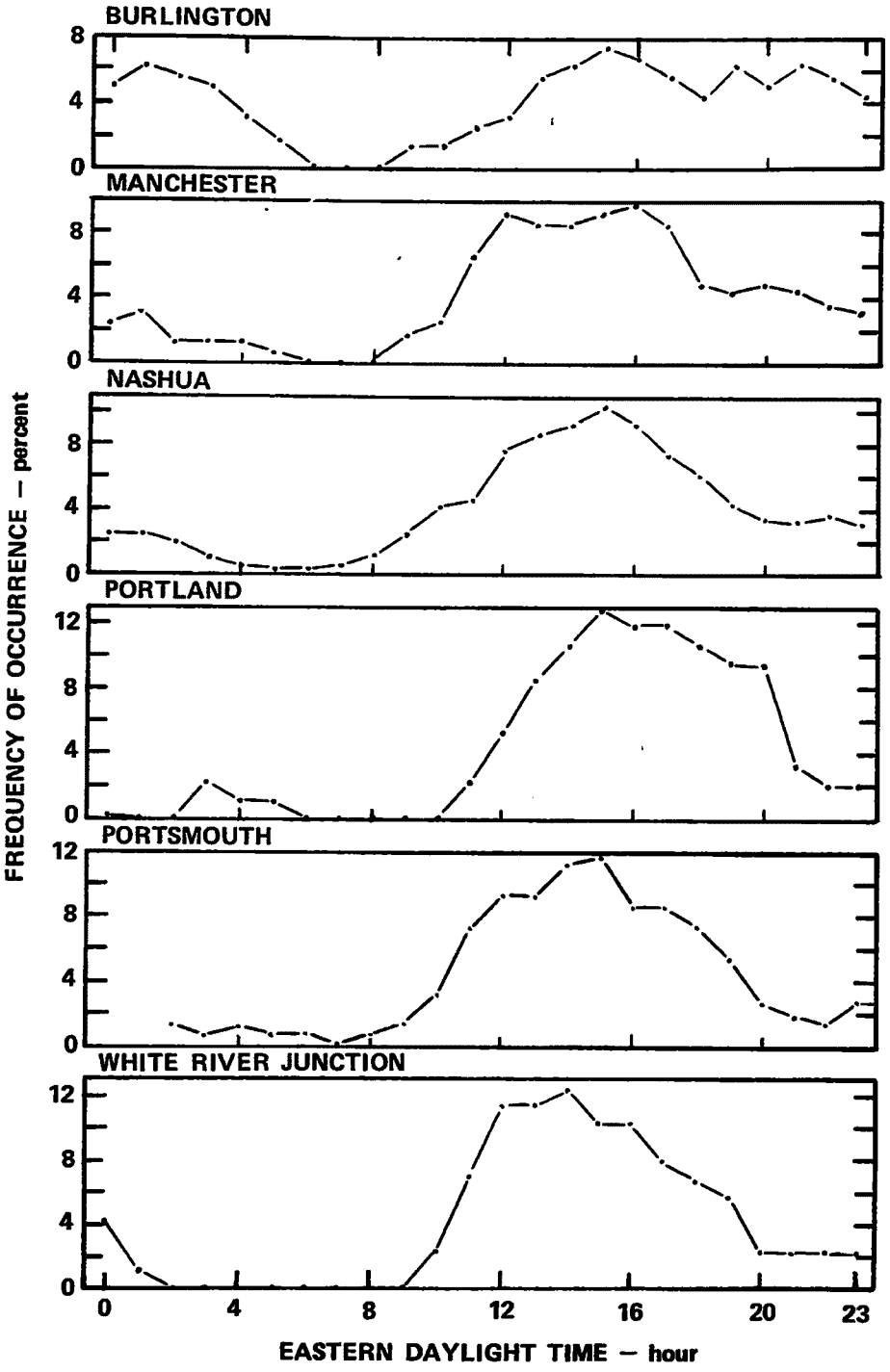


FIGURE 6 DIURNAL VARIATION OF OZONE CONCENTRATIONS OF 80 ppb OR GREATER FOR SELECTED STATIONS

hours--around 2200 or 2300 EDT for Portsmouth, Nashua, and Manchester, and 0100 to 0300 hours for White River Junction, Portland, and most pronounced of all, Burlington. The time least likely to experience violations was between 0400 and 0800.

As with seasonal variations, the diurnal patterns of high ozone concentration are to be expected from a consideration of diurnal cycles of the precursors to ozone formation, especially nitric oxide (NO). Emissions of NO and HC during early morning hours will scavenge oxidant present during this time (oxidant probably of natural origin, or left from the previous day). With little photochemical activity at this time, concentrations will be low, and violations exceptional. Photochemical activity will be most intense around noon, and the chance of violations greatest during early afternoon hours. Concentrations will fall as photochemical production of ozone decreases, and finally ceases after sunset. It is often the case that ozone produced in the urban plume during the day becomes isolated in or above a stable layer formed during night hours. If vertical mixing occurs at night, this ozone can be mixed to ground level. Advection of an urban plume would mean that nighttime violations can occur well downwind of the source. It may be that the difference in nightime patterns of violations for Nashua and Burlington reflect this point.

Thus, although daytime violations of the standard may well occur as the result of normal diurnal cycles in precursors and meteorological variables, nighttime violations perhaps more often reflect particular synoptic situations that can cause ozone aloft to be mixed down to ground level. Examination of the weather situation associated with days when ozone levels exceeded the standard shows that 50% of these occasions occurred either with a warm air mass near a cold front, or in the warm sector of a frontal wave (see Section IV-B-1-b, Table 5).

B. *Possible Origins of Oxidant Concentrations in Excess of the Standard*

The preceding section has shown that violations of the NAAQS occur in all parts of Northern New England, including those that are well away from any highly urbanized area. When violations occur near urban areas, with large emissions of known precursors to ozone, then the natural assumption has been to link the observed high ozone concentrations causally with the nearby emitters. This assumption underlies the philosophy behind the NAAQS. It has been tacitly assumed that air quality could be improved by locally instituted abatement programs. The originally published EPA procedures for determining the necessary precursor reductions (Federal Register, 1971) applied to local areas where measureable oxidant problems exist. At the time that the procedures were devised, it was believed that ozone was only a local urban problem and that diffusive and destructive processes reduced the oxidant concentrations in rural areas to insignificant levels. However, by the early 1970s it had been observed that high oxidant concentrations were quite widespread within rural areas. The situation described in the preceding section is not unusual.

The sources of the high concentrations of ozone outside urban areas are subject to some controversy, especially with regard to their relative magnitude. The importance of the sources to the problem of formulating control strategies is obvious. If the major sources are anthropogenic, then a control strategy can presumably be formulated, but it is absolutely necessary that the controls be applied in the proper place. If the observed ozone concentrations are the result of transport over long distances, then the controls must be applied at suitable places, possibly far upwind. If major sources are natural, then control measures are unlikely to be of any use and the considerable cost of their implementation should be avoided.

The several possible processes that might cause high non-urban ozone concentrations are

discussed in the following sections. The major natural possibilities are transport from the stratosphere and photochemical production from natural precursors within the troposphere. The two basic anthropogenic possibilities are generation from locally emitted precursors, or transport over long distances. Much of the discussion of natural processes that follows has been extracted from a report by Singh et al. (1977). The discussion is intended to provide some background for the understanding and interpretation of the available data.

1. *Natural Sources and Sinks of Tropospheric Ozone*

a. *Tropospheric Synthesis*

Went (1960) suggested that tropospheric ozone might be synthesized photochemically from natural terpenes and natural NO_2. Ripperton et al. (1971) tested this hypothesis under controlled conditions and confirmed that terpene and NO_x can result in ozone formation processes similar to those in polluted atmospheres. Although terpenoid compounds and NO_2 have been measured at relatively remote locations, their involvement in the tropospheric balance of ozone is uncertain. This uncertainty arises from inadequate data bases, the inhomogeneous distribution of trees, the extreme reactivity of the terpenes, the the temporal and seasonal variations of natural emissions, and the inability to measure NO accurately at less than part-per-billion concentrations.

Crutzen (1971) hypothesized that methane oxidation chains should also lead to the net production of ozone in the troposphere. This is an important proposition because methane is ubiquitous and occurs at fairly high concentrations, about 1.4 ppm. There is no consensus on the effectiveness of methane oxidation chains in producing ozone. In fact, they can either produce or destroy ozone, depending on the chosen NO_x levels (see, for example, Chameides and Stedman, 1976; Fishman and Crutzen, 1976; and Weinstock and Chang, 1976). Although natural reactive hydrocarbons (e.g., terpenes) and less reactive hydrocarbons (e.g., methane) are widespread in the atmosphere, their relation to the production of ozone appears to be controlled critically by the availabilty of oxides of nitrogen.

b. *Transport from the Stratosphere*

Large amounts of ozone are known to be produced in the stratosphere. Some of this stratospheric ozone gets transferred to the troposphere by various meteorological processes. There are seasonal variations in the rate at which ozone is transferred to the troposphere. The greatest rates occur in the late winter and spring. It appears that background ozone concentrations in the lower troposphere tend to have a phase lag of one or two months behind the injection cycle from the stratosphere to the troposphere. The major sink for the tropospheric ozone is the destruction that takes place at the surface. There is some uncertainty about the amount of ozone in the troposphere that can be attributed to stratospheric sources. Reiter (1977) provides an estimate of 10 to 15 ppb as the average contribution of stratospheric ozone to the background at ground level. Singh et al. (1978) and Mohnen (1977) have estimated the yearly mean tropospheric background ozone concentration to be about 30 ppb, and that nearly all of this can be attributed to a stratospheric source. In the springtime, concentrations are likely to be higher, than the annual average value, and in the fall, lower. In any event, there appears to be a natural background of ozone in the troposphere at a level of a few tens of parts per billion. This represents an appreciable fraction of the NAAQS for oxidant.

It is worth examining how this natural ozone behaves, because it is quite easy to mistake the natural ozone for ozone of anthropogenic origin. Singh et al. (1977) have provided an idealized picture of the behavior of natural ozone in remote locations. Figure 7 is a

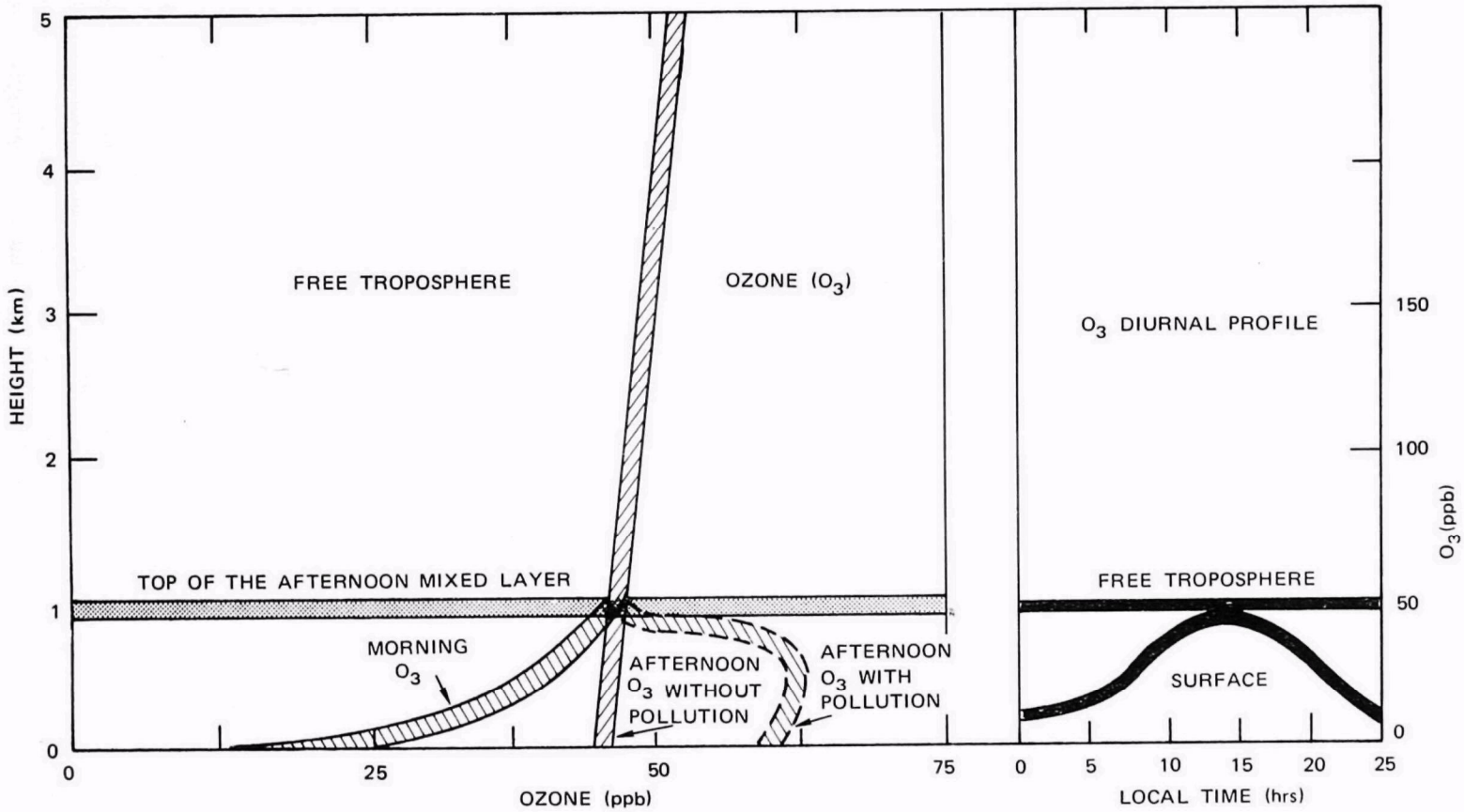


FIGURE 7 SCHEMATIC REPRESENTATION OF OZONE VARIATIONS AT THE SURFACE AND IN THE FREE TROPOSPHERE

schematic representation based on a figure from their report. It shows a large reservoir of ozone aloft. That reservoir is relatively unaffected by daily short-term changes. Above the mixed layer, there is little diurnal variation of ozone concentration. However, as shown in the right-hand side of the figure, there is considerable variation of the concentration at the surface during the day. This diurnal variation of surface concentration occurs because the ozone that is within, or below, the nocturnal inversion is destroyed and is not replaced by ozone from aloft. As the sun rises and the warming of the ground progresses, there will be convective mixing that brings ozone from the reservoir aloft down to ground level to replace that which is destroyed. Hence, the ground level concentrations will increase during the times of day when there is mixing. Although a diurnal profile at the surface such as that shown in Figure 7 is much the same as that produced by photochemical processes, it can arise solely from the changes in diurnal mixing. Figure 7 also shows how the vertical profile of ozone might look in the afternoon if the natural ozone were supplemented by ozone produced from nearby emissions through photochemical processes.

Singh et al. (1978), have also provided a picture of the annual variations in the natural tropospheric ozone burden. These are shown schematically in Figure 8. At very remote sites, unaffected by anthropogenic emissions, the ozone concentrations reach their maximum in the early spring. In general, the natural ozone falls somewhere in the shaded area marked A in the figure. Natural concentrations reach their minimum in the late fall or early winter. The decline of ozone concentrations in these remote locations is in part due to the decrease in stratospheric injection into the troposphere; it is also possible that photochemical processes destroy the natural ozone when no NO_x is present. If oxides of nitrogen are present, either from natural or anthropogenic sources, then the situation is quite different and photochemicl reactions will cause a net increase in ozone. We will return the discussion of these effects in the next section.

To this point, the stratospheric contribution has been discussed only in terms of averages. An important question is whether stratospheric air, rich in ozone, ever reaches ground level before ozone concentrations have been diluted below the NAAQS. Danielsen (1964) has proposed a mechanism involving the folding of the tropopause that brings relatively undiluted stratospheric air deep into the troposphere, perhaps down to levels of 3000 m or so. Danielsen and Mohnen (1976) have presented data documenting such events, but the ozone concentrations are generally diluted before reaching altitudes near sea level. This does not mean that stratospheric ozone never causes violations of the NAAQS standards for oxidants at ground level. Reiter (1977) has attributed one instance where concentrations of nearly 200 ppb were observed at the 3000 m peak, Zugspitze, in Germany to an intrusion of stratospheric air. Singh et al. (1977) present another example from Mauna Loa in Hawaii when concentrations of nearly 100 ppb were observed.

Both the above examples were observed at rather high altitudes, but Lamb (1976) has conducted a detailed analysis of an incident near sea level in Santa Rosa, California. In this incident hour-averaged ozone concentrations of about 220 ppb were observed during the early morning hours of 19 November 1972. Lamb's analysis suggested that these high concentrations were the product of a rather unusual sequence of events. The ozone was brought into the troposphere from the stratosphere by rather large-scale circulations associated with the advance of the frontal zone. However the ultimate transport to the ground resulted from smaller scale air circulations around a shower cloud. Although the events produced very high concentrations, those concentrations were short-lived and affected only a relatively small area within a few tens of kilometers of the observation site.

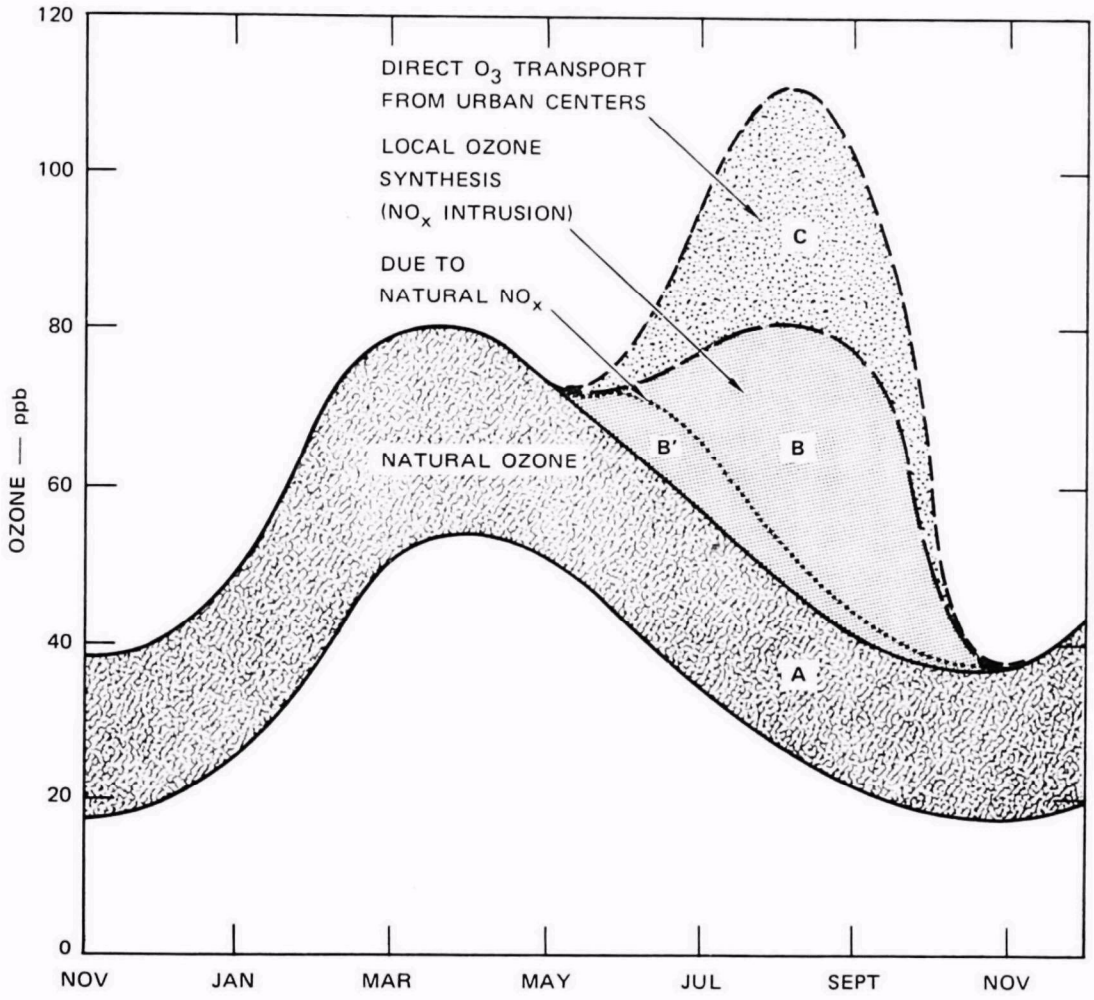


FIGURE 8 IDEALIZED OZONE VARIATIONS AT REMOTE LOCATIONS

Although it appears that violations of the air quality standards due solely to the introduction of stratospheric ozone into the lower atmosphere are rather rare, and we were unable to identify such events in the data that we analyzed, they should not be dismissed altogether. Occurrences of violations induced by stratospheric air are likely to be associated with meteorological conditions that are different from those that produce photochemical ozone; and any control strategies based on these anomalous conditions are not likely to be very effective. Strong outbreaks of cold air during cyclogenesis in the late winter or spring are candidate events for intrusion of stratospheric air, but are unlikely to be associated with the photochemical production of ozone. For purposes of policy formulation, it is extremely important to differentiate between ozone of natural origin and that produced photochemically from anthropogenic emissions.

2. *Anthropogenic Sources of Tropospheric Ozone*

Intelligent formulation of control policy requires not only the differentiation between natural an anthropogenic causes of standards violations, but also the differentiation among several different kinds of anthropogenic causes. As noted before, anthropogenic causes of ozone standard violations can be classified in three categories. The first involves those cases where the precursor emissions and the standards violations take place reasonably close to each other--i.e., the problem is localized. The second category involves cases where problems are almost solely of anthropogenic origin, but the ozone is transported over long distances so that the problem is widely separated from its cause. The third category includes those cases where appreciable amounts of ozone are advected into an area and the standard is violated when the advected ozone is supplemented by that produced from local emissions.

Ludwig and Shelar (1978a) examined the problem of determining where the greatest amounts of locally produced ozone are found relative to a city. They concluded that such areas are apt to be where the air will be after it has traveled 5 to 7 hours from the upwind side of the city. When conditions are favorable to the formation of photochemical oxidants--i.e., warm, sunny days with light winds. They note that for a smaller city (as is the rule in Northern New England) the maximum effects are likely to be observed closer to the city. In any event, maximum concentrations of locally produced ozone are apt to occur within a few tens of kilometers of the source region, but outside the area of NO emissions because the short-term effects of NO are to reduce ozone concentrations.

Although the maximum effects occur within a few tens of kilometers of the city, a detectable effect can extend much farther downwind. Ludwig and Shelar (1977) have concluded that appreciable effects could be observed for more than 100 km downwind of some large cities in the northeastern United States. This is in general agreement with findings of many others (e.g., Cleveland et al., 1976; Zeller et al., 1977) the latter authors have reported observing the plume of ozone generated from emissions in the Boston area over the ocean 200 km downwind of Boston. Another example is discussed later.

There are likely to be differences in the diurnal patterns of ozone concentrations between the locally generated ozone and that which is advected from cities long distances away. Figure 9 is a schematic illustration of what one might expect to observe in the plume of emissions from a city. The top part of the figure shows the plume of hydrocarbons and oxides of nitrogen emitted during the morning rush hour. These emissions are reasonably well mixed and have traveled some distance downwind of the city. At the greater downwind distances the densities are much less, showing the dilution that has taken place and the effects of the much smaller nighttime emissions. There is some ozone scattered among the oxides of nitrogen and the hydrocarbons. At this morning hour, some of this ozone is likely to have been produced by photochemical activity, but most is apt to have been advected or to be of natural origin. The second panel of the figure shows the situation at about midday. The plume is dense with oxides of nitrogen and hydrocarbons for some distance downwind. Of considerable significance is the fact that much ozone has been produced by photochemical processes during the day. This ozone is distributed nearly uniformly in the vertical because of the strong daytime mixing. In the horizontal, we see the concentrations increasing downwind of the city and then falling off.

The third panel of Figure 9 shows the situation in the late afternoon or early evening, when the oxides of nitrogen and hydrocarbons are uniformly mixed in the vertical and are seen to be fairly dense for considerable distances downwind of the city. However, there are few ozone symbols scattered among emissions that occurred later in the day (and are still close to

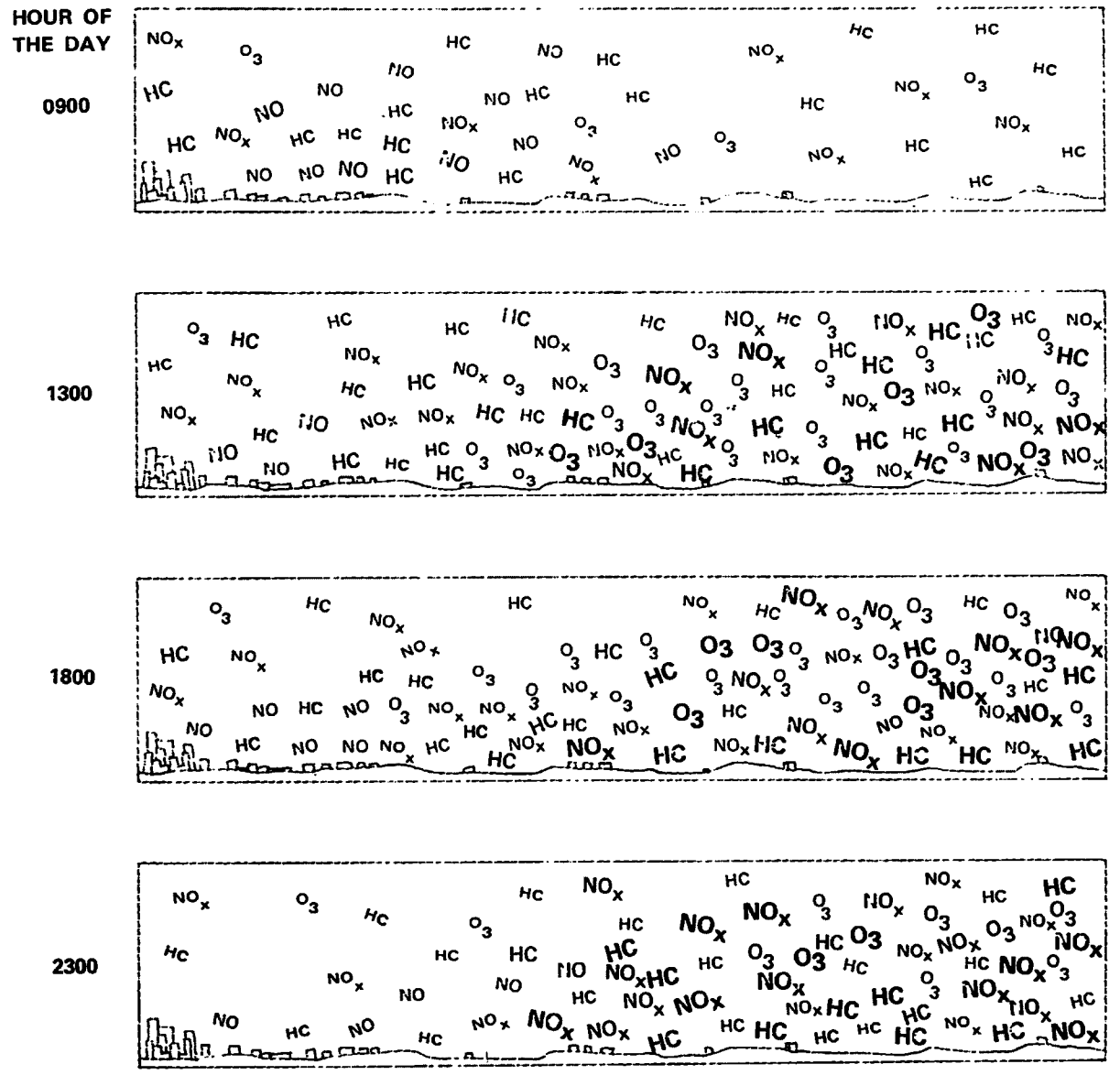


FIGURE 9 SCHEMATIC DIAGRAM OF THE TRANSPORT OF PRECURSORS, OZONE PRODUCTION, AND OZONE DESTRUCTION DOWNWIND OF A CITY

the city), because photochemical processes are rather ineffective in producing ozone in the late afternoon. Another important characteristic of this diagram is the fact that ozone is confined to the upper parts of the plume at the greater downwind distances; by the late afternoon or early evening a stable layer is likely to have formed at ground level and this prevents mixing of the ozone throughout the entire depth of the plume. The ozone that was in the lowest layers is destroyed at the ground and is not replaced by mixing from above.

The final panel of Figure 9 is an extension of the situation shown in the the preceding panel. The concentrations of oxides of nitrogen and hydrocarbons begin to drop as the emission rates decline later at night. No ozone is produced after sunset, and only that which occurs naturally or has been advected from elsewhere, will be found in the part of the plume that is close to the city. Farther downwind, in the part of the plume that was released earlier in the day and in which photochemical activity has taken place, one sees the ozone that was produced during the afternoon. As before, this ozone is confined to the upper parts of the the plume; the ozone in the lower parts has been destroyed at the surface.

Figure 9 shows that a large part of the transport of ozone may take place in elevated layers. Hence it will be very difficult to estimate the contribution of advected ozone to observed concentrations unless data from aloft are available. Some estimates can be made when vertical mixing is good and the data are free of urban influences. Since the extent of urban influence is very difficult to quantify and virtually no aircraft data were available, it has been nearly impossible to determine the exact magnitude of the concentrations of ozone imported into the northern New England states.

If the vertical mixing associated with a weather system were to occur at night, then the ozone isolated aloft would be mixed to ground level and high concentrations would be observed. Looking at the last panel of Figure 9, it is evident that the highest concentrations would occur far downwind of the source area if the vertical mixing were a widespread phenomenon. Ludwig and Shelar (1977) have shown two examples of this kind of nighttime behavior in the area downwind of New York City. One of the implications of the behavior shown in Figure 9 is that the emissions causing high concentrations of ozone at night probably occurred many hours earlier. Even under very light wind conditions, where the wind speed averaged through the mixing layer may be only 5-15 km per hour, the high nighttime ozone concentrations may be found 100 to 200 km from the source area. In fact, it appears that high concentrations of ozone are more likely to occur at night at great distances from source areas than close to them.

3. *Combined Natural and Anthropogenic Effects*

Figures 7 and 8, which were shown earlier to illustrate the diurnal and annual cycles of ozone concentrations in the lower troposphere, also include a schematic representation of the changes in concentrations that occur when anthropogenic effects are introduced. Figure 7 shows that one might expect larger diurnal variations in ozone concentrations when there is photochemical production from emissions near the monitoring site. As was discussed before, if there is appreciable vertical mixing during the evening, then night and day ozone concentrations at ground level will not differ by very much when the only source of ozone is the tropospheric background. When there is local photochemical production of ozone, then afternoon values are likely to be much higher than nighttime values, even in the presence of nighttime mixing.

If anthropogenic ozone is transported over long distances before reaching the station, then it is quite possible to have nighttime ozone concentrations higher than those that occurred during the afternoon. This is very unlikely to happen when the sources are natural background or local photochemical production. In fact, if the station is located on a hill or a mountain, away from the destructive surface processes, and it is subject to receiving ozone that has been transported over long distances, then it may well be that the highest concentration will quite regularly occur during the night. The monitoring site at White Face Mountain is an example of such a site. There are few local anthropogenic sources of ozone precursors, and the site is on a mountain top. It is frequently downwind of several of the urban centers in the east--e.g., Pittsburgh, Cleveland, Toronto, Montreal, and New York. Figure 10 shows the frequency with which the maximum daily ozone concentrations occurred during different hours of the day for three recent years at White Face Mountain. When the highest hour-averaged concentration occurred more than once during a day, these occurrences were distributed among the several hours in which that maximum occurred. For example, if the maximum occurred during two hours, each of those hours was credited with half an occurrence for that day.

In 2 of the 3 years shown in Figure 10, the maximum was most likely to occur between 10 p.m. and 4 a.m. EST. In the third year shown, there were also an appreciable number of maxima during the afternoon hours.

The principal reason for the preceding discussion is to provide some information about what one might look for in the data in order to recognize the nature of the sources producing high ozone concentrations. Unfortunately, the connections between the causes and the observed diurnal and annual cycles of ozone are not always unique. The changes from season to season and from hour to hour provide a useful, but not infallible, guide to the understanding of what is happening.

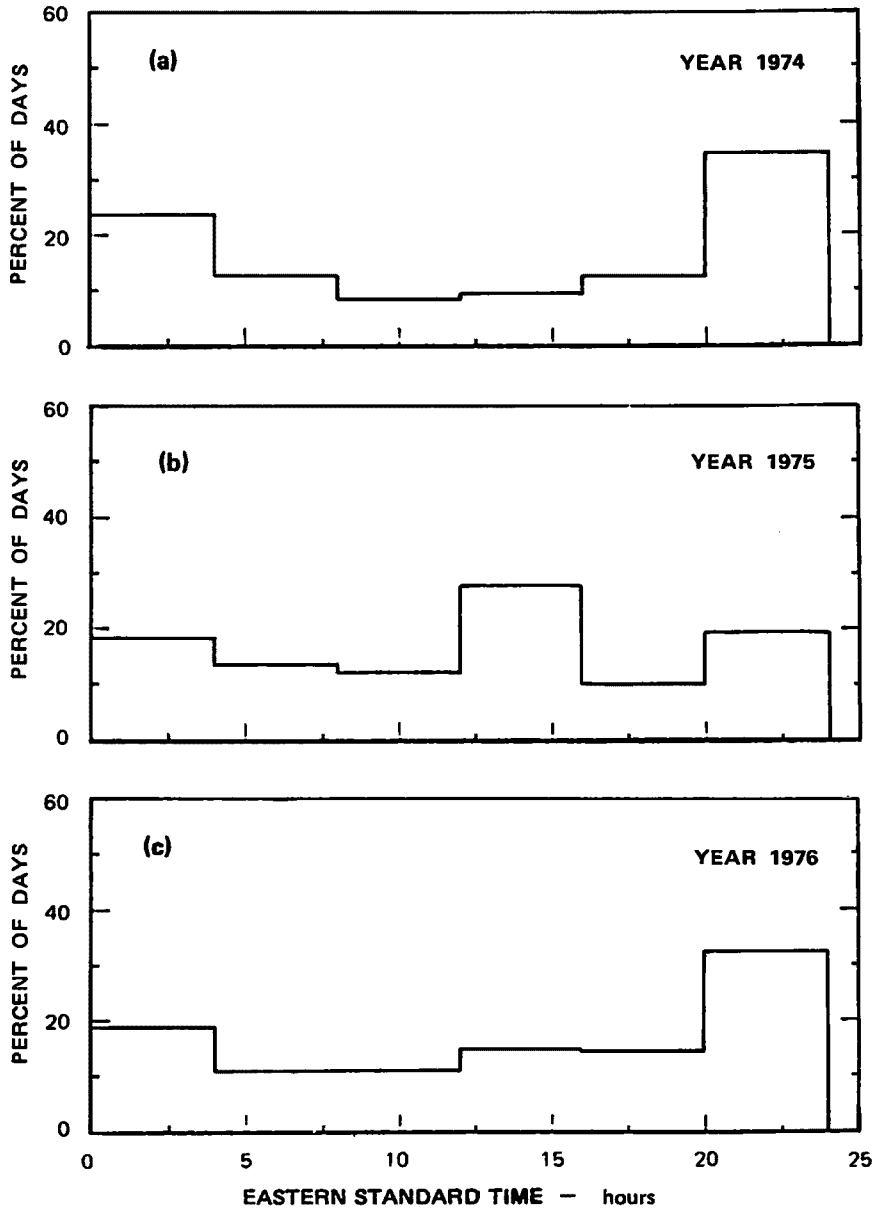


FIGURE 10 DIURNAL DISTRIBUTION OF DAILY 1-HR O_3 MAXIMUM OCCURRENCE AT WHITE FACE MOUNTAINS, N.Y. FOR 1974, 1975, AND 1976

IV ANALYSIS OF THE ORIGINS OF THE AIR AS RELATED TO OZONE CONCENTRATIONS

A. *Governing Factors*

It should be evident from preceding discussions that two very basic requirements have to be met before high oxidant concentrations will be observeed. First, the oxidant must be produced, and second, it must be brought to the place of observation without too much destruction or dilution. The major production process of concern here is photochemical, operating on precursor materials (hydrocarbons and oxides of nitrogen) emitted into the lower atmosphere. To be operative, this production mechanism has some well defined requirements--sunshine, warm temperatures, and an accumulation of precursors, Some of the meteorological situations that are accompanied by conditions conducive to oxidant formation are examined in this section.

In particular, examples of the stagnation conditions conducive to the accumulation of high concentrations of precursors are discussed, as are cases involving the change from warm, sunny air masses conducive to photochemical activity, to cooler air masses. The change from one air mass type to another is generally marked by the passage of a weather front. Several of the cases discussed on the following pages involve the behavior of ozone concentrations during frontal passages.

The transport of ozone in the troposphere is also dependent on the prevailng meteorological conditions. The following sections discuss the transport of ozone in the Northern New England states. Transport must be considered not only as a means by which ozone is moved from one place to another, but also in terms of its effect on the destruction and dilution of preexisting ozone.

B. *Formation and Transport in the Lower Atmosphere*

1. *Winds and General Weather Patterns Associated with Oxidant Concentrations above the NAAQS*

a. *Winds and Trajectories*

Ludwig et al. (1977a) classified days on which the ozone standards were violated according to the wind conditions and the large-scale meteorological patterns that prevailed in different parts of the eastern United States during 1974. Table 3 from that report summarizes the results that they obtained when the days were classified according to the winds. It is apparent from Table 3 that the heavy preponderance of high concentrations in New England occurred with winds from the southwest quadrant. The data from Northern New England have been examined in a simlilar fashion.

Figure 11 shows schematically the number of hours when observed ozone concentrations in excess of 80 ppb at different sites were associated with winds from different directions. The winds at the 850-mb level, about 1500 m above sea level, were estimated from U.S. Weather Service analyses. The lengths of the sector radii in Figure 11 are proportional to the numbers of hours that the air was moving from the corresponding directions. The 850-mb winds were used because they are less influenced by local topography and tend to give a truer picture of general air motions through the region. The importance of air motions from the southwest is evident, but westerly winds in general seem to be about equally important. Similar

Table 3

WINDS REPORTED ON MORNING WEATHER MAP IN AREAS
WHERE PEAK-HOUR OZONE EXCEEDED 80 ppb DURING THE DAY
(Number of days from June through August, 1974)

Region	Surface Winds				
	Calm	≥ 2 m/s			
		N to E	E to S	S to W	W to N
Florida Peninsula	11	5	4	2	0
Texas-Louisiana Gulf Coast	17	10	0	7	1
New York-New England	3	4	7	26	2
Western Oklahoma, Kansas, Nebraska	1	7	13	36	11
SE of Lakes Erie and Ontario	20	1	10	6	1
Washington-Philadelphia Corridor	9	5	7	7	4
S or SW shore of Lake Michigan	7	0	5	6	1
Ohio River Valley & Surroundings	21	2	1	7	0

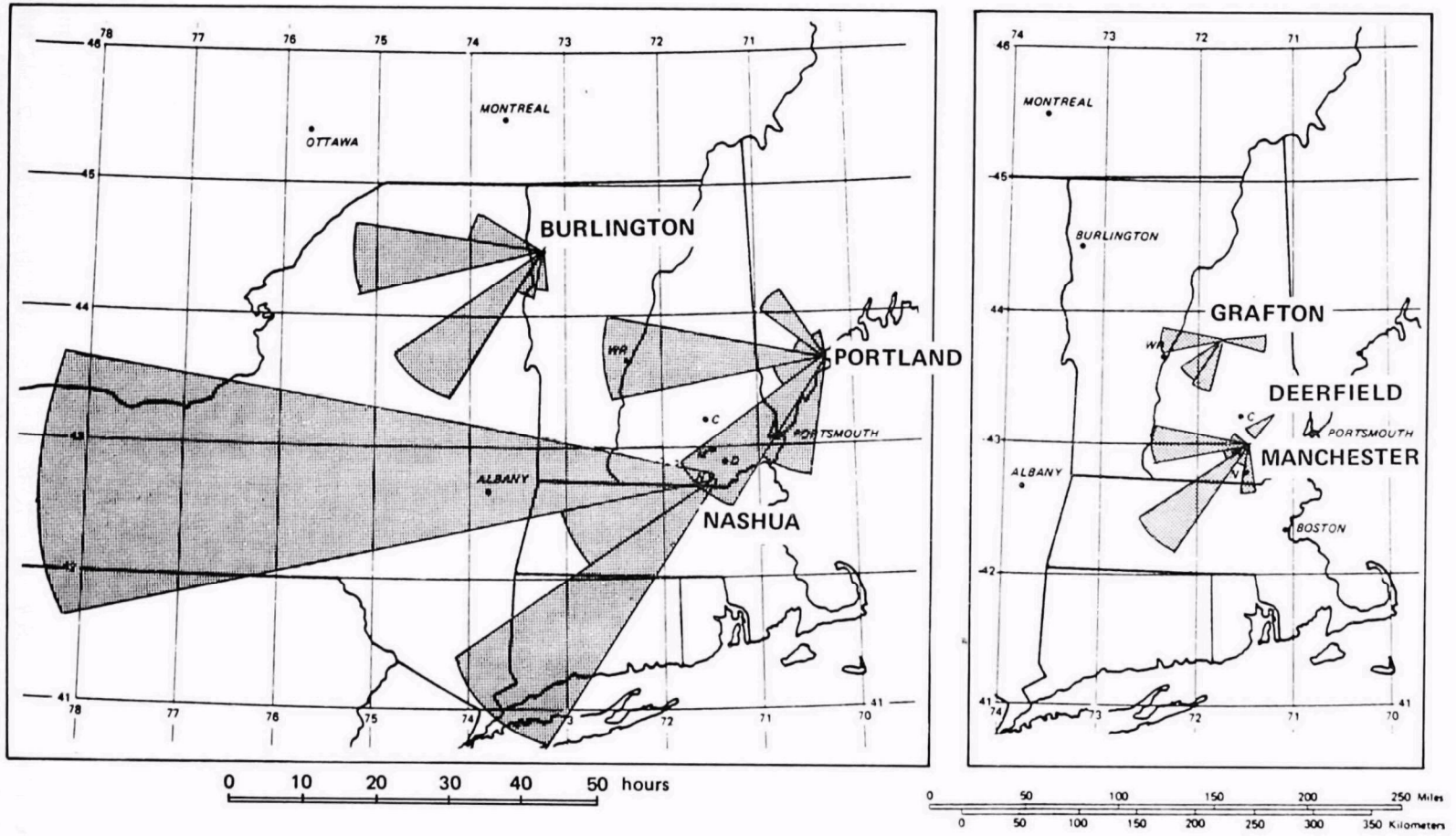


FIGURE 11 NUMBER OF HOURS WHEN OZONE CONCENTRATIONS VIOLATED THE NAAQS FOR OXIDANTS AS A FUNCTION OF 850-MB WIND DIRECTION—1976

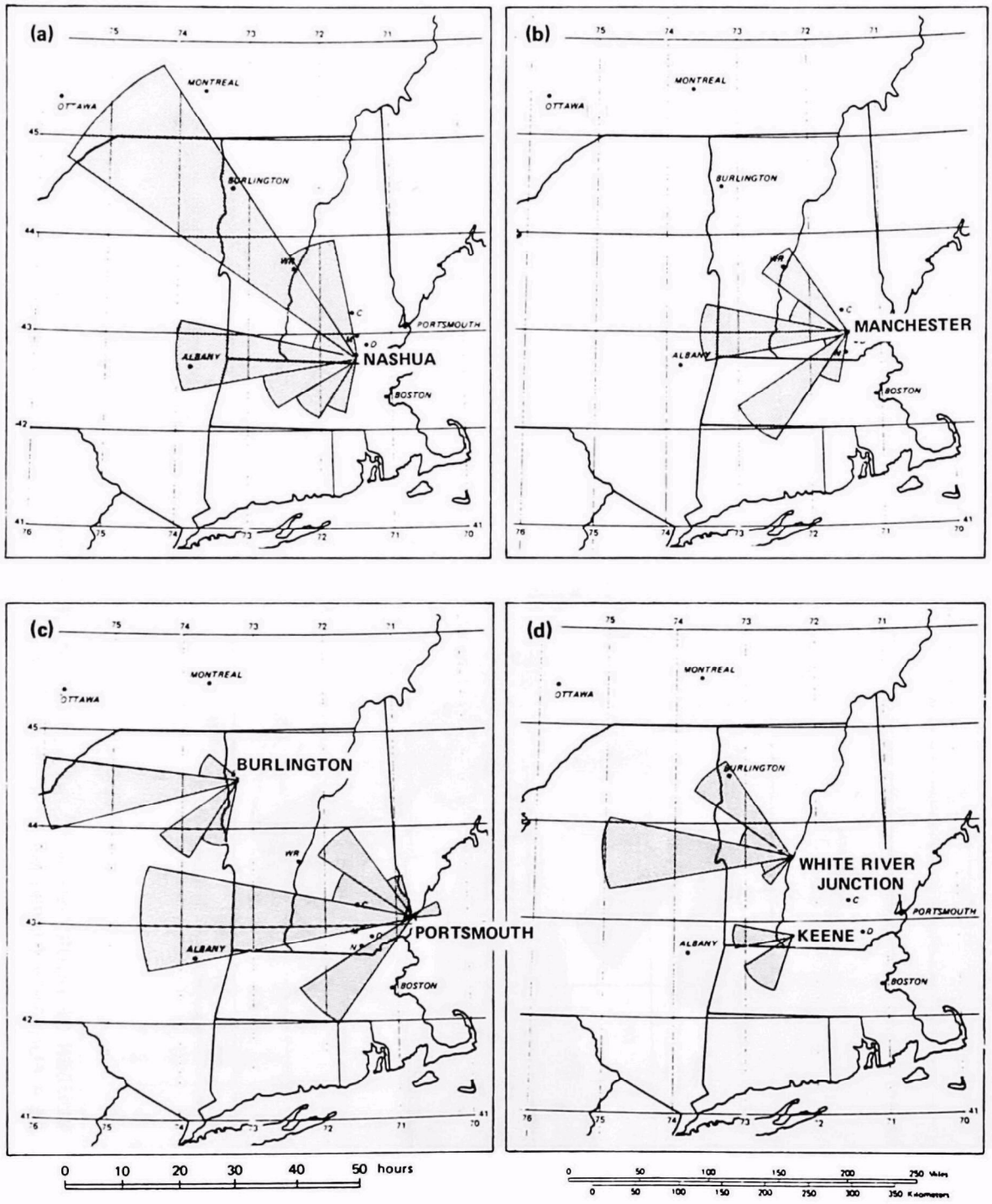


FIGURE 12 NUMBER OF HOURS WHEN OZONE CONCENTRATIONS VIOLATED THE NAAQS FOR OXIDANTS AS A FUNCTION OF 850-MB WIND DIRECTION—1977

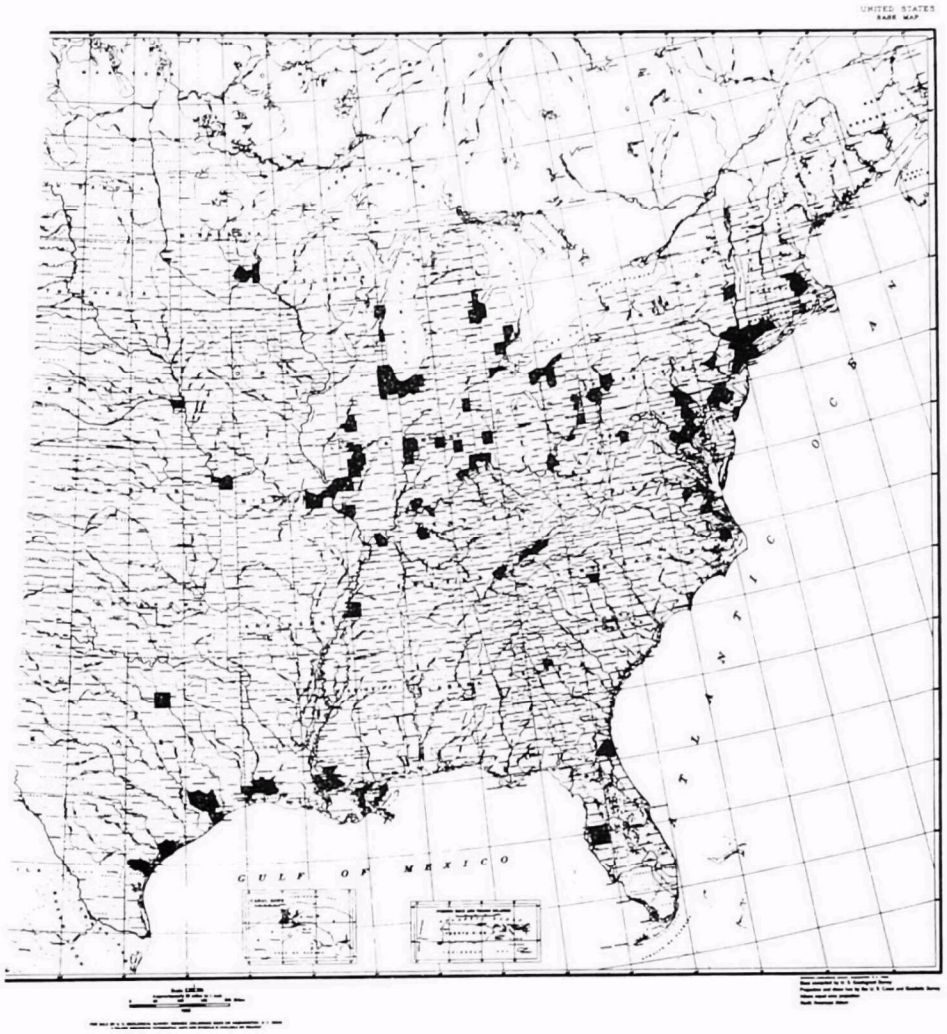


FIGURE 13 COUNTIES WITH AVERAGE ANNUAL NO_X EMISSIONS GREATER THAN 75 TON M^{-2} YR^{-1}

displays, based on the 1977 data, are shown in Figure 12. In the 1977 data set, winds from the northwest assumed greater importance than for 1976.

It should be remembered that the results shown in the figures reflect three factors: first is the size of the data set (see Table 1), second is the overall frequency of winds from the various directions, and the third is the frequency with which winds from a given direction are associated with conditions suitable for oxidant concentrations in excess of 80 ppb. The two figures also seem to display evidence of a bias against wind directions other than the eight major directions; there seems to have been a preference for labeling winds W or SW rather WSW, for example. This may reflect a real physical effect, because the emissions of oxides of nitrogen tend to be greater toward the southwest and the west for most of the stations. Figure 13 summarizes county-wide NO_x emissions in the northeastern United States for 1974. Greater emissions are found to the west or the southwest than to the west-southwest for many of the stations.

The cases associated wih northwesterly winds in 1977 were nearly all connected with a very few episodes in April and May. It appears that the air arriving from the northwest

was usually part of a high pressure circulation that had persisted long enough for there to be an accumulation of emissions from many sources in the northeastern United States. The accumulated emissions could have moved to the north and then have entered the northern New England area from the northwest. This serves to illustrate the fact that wind directions over a limited time interval are not always accurate indicators of the origins of the air.

Air trajectories were calculated from upper air wind data for selected cases in order to provide a better estimate of the origins of the air. The calculations were prepared by Mr. Dale Coventry of the EPA in Research Triangle Park, North Carolina. The calculations are based on the computer program described by Heffter and Taylor (1975). The application of this program to problems of this type has been discussed by Ludwig et al. (1977b). Briefly, the winds are interpolated horizontally and averaged vertically through the mixing layer, The air motions are calculated from these averaged, interpolated winds for the periods between observations. The program provides calculated air positions at 6 hour intervals.

It was beyond the scope of this project to calculate trajectories for every day and for every ozone monitoring site. Trajectories terminating at Burlington, Vermont and Manchester, New Hampshire were calculated for all the days shown in Table 4. The time periods were selected to include one or more instances of widespread violations of the oxidant standard in northern New England or some period that was being considered for special analysis because of the prevailing meteorology or high nighttime ozone concentrations.

Table 4

TIME PERIODS FOR WHICH AIR TRAJECTORIES WERE CALCULATED

17 April 1976	to	20 April 1976
27 May 1976	to	30 May 1976
13 June 1976	to	17 June 1976
8 July 1976	to	12 July 1976
24 August 1976	to	29 August 1976
8 September 1976	to	11 September 1976
9 March 1977	to	12 March 1977
18 April 1977	to	25 April 1977
29 April 1977	to	24 May 1977
12 June 1977	to	29 June 1977

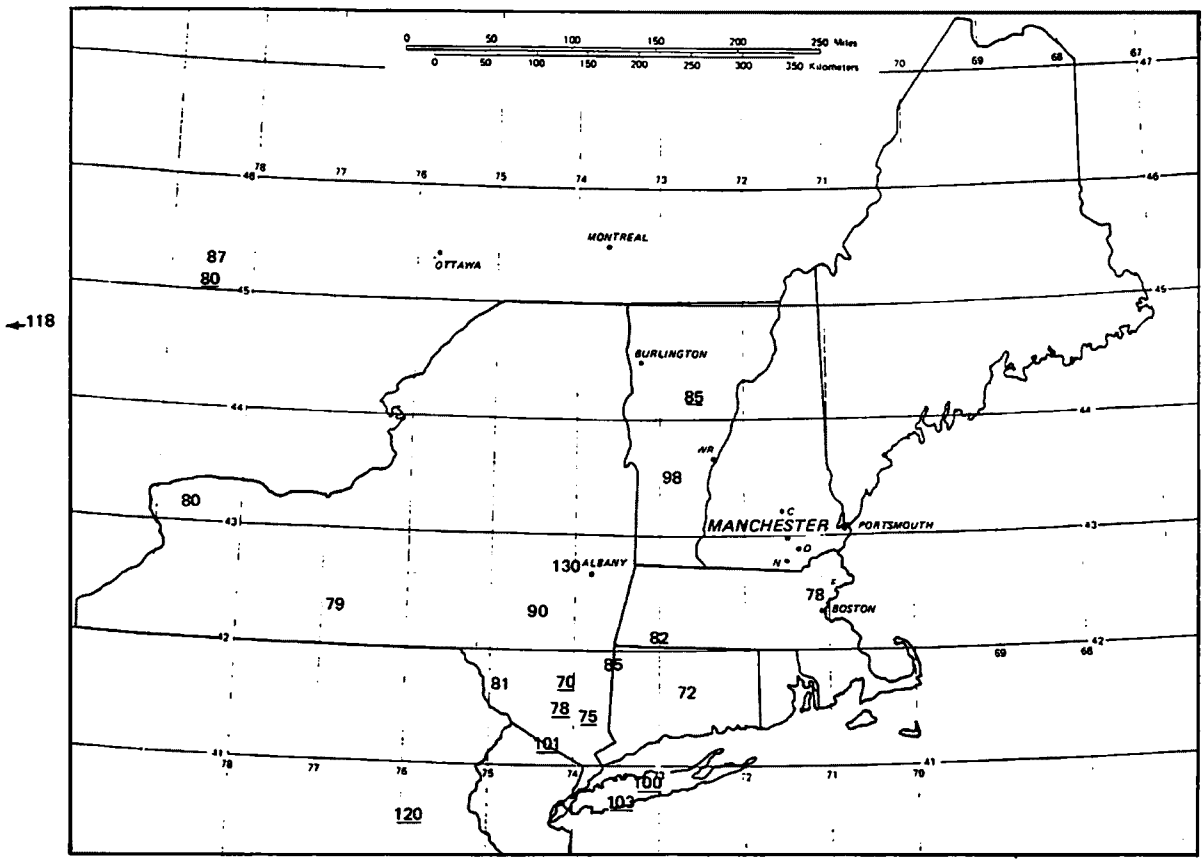


FIGURE 14 LOCATIONS OF AIR THAT ARRIVED AT MANCHESTER IN 12 HOURS WITH AN OZONE CONCENTRATION OF 70 PPB OR GREATER UPON ARRIVAL
Ozone concentrations are shown for time of arrival. Underlined figures show arrival at 1900; others, at 1300

The ozone concentration at the terminus of each trajectory (Burlington or Manchester) was plotted at the location of the air 12 hours earlier. This was done for every available trajectory that terminated at 1300 or 1900. Figures 14 and 15 show those cases where the air arrived at the target location with an ozone concentration in excess of 70 ppb. For example the numeral 78 plotted near Boston in Figure 14 means that the air at that location arrived in Manchester 12 hours later (at 1300 EST) and the ozone concentration observed in Manchester at the time of arrival was 78 ppb.

It is evident from Figure 14 that the higher ozone concentrations measured at Manchester were frequently associated with air that had passed over the high population density areas of New Jersey, Connecticut, and southeastern New York during the preceding 12 hours. Another favored corridor stretched over the Buffalo, Toronto, and Rochester areas. It is somewhat surprising that the nearby Boston area was not involved in very many instances of higher ozone concentrations at Manchester.

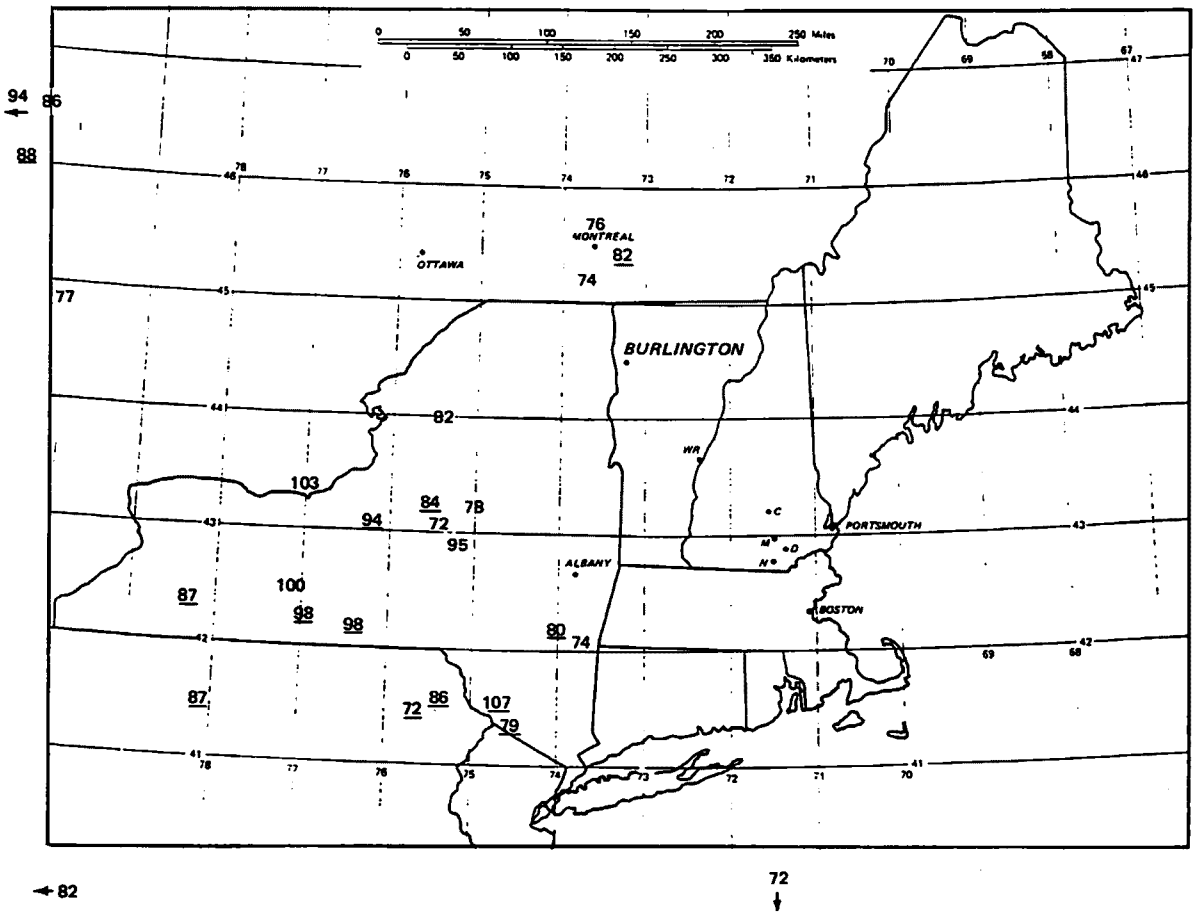


FIGURE 15 LOCATIONS OF AIR THAT ARRIVED AT BURLINGTON IN 12 HOURS WITH AN OZONE CONCENTRATION OF 70 PPB OR GREATER UPON ARRIVAL

Ozone concentrations are shown for time of arrival. Underlined figures show arrival at 1900; others, at 1300

It should be noted that Boston may well influence some areas in northern New England especially those to the northeast, such as Portland, Maine. For example, Figure 11 shows that high ozone concentrations at Portland are frequently associated with winds from the direction of Boston. In that same figure, Manchester shows no occurrences from that directon, but consistent with the trajectory results, Manchester shows frequent occurrences with winds from the southwest and west. The subject of transport toward Portland along a path parallel to the coast will be discussed again later.

Figure 15 shows that even Burlington is influenced on occasion by air arriving from the direction of New York and New Jersey. However, it is more common that the higher afternoon and early evening ozone concentrations are associated with air that has passed over the areas southeast of Lakes Erie and Ontario. This swath includes metropolitan areas such as Pittsburgh, Cleveland, and Buffalo. There were three instances in this sample when concentrations above 70 ppb were connected with air that had been in the vicinity of Montreal twelve hours earlier. It appears that when there are light north-northwesterly winds the influence of Montreal just extends to Burlington.

Those cases in which air coming from the area north of Lake Huron produced high ozone concentrations are somewhat puzzling because of the long travel distances involved. The long distance of travel implies very high wind speeds, which in turn indicates very little time for emissions to accumulate and reach the high concentrations that are usually presumed to be needed for the formation of high ozone concentrations. The time and data available for this project have not been adequate to determine whether the observed ozone concentrations are connected with smelting or other industrial activities north of Lake Huron. If more comprehensive trajectory analysis showed that air from that area is regularly associated with high ozone concentrations, then special measurement programs to clarify the effects might be warranted.

b. *Weather Patterns*

Ludwig et al. (1977b) prepared analyses of ozone concentrations in the eastern United States for each day of 1974. The areas where the NAAQS for oxidant were violated were classified according to the weather type in the same area. Table 5 from Ludwig et al (1977a) shows the weather patterns that were most frequently associated with high ozone concentrations. A similar analysis has been prepared for the Northern New England States.

Table 5

METEOROLOGICAL FEATURES ASSOCIATED WITH VIOLATIONS OF THE NAAQS FOR OZONE DURING 1974 IN THE EASTERN UNITED STATES

(Number of Cases per Month)

	January	February	March	April	May	June	July	August	September	October	November	December
Warm air mass near front	1	0	6	5	15	8	19	23	9	8	2	0
Warm sector of frontal wave	0	1	1	0	4	4	8	4	2	2	1	0
West side of anticyclone	0	1	2	12	11	22	35	30	18	14	0	2
Center or east of anticyclone	0	2	2	4	14	15	44	20	11	10	2	1
Squall line	0	0	0	0	1	1	0	0	0	0	0	0
Behind strong cold front	1	0	2	2	1	6	7	10	0	2	2	0
Other	0	0	1	6	10	15	15	21	7	2	0	0

Weather maps from the "Daily Weather Map" series (National Oceanic and Atmospheric Administration; 1976, 1977) were subjectively classified for those days during which the NAAQS were observed to be violated somewhere in the three Northern New England States during 1976 and the first half of 1977. Table 6 summarizes the number of days of violation associated with each of several different weather types. The weather pattern classifications are the same as those used by Ludwig et al. (1977a).

Table 6 shows that the northwest quadrant of a high-pressure system, or anticyclone, is the most common location for high ozone concentrations in the Northern New England States, as it is elsewhere in the eastern United States according to Table 5. The extreme western boundaries of high-pressure systems are often marked by approaching frontal systems. The warm air mass ahead of the front is often amenable to ozone formation, especially in areas where the air moving from the southwest passes over an extended emissions area. Table 6 shows that the Northern New England States have an appreciable number of days when the NAAQS are violated and the weather pattern fits into this category.

Table 6

METEOROLOGICAL FEATURES ASSOCIATED WITH OBSERVED OZONE CONCENTRATIONS OF 80 ppb OR GREATER IN THE THREE NORTHERN NEW ENGLAND STATES

(Number of Cases)

Weather Feature	Number of Days
Warm air mass near front	16
Warm sector of a frontal wave	11
West or northwest side of an anticyclone	25
Center or east side of an anticyclone	6
Other	12

Another weather category of importance is the warm air region of the wave between a cold front and a warm front. Eleven violations of the NAAQS were found in such a region. Six days of violations for ozone occurred when the central or eastern parts of a high-pressure system were over the states of Maine, New Hampshire, or Vermont. As shown in Table 6, 12 days could not be categorized.

The following text presents some specific cases when the high ozone concentrations were associated with light winds or stagnation in a high- pressure system or with a weather front and its associated air circulations.

2. *The Effects of Weather Fronts*

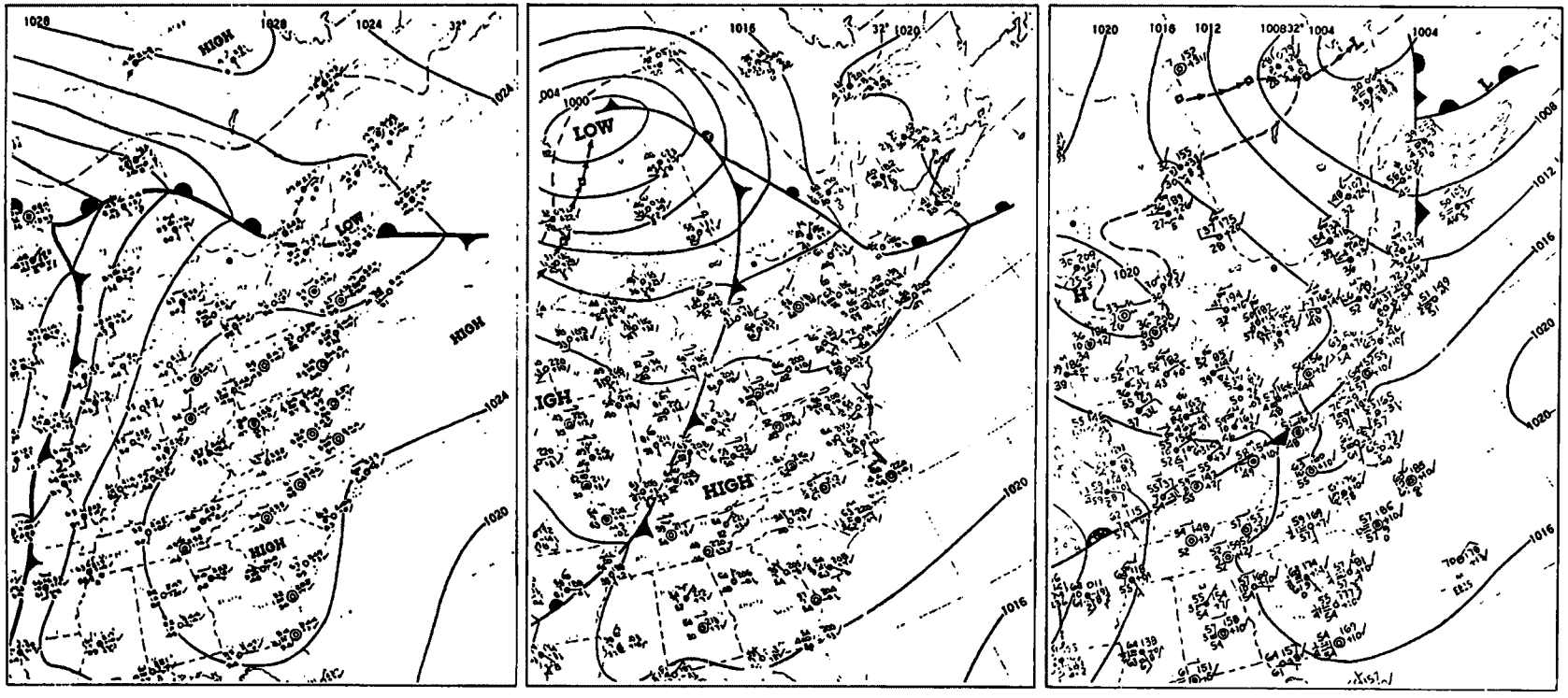
Weather fronts mark the boundary between two bodies of air of different properties (air masses). In meteorology the emphasis is on the contrast in temperature and humidity across the weather front. However, there will also be contrasts in the amounts of pollutants in the air and the origins of those pollutants. Thus, the changes in pollutant concentration during a frontal passage or the variation of concentrations in the vicinity of a front are indicators of the relative importance of the sources that contributed to the concentrations on either side of the front. Ludwig and Shelar (1977, 1978b) have presented some dramatic examples of changes in ozone concentration during frontal passages over Southern New England. In those cases, warm air laden with the emissions from the New York and New Jersey areas was contrasted with cooler, relatively cleaner air from the north. The results of the trajectory analysis suggest that similar events might occur farther to the north.

Several days when frontal passages occurred have been chosen for detailed analysis. One of the objectives of the analysis is to obtain an estimate of the relative importance to the production of oxidants of the sources in the two different air masses. One of the problems that arises in such an analysis is that the concentrations of ozone are controlled by more than just precursor concentrations. In particular, photochemical production of ozone varies with the time of day, and it is not always easy to separate the diurnal variations of ozone production, destruction, and dilution from the variations caused by differences between the air masses on either side of a front as it passes. We have been fortunate to find some examples where a front moved back and forth through the area, providing more than one sample of the differences between the air masses. These cases are discussed on the following pages.

a. *18-20 April 1976*

This was an interesting period for two reasons. First, it happened relatively early in the year for violations of the oxidant NAAQS, and second, the behavior of the warm front that affected the area on the 19th was unusual. Although violations were recorded only at Nashua and Portland, concentrations approaching the 80 ppb standard for ozone were recorded throughout the area.

This was an unusually warm period for mid-April, with temperatures reaching the upper 80's (F) and low 90's on the 18th and 19th. Surface wind speeds were generally low. The daily weather map for 0800 EDT on the 18th [Figure 16(a)] shows that Northern New England was influenced by high pressure to the south, and a weak warm front to the northeast. By 0800 EDT on the 19th [Figure 16(b)] the area was lying in the warm sector of a more well defined depression. Figure 17(b) shows the movement of the warm front during the morning hours of the 19th. As the afternoon progressed, the front behaved in a rather unusual manner,



(a) 18 APRIL 1976 (b) 19 APRIL 1976 (c) 20 APRIL 1976

FIGURE 16 WEATHER MAPS FOR 18–20 APRIL 1976, 0800 EDT

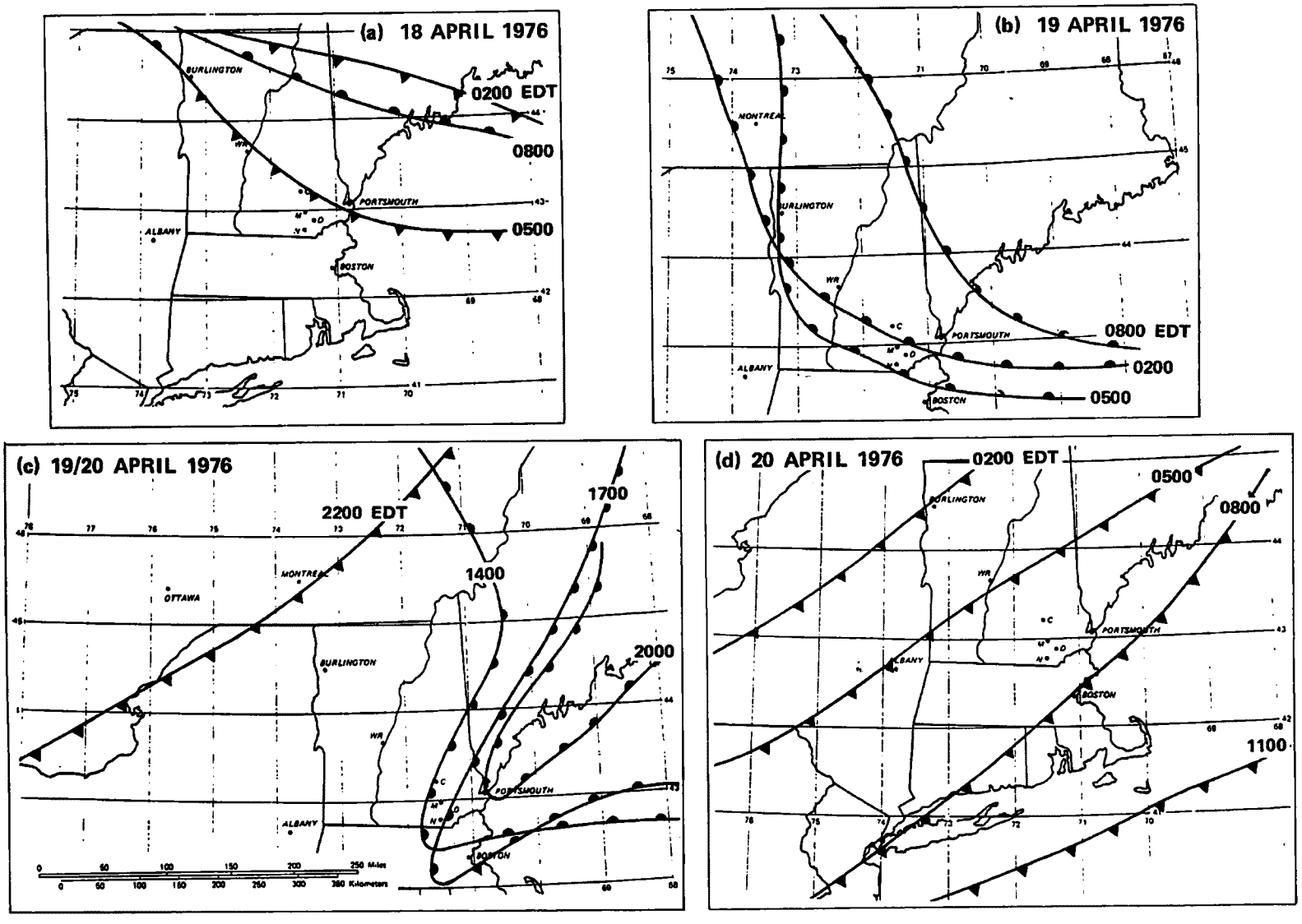


FIGURE 17 FRONTAL POSITIONS IN NORTHERN NEW ENGLAND, 18-20 APRIL 1976

looping back over the southern part of the area [Figure 17(c)] to affect sites in Southern New Hampshire, and Maine. The cold front of the system moved southeast across the area on the 20th, clearing Portsmouth and Portland by 0800 EDT [Figure 16(c)].

The variations in ozone concentrations during this time are shown in Figure 18. There is a marked contrast between the smooth diurnal cycle of the 18th (especially at Manchester and Nashua) and the much more variable cycle on the 19th. The low wind speeds and clear skies together with the high temperatures provided near ideal conditions for the photochemical production of ozone on the 18th. All sites show rises in concentration between 0600 and 0800 EDT on the 18th. On the 19th, however, the initial rise in concentrations happened earlier (0300, 0400 at Manchester and Nashua) and was followed by a series of increases and decreases throughout the day and into the night hours. These variations can be ascribed to the influence of the warm and cold sectors of the depression as the warm front moved back and forth over the area. The estimated times of influence of each air mass have been marked on the graphs of Figure 18.

The relationship between the air masses and the ozone concentration was most pronounced at Nashua, but all the sites showed the effect to some extent. The obvious tendency is for ozone concentrations to increase as the sites come under the influence of the warm air and decrease when the cold air mass arrives. The warm air was richer in ozone, probably for two reasons. First, the meteorological conditions were more suitable for photochemical activity, and second, the warmer mass had been exposed to more precursor emissions from the heavily populated areas to the south than had the cold air.

b. *11, 12 July 1976*

There were widespread violations of the standard in Northern New England during daylight hours on 11 July 1976. The area was influenced by the development of a low-pressure system just to the north of New Hampshire. Highest concentrations were recorded around 1400 EDT on the 11th; the period was broken up by the passage of the cold front across the area on the 12th.

The surface weather map (Figure 19) for the 11th shows extremely weak pressure gradients over the Northeast. At 0800 EDT there was a weak front lying to the west of the New England Area. Figure 20 shows the movement of this front during the 11th. The whole area was within the warm air mass by 2000 EDT. The surface wind speeds (Figure 21) were low until 0900; wind directions were variable. As the wind speed increased around 0900, the wind directions became steadier, and from the south.

The observed ozone concentrations for individual sites are shown in Figure 22. The initial sharp rise in concentrations around 0600 EDT at Portland, Manchester, and Deerfield cannot be attributed to photochemistry, because of the early hour and consequent low level of insolation. The rise does correspond with the invasion of warm air from the south. The observed ozone had probably been formed in the warm air mass the previous day and then was isolated aloft by the stable layer associated with surface cooling; finally, it was transported northward. There was probably some increase in vertical mixing associated with the area near the front and the onset of surface heating at sunrise. This vertical mixing brought ozone stored aloft in the warm air down to ground level and caused the observed rise in concentrations.

Burlington concentrations remained at about 50 ppb through the night, but also began to rise somewhat later, at around 0800 EDT. Burlington seems to have remained in the cold air mass until early afternoon, so the morning rise reflects the photochemical production of

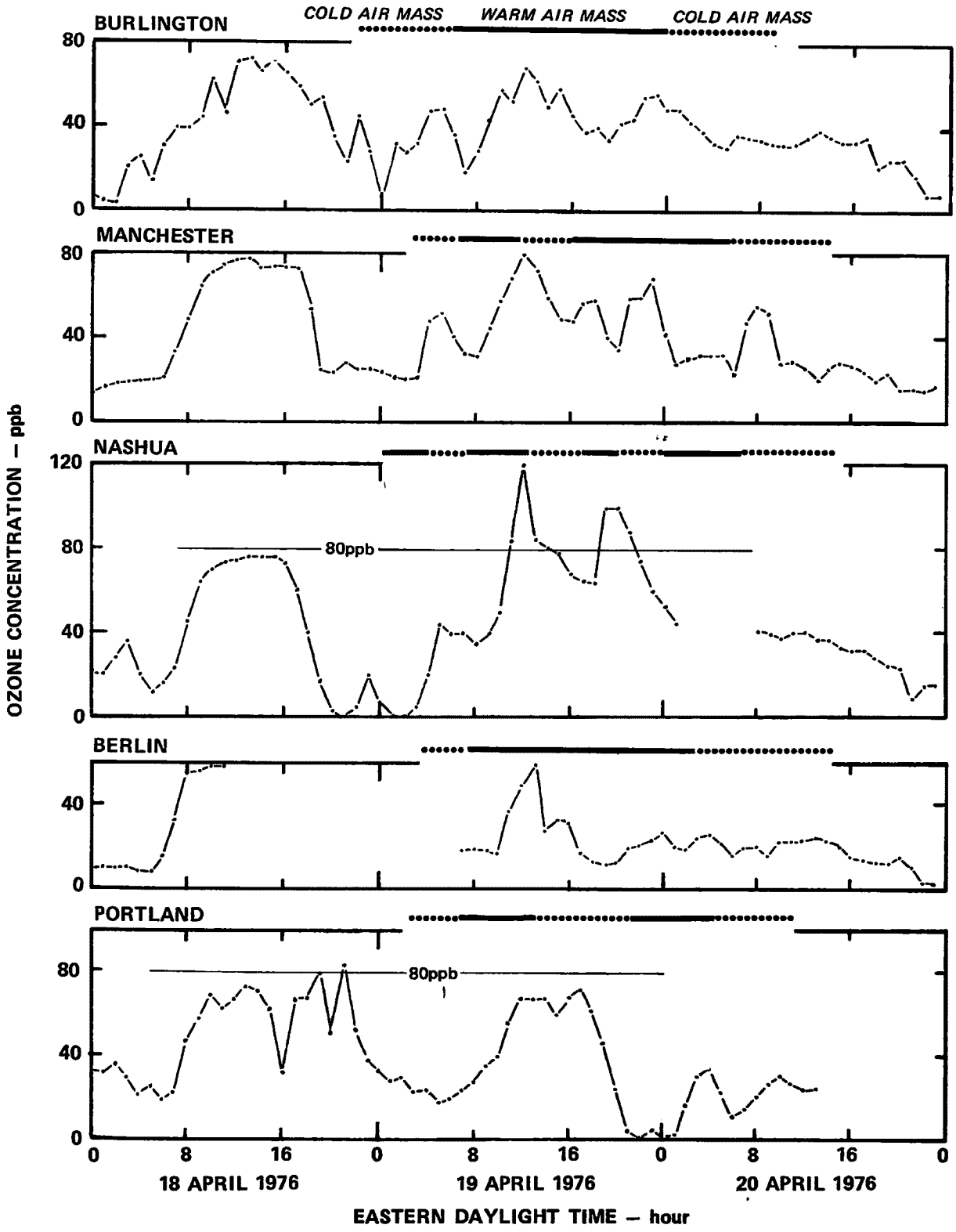
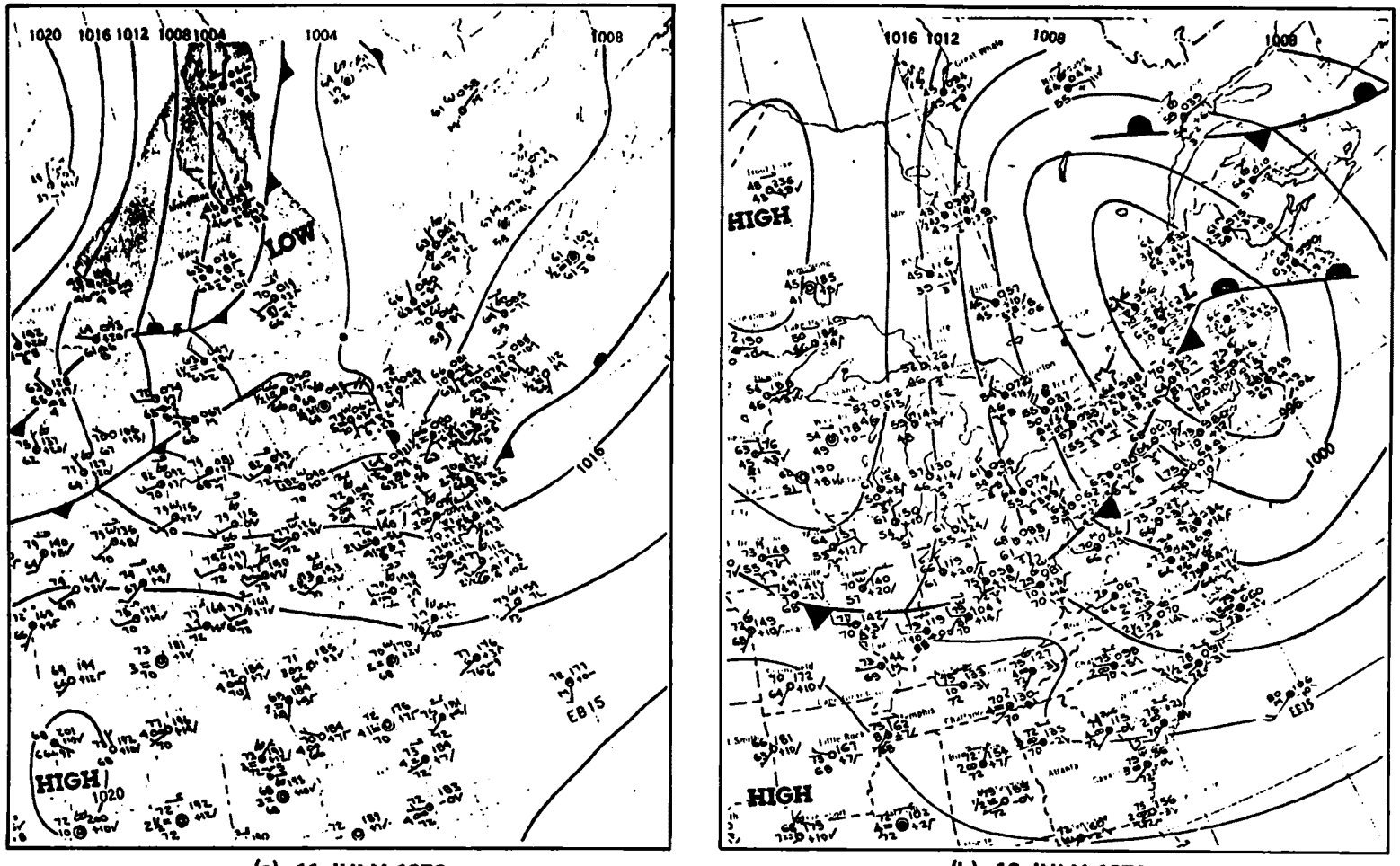


FIGURE 18 TIME HISTORIES OF OZONE CONCENTRATIONS IN NORTHERN NEW ENGLAND, 18-20 APRIL 1976



(a) 11 JULY 1976

(b) 12 JULY 1976

FIGURE 19 WEATHER MAPS FOR 11-12 JULY 1976

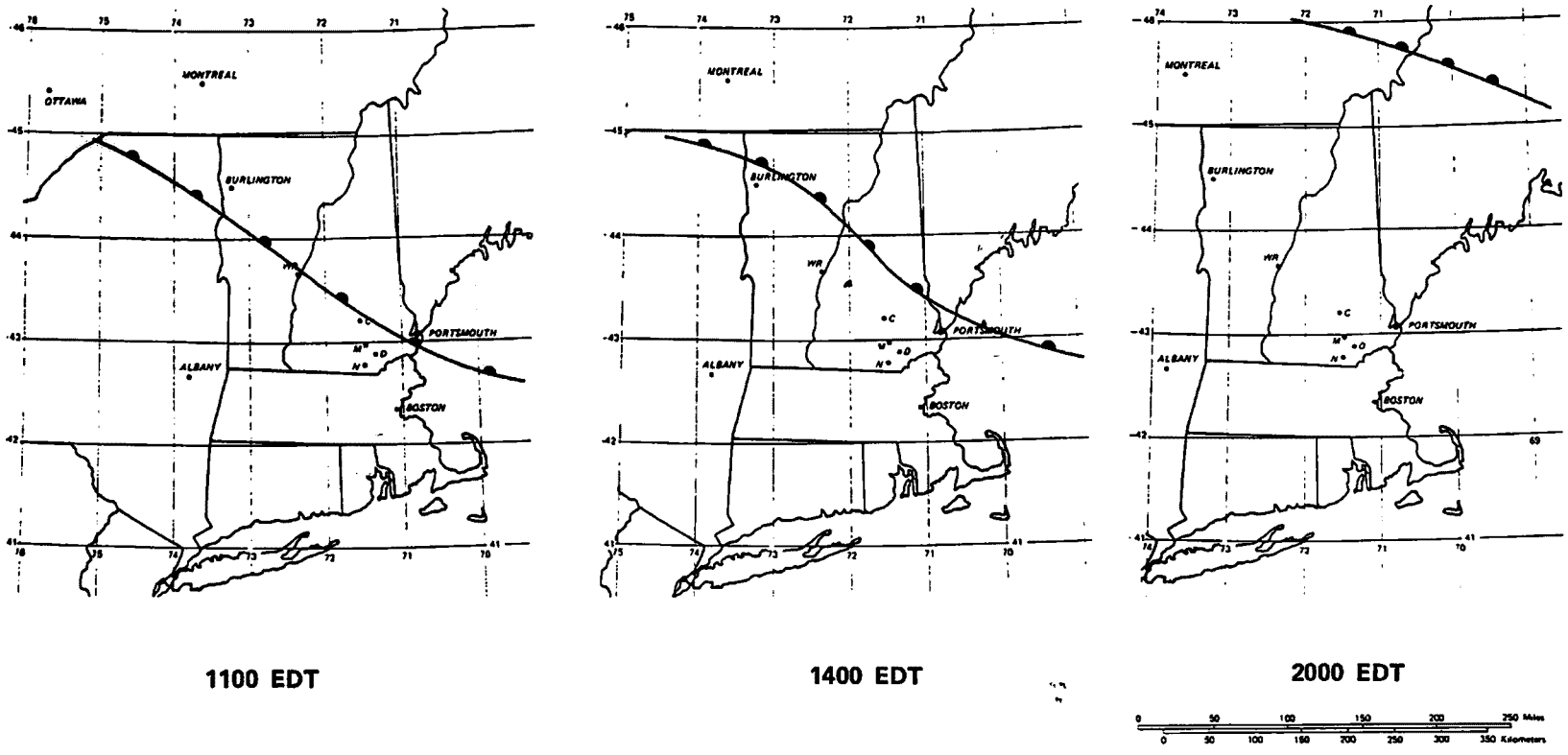


FIGURE 20 FRONTAL POSITIONS IN NORTHERN NEW ENGLAND, 11 JULY 1976

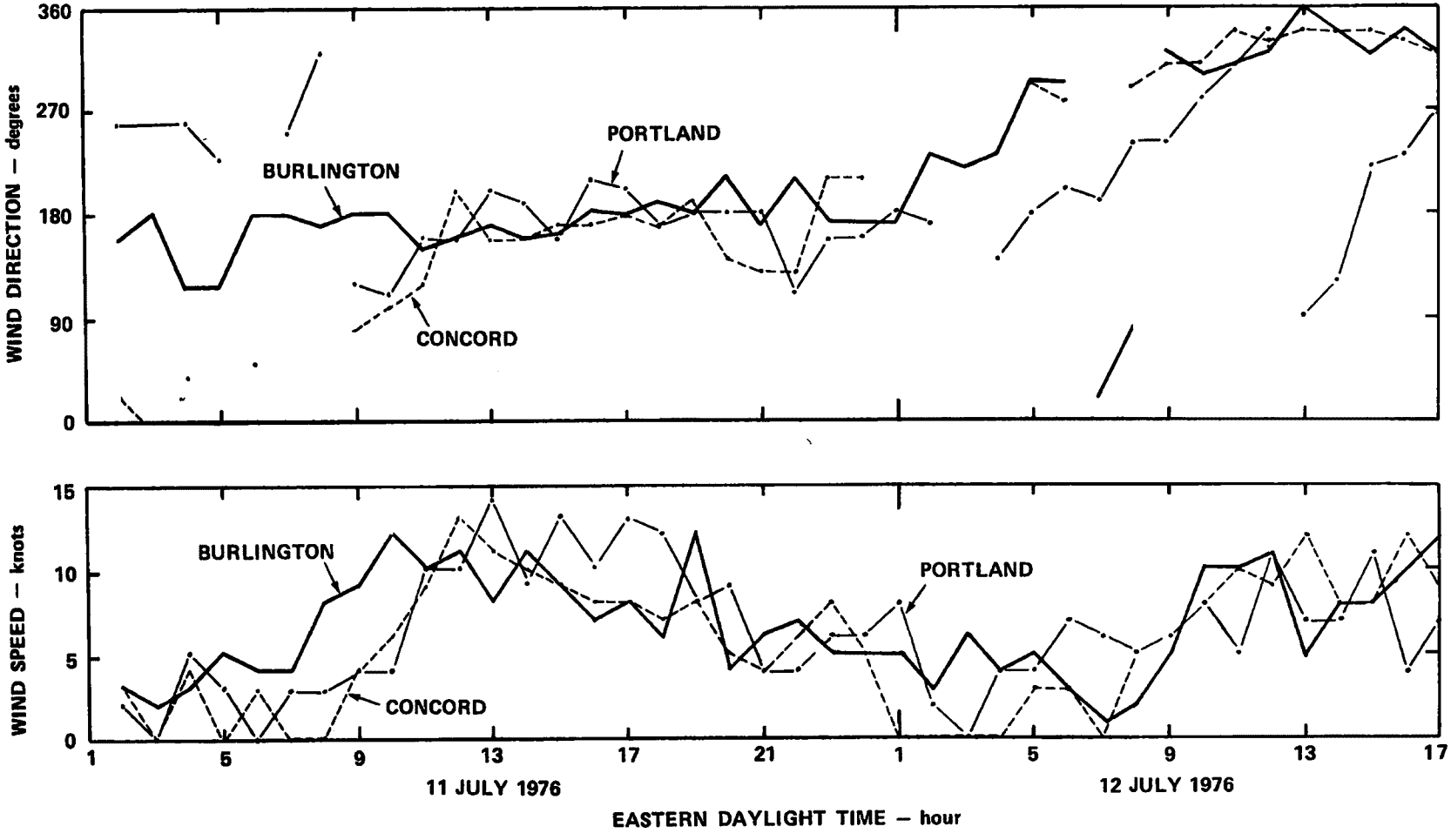


FIGURE 21 TIME HISTORIES OF WINDS AT SELECTED NORTHERN NEW ENGLAND SITES, 11-12 JULY 1976

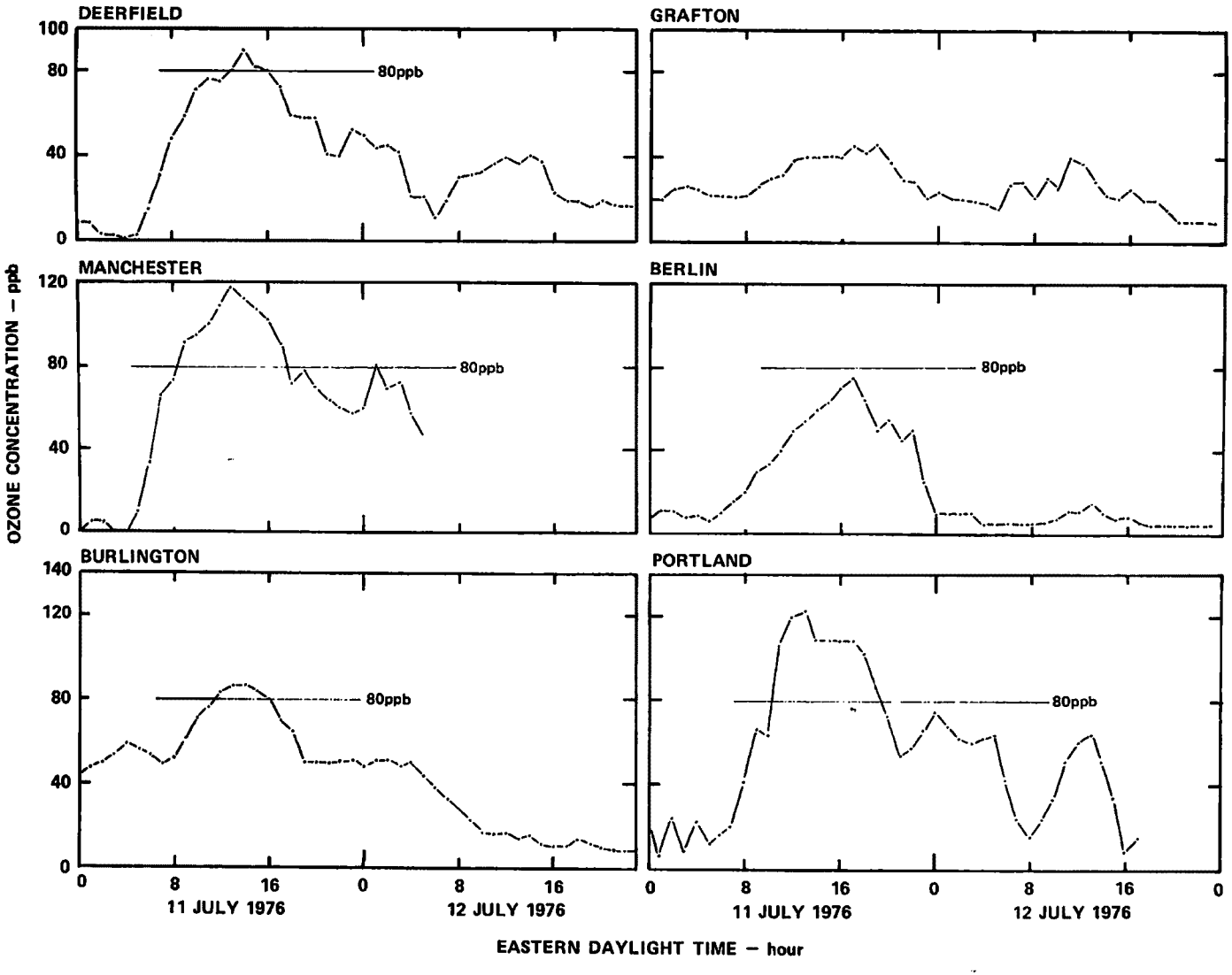


FIGURE 22 TIME HISTORIES OF OZONE CONCENTRATIONS IN NORTHERN NEW ENGLAND, 11-12 JULY 1976

ozone from precursors within that air mass. The transition from the cold air ozone concentrations to the warm air concentrations that takes place in the early afternoon is quite smooth. This suggests that the ozone in the warm air mass had been diluted to the point where it was about the same as cool air values by the time it reached this northerly station. This gives some indication of how rapidly the ozone concentrations decrease (by dilution and destruction) with distance from the areas where precursor emissions originate.

The graphs for Grafton County (Fraconia Notch) and Berlin show a much more gradual increase, with Grafton never rising much above 40 ppb. Berlin gradually approached the standard by 1600 EDT. As discussed in Appendix A, both these sites are rather anomalous.

Conditions were extremely suitable for production of ozone. It is likely that concentrations at all sites were reinforced by remoter sources of ozone upwind moving from the urban complexes to the south.

Concentrations were considerably less at all sites on the 12th than they had been on 11 July 1976. The surface wind data (Figure 21) showed a gradual increase in speed around 0900 EDT, and a change in wind direction to the northwest. This is consistent with the development and movement of the low pressure system, and the passage of the cold front across the area (Figure 19). The air behind the front had different origins than that ahead of it on the preceding day. The postfrontal air did not have the recent exposure to heavy precursor emissions from the conurbation to the south. Therefore it is not surprising that the photochemical reactions on 12 July did not produce concentrations that were as great as they had been the day before. To some extent the difference between the two days reflects the influence of sources to the south and southwest of the Northern New England states. However, it should be remembered that the differences also reflect differences in the meteorolological conditions on the two days.

c. *17-18 June 1977*

These two days were a time of late afternoon and early evening violations associated with the movement of a depression across Northern New England. The surface weather charts indicated that the warm front of a slow moving low-pressure system entered the area from the southwest around noon on the 17th (Figure 23). However, the surface wind data at sites through the area (Figure 24) show that the front was weak, hardly affecting speed or direction. At 1400 EDT, Portsmouth and Portland were still in the cold air according to the National Weather Service analysis. The warm front of the system passed over these coastal locations by 1700. The cold front of the system had a much more definite impact on wind speeds and directions, particularly at Burlington (Figure 24). The front passed Burlington around 2300 EDT on the 17th, shifting wind directions to the northwest. It probably crossed the White River Junction area some 3 to 7 hours later, and cleared southern New Hampshire by 1400. Portsmouth was still in the warm sector at this time. Another system began to develop, and toward the end of the 18th the area was once again in a warm sector.

Ozone concentrations for sites with data at this time are shown in Figure 25. Violations were recorded between 1600 and about 2300 on the 17th at all but Portsmouth which showed a pronounced peak of violations around 1700 EDT on the 18th at a time when Manchester and Nashua experienced a sharp drop in concentrations.

The observed variations can be explained in part by the movement of the depression across the area. Concentrations began rising steadily at all sites except Burlington

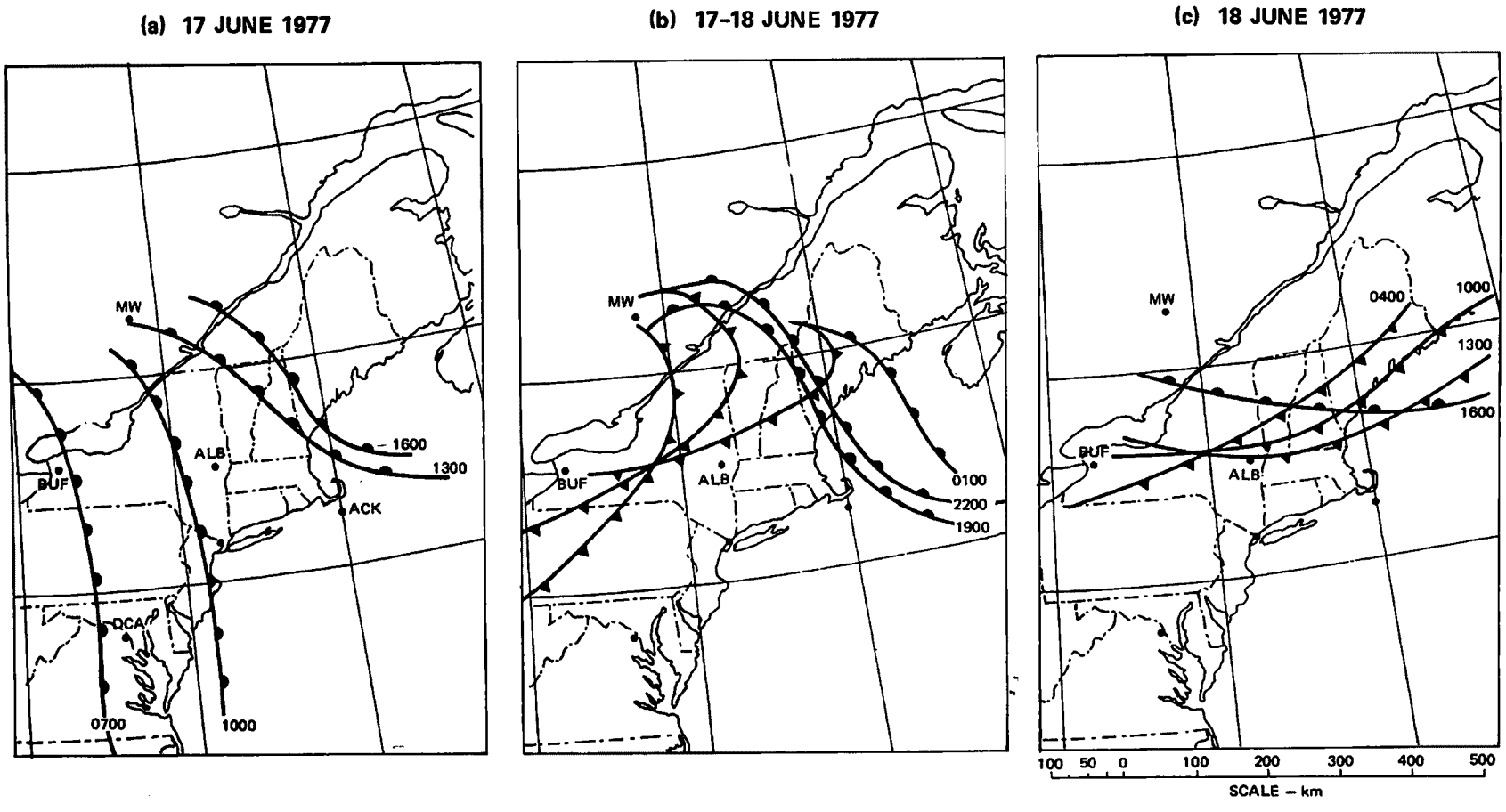


FIGURE 23 FRONTAL POSITIONS IN NORTHERN NEW ENGLAND, 17-18 JUNE 1977

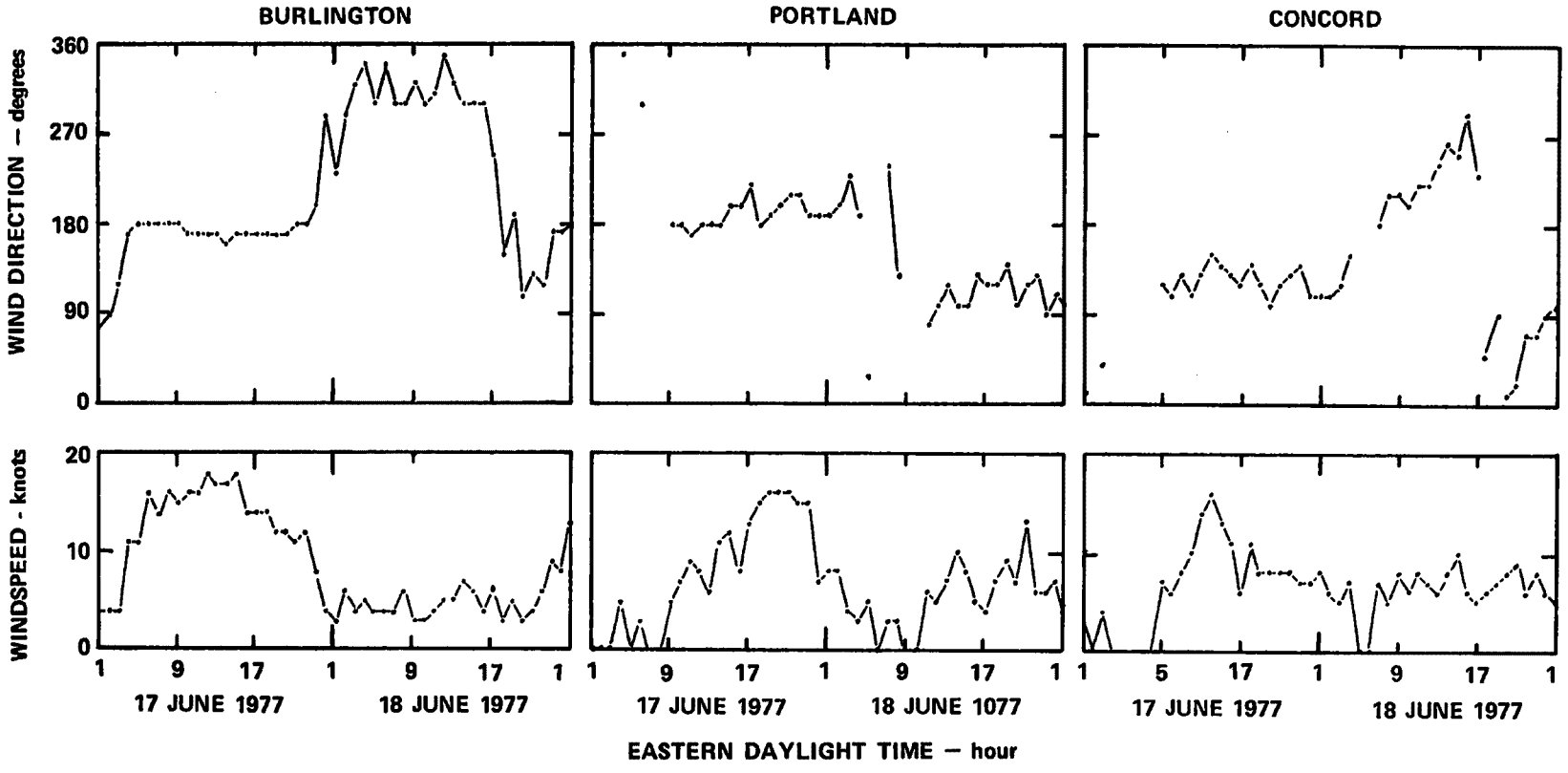


FIGURE 24 TIME HISTORIES OF WINDS AT SELECTED NORTHERN NEW ENGLAND SITES, 17-18 JUNE 1977

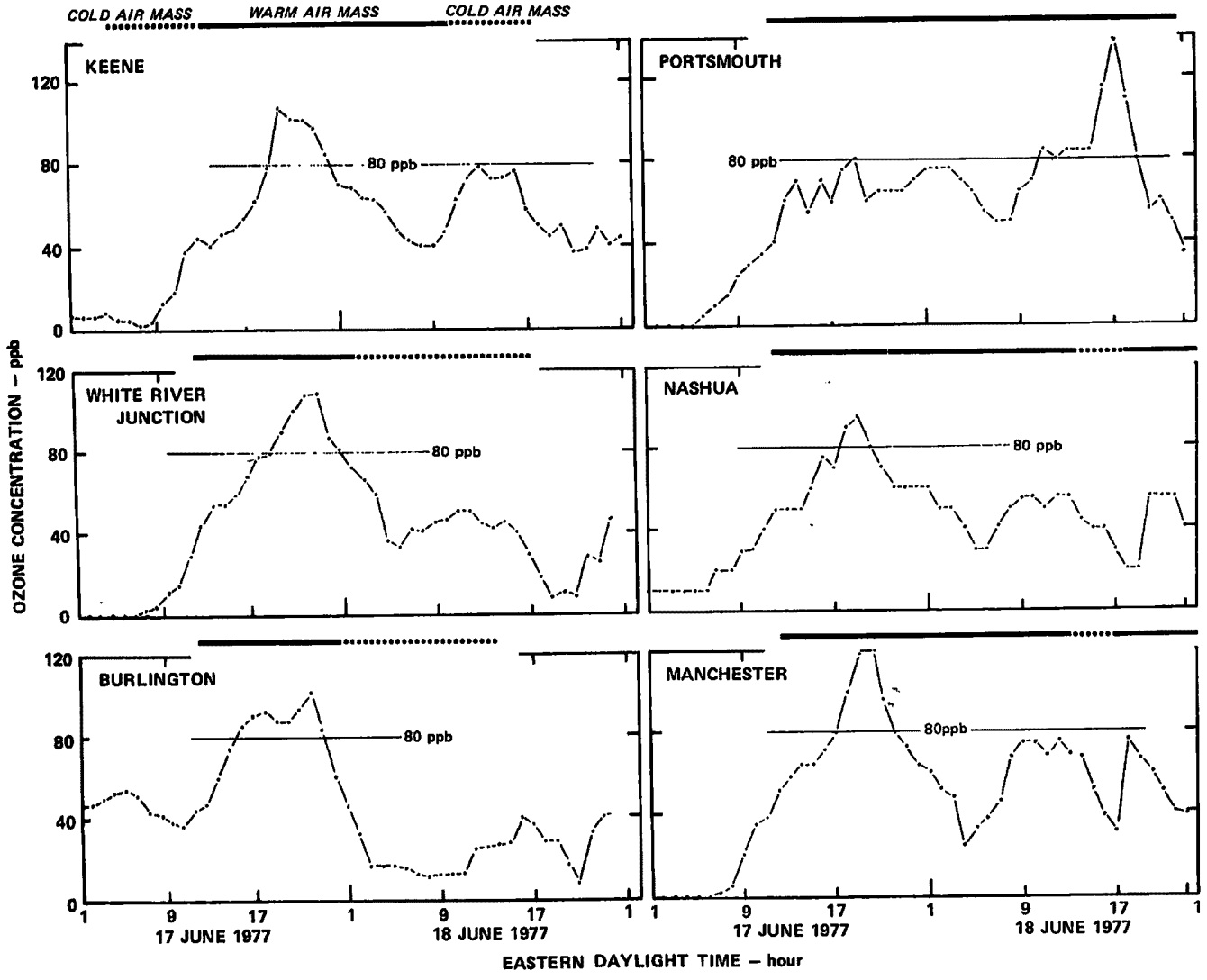


FIGURE 25 TIME HISTORIES OF OZONE CONCENTRATIONS IN NORTHERN NEW ENGLAND, 11-18 JUNE 1977

around 1900 EDT on the 17th. Conditions were not exactly favorable to the formation of photochemical ozone; skies were almost totally overcast, and wind speeds were in excess of 10 knots for most of the day. Figure 24 shows that wind speeds at Burlington had been relatively high since 0400 EDT, indicating vertical mixing that was transfering momentum groundward. The higher concentrations observed at this time may reflect this nighttime vertical mixing that was not present at the other sites. Any ozone aloft would have been brought down to replace that destroyed at the surface. The late occurrence of violations suggests that the ozone may have been transported into the area from the large urban complexes to the south and arrived later at this site than elsewhere. Wind directions remained steadily from the south during much of this time. The concentrations at Portsmouth approached, but did not reach 80 ppb. Portsmouth may have been away from the center of the polluted plume.

Wind speeds decreased during the evening of 18 June 1977, and ozone concentrations also fell gradually. All sites showed a minimum in concentration around 0500 EDT on the 18th. The one experience of violations at Portsmouth on the 18th seems to be from the movement of the cold front. The other sites in Southern New Hampshire seem to have had the warm polluted air replaced by cooler, cleaner air behind the front sometime during the early afternoon. Later, they were again overrun by the warm air according to the National Weather Service analyses. The period in the cool cleaner air corresponds to the concentration minima at Manchester and Nashua. Portsmouth probably remained in the warm sector during this period and the violations were the result of transport of materials from the south. This case shows the effect of transport from areas to the south at a time of day when local production of ozone was minimal.

3. *The Effects of Stagnation*

If air remains in the same area with little or no motion for prolonged periods of time, the emissions tend to accumulate, and if weather conditons are right, copious amounts of ozone may be formed. Light winds tend to be most often associated with high-pressure cells, and high-pressure cells are also noted for sunny conditons so the weather accompanying stagnation conditions is probably conducive to ozone formation. True stagnation for extended periods of time is highly unusual, but it has been possible to identify two instances where the air that arrived in Northern New England had traveled only about 300 km or less in two days. These two cases are discussed below. It was not possible to identify any cases where the air had remained in Northern New England for more than a day.

a. *20-22 April 1977*

This period provides an example of an instance when the Northern New England states remain in the northwest quadrant of a high-pressure cell for an extended period of time. Eventually, on April 22, a cold front passed through the region, bringing an end to the period of light southwesterly winds that had prevailed. Trajectory calculations show that the air arriving in the area of interest about midday on 21 April had been traveling very slowly from the southwest at an average speed of only about 4 m/s for the preceding 24 hours.

Figure 26 shows the ozone concentrations for these days at the six sites with data. A striking feature of the figure is the marked diurnal cycle at all sites, peaking around 1200 to 1600 EDT, with a minimum around 0000 to 0400. The violations occurred at Manchester and Portsmouth on the 21st and 22nd, on all three days at White River Junction, and for an extended period between the 21st and 22nd at Burlington where, unfortunately, data were missing on 20 April 1977. The regular diurnal cycle shows the effects of photochemical production with its midday to early afternoon peak. The fact that the concentrations were

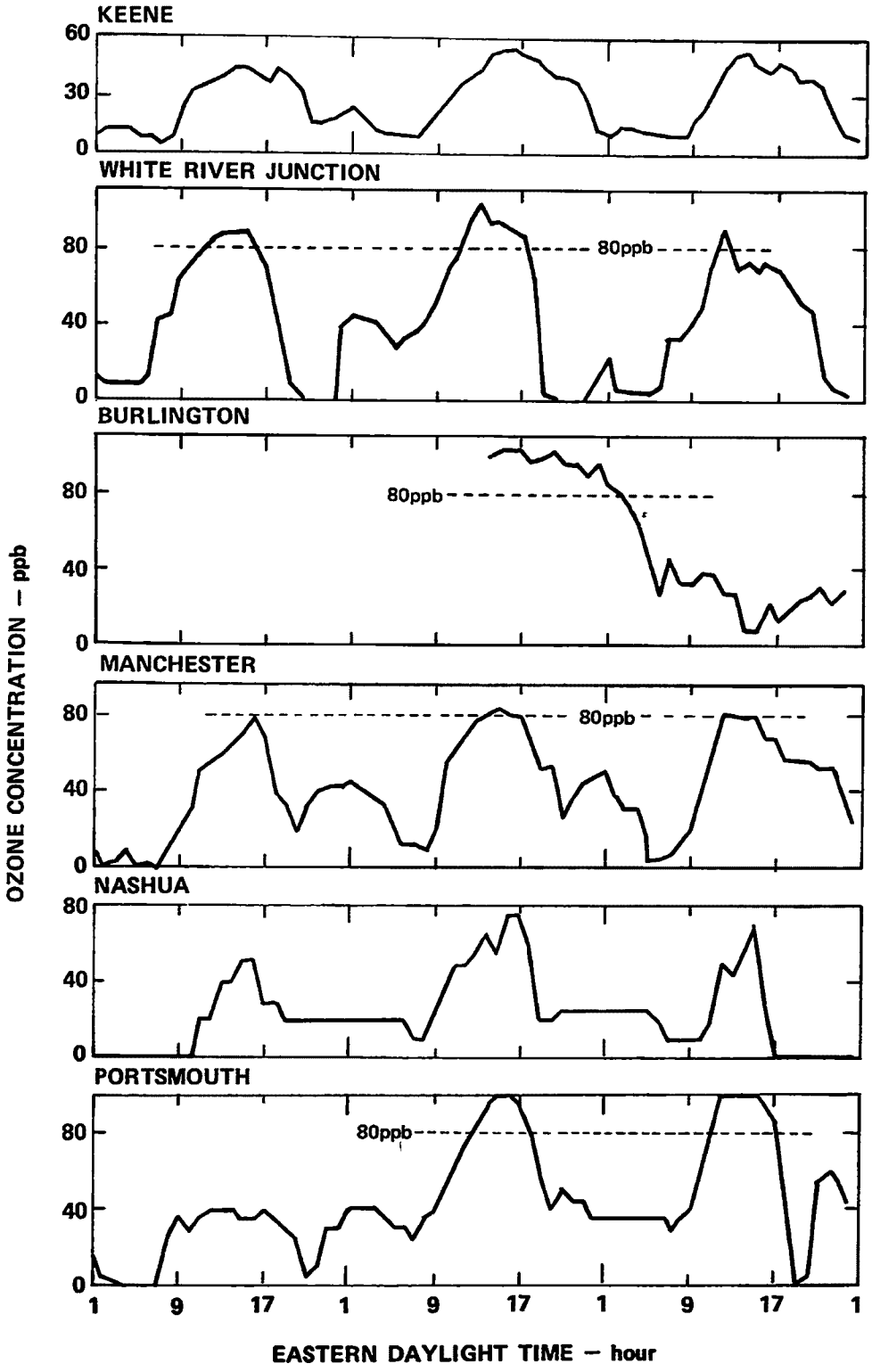


FIGURE 26 TIME HISTORIES OF OZONE CONCENTRATIONS IN NORTHERN NEW ENGLAND, 20-22 APRIL 1977

rather low, in spite of the near-ideal opportunity for the accumulation of precursors from major urban areas, is probably because skies were cloudy in the area.

The minima observed in the early evening at several of the sites may be effects of local emissions of NO during the evening hours. These were weekdays, so an increase in evening traffic is a plausible explanation. Wind speeds (Figure 27) increased during the late evening and early morning hours at Concord and Burlington, suggesting that some vertical mixing may have been going on that would have brought ozone formed earlier down to ground level.

b. *20-24 May 1977*

This is a second example of violations associated with the prolonged presence of a high-pressure system, in this case generally to the southeast of Northern New England. Although regular diurnal cycles were present in the ozone concentrations at each site (Figure 28), they were less distinct than those of the April example. NAAQS were violated for extended periods during daylight hours on the 21st, 22nd and 23rd. To illustrate how slow the air motion was during the period, calculated trajectories ending at Manchester showed that the air that arrived at the beginning of the period had been about 250 km to the north-northeast two days earlier. Air arriving at midday on the 21st had been about 1300 km to the west two days before. However, the intervening trajectory brought it just north of the New York City area. The air arriving at Manchester at midday on 22 April and on 23 April had been near Philadelphia the day before in both cases.

Although the average air motion was less for air arriving at Manchester on the 21st, the ozone concentrations were lower than on subsequent days when the air had moved faster, but had passed over the high emissions areas toward the southwest. Obviously, stagnation without emissions is not sufficient to be an effective producer of ozone. The alignment of airflow with the elongated axis of the East coast emissions area seems to offset the high ventilation rates even in distinctly non-stagnant conditions like those ahead of a front.

4. *Special Meteorological Situations*

a. *Nighttime Effects*

As has been noted before, the commonly observed diurnal cycle in ozone concentrations at ground level is largely the result of two mechanisms. The first is the production of ozone during daylight hours from the photochemical reactions of its precursors, such as HC and NO. Such production requires certain meteorological conditions, primarily a sufficient intensity of sunlight, and therefore is confined to hours with light winds between sunrise and sunset. Production is generally greatest around midday, with peaks in ozone concentrations during early to midafternoon hours. The second factor is the vertical temperature structure of the atmosphere. This will tend to promote vertical mixing during daylight hours when the surface is warmer than the air above and mix down to ground level both locally produced ozone and any ozone from natural or more remote anthropgenic sources that has been advected into the area. During night hours, vertical mixing is usually inhibited because the surface cools more rapidly than the surrounding air. This difference of cooling rates can lead to the formation of a temperature inversion near ground level, and prevent the mixing of any ozone trapped above the lowest layers down to the ground. Any ozone that has remained below the inversion after sunset will be destroyed by the scavenging action of HC, NO, and contact with surfaces, but that at higher altitudes will be isolated from the surface destruction.

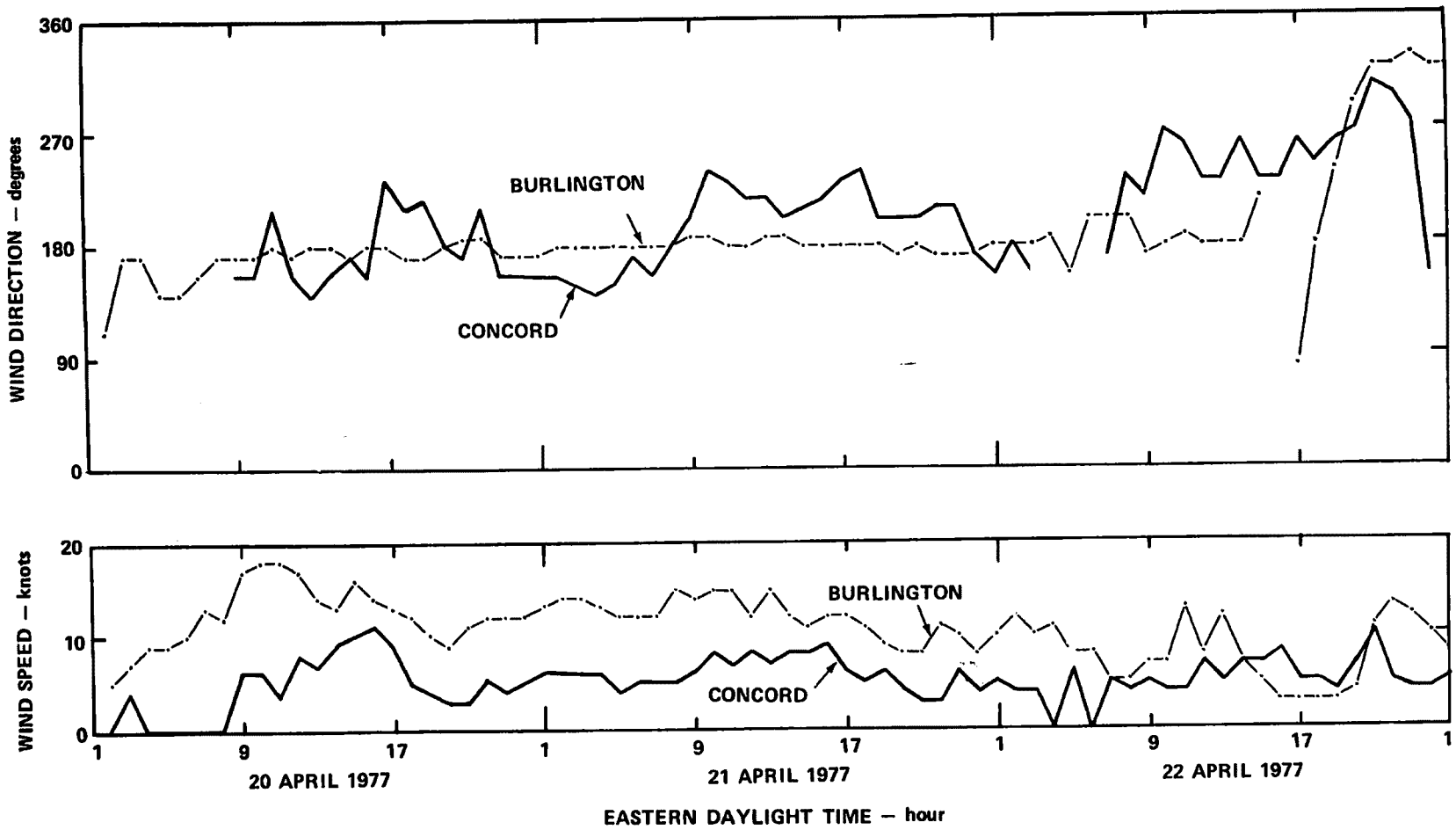


FIGURE 27 TIME HISTORIES OF WINDS AT BURLINGTON, VERMONT AND CONCORD, NEW HAMPSHIRE 20-22 APRIL 1977

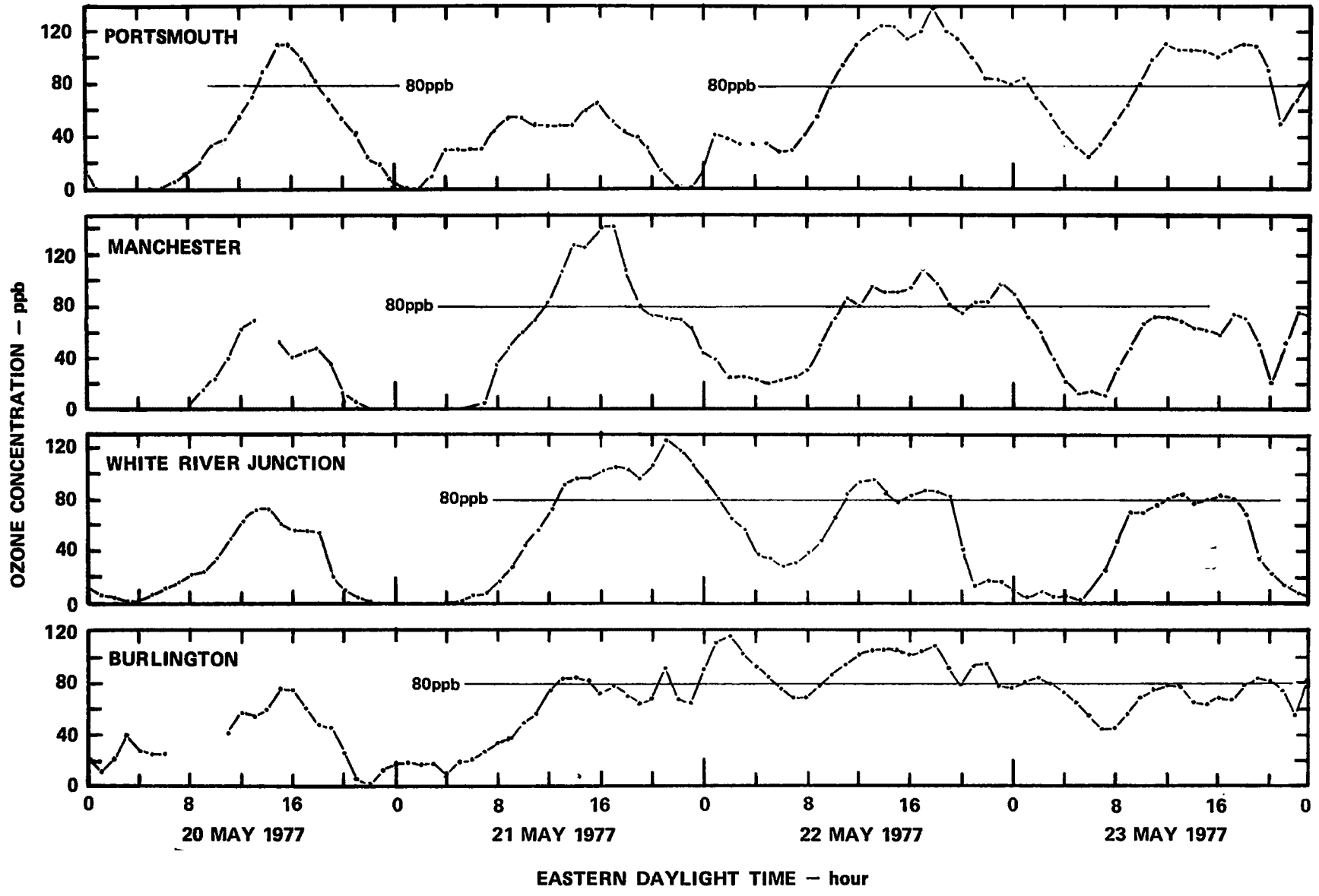


FIGURE 28 TIME HISTORIES OF OZONE CONCENTRATIONS AT FOUR NORTHERN NEW ENGLAND SITES, 20-23 MAY 1977

The occurrence of NAAQS violations during night hours therefore suggests two prerequisites: (1) an initially sufficient source of ozone above ground level, which in turn requires that conditions have been conducive to the formation and transport of ozone from urban areas upwind for a period of time beforehand; and (2) the presence of vertical mixing in order to bring the elevated ozone source to ground level. Usually the onset of vertical mixing at night will be accompanied by certain symptomatic meteorological conditions. Symptoms include cloudy skies, rises in temperature, or medium to strong winds. Increased temperatures and winds mark the downward flux of heat and momentum, and cloudy skies will inhibit the cooling at the surface that is required for the formation of temperature inversions.

A feature in the variation of ozone concentrations that follows from this reasoning is the decrease in concentrations as mixing continues. This results because the nighttime ozone source represents the daylight production from urban areas upwind, and as such it would eventually become diluted or exhausted. There is no photochemical activity at night to replace the ozone destroyed at the surface.

Referring back to Figure 6, the only site with frequent occurrences of violations during night hours was Burlington. Periods when more than just the odd hour or so exceeded the standards were not common at most sites, as can be seen by reference to Appendix B. However, two examples will now be discussed that serve to illustrate the points outlined above.

i. *28-29 June 1977*

This a period of violations of the standards at Nashua, Manchester, Burlington, and Keene extending from about 1000 EDT on the 28th to as late as 0500 on the 29th at Burlington. At all the sites, violations were recorded until about midnight on the 28th (see Figure 29). It should be noted that no data were available from Berlin, Portsmouth, and White River Junction for this time.

The daily weather maps for these days (Figure 30) show a rather unusual situation with a warm front lying within the warm sector of a larger frontal system. By 0800 EDT on the 29th, this front was straddling the area on roughly a NNW-SSE line. The movement of the front for 9 hours previous is shown in Figure 31.

The surface wind data for these days (Figure 32) shows that there were consistent southerly winds for most of the 28th and the morning hours of the 29th until the passage of the cold front, when wind directions shifted to the W and NW. Wind speeds, after an initial low on the 28th, remained relatively high at Burlington and Albany (10 to 15 knots), and a little lower at Portland and Concord (5 to 10 knots).

Ozone concentrations at all sites (Figure 29) showed a sharp increase at around 0700 on the 28th, probably the result of increased mixing. The increased wind speeds indicate a downward transfer of momentum along with ozone from aloft as well. Photochemical activity was probably under-way by this hour. Standards were exceeded by 0900 EDT at Keene, by 1000 at Burlington, and by 1300 at Manchester and Nashua. The timing of the violations is consistent with the advection of warm dirty air behind the warm front.

The continuation of levels above 80 ppb well into night hours suggests that the mechanisms outlined earlier were in operation. The area between the warm and cold fronts was probably unstable so that vertical mixing was encouraged, even after sunset. Wind speeds had remained high during night hours throughout the area, suggesting that vertical mixing was

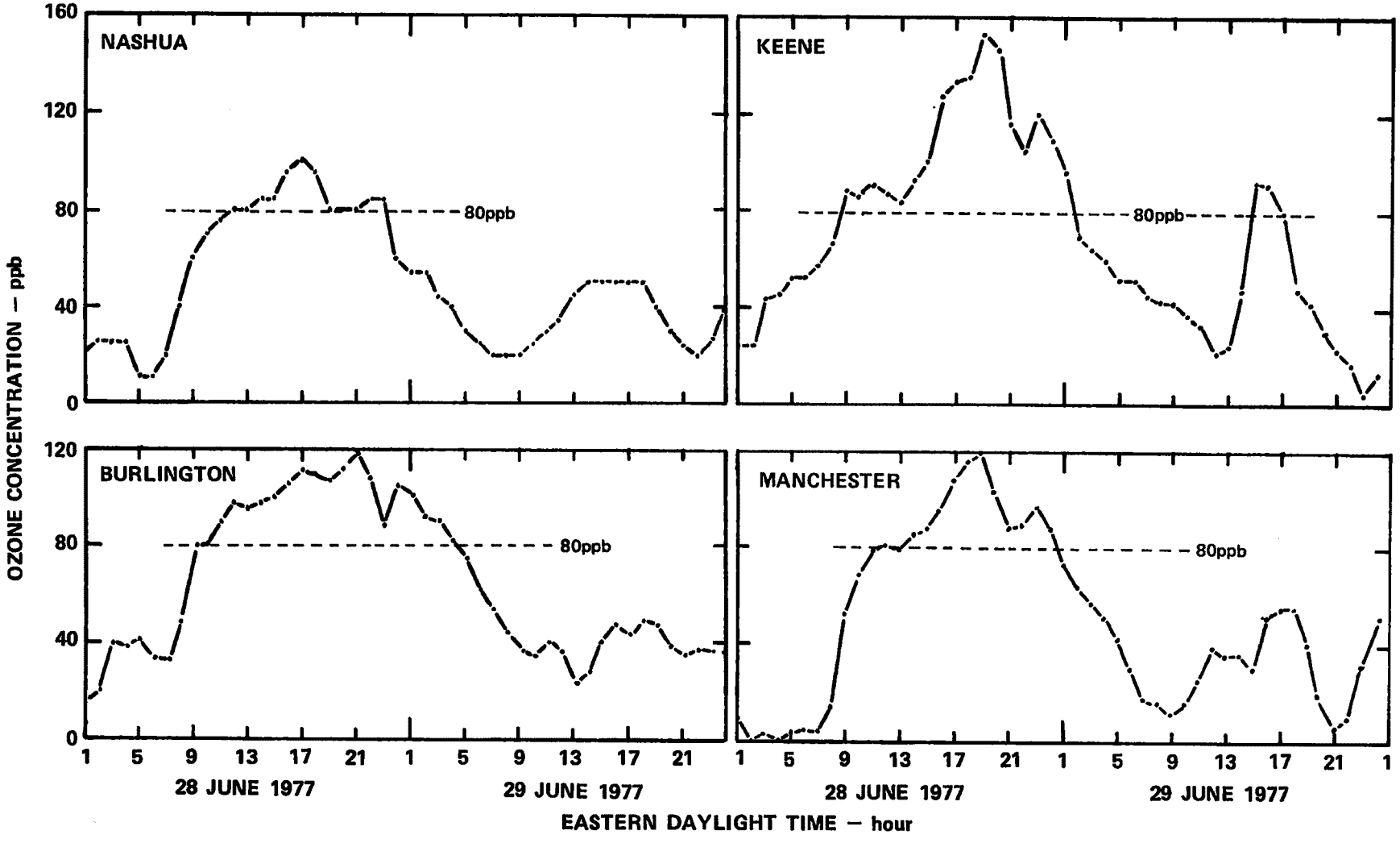
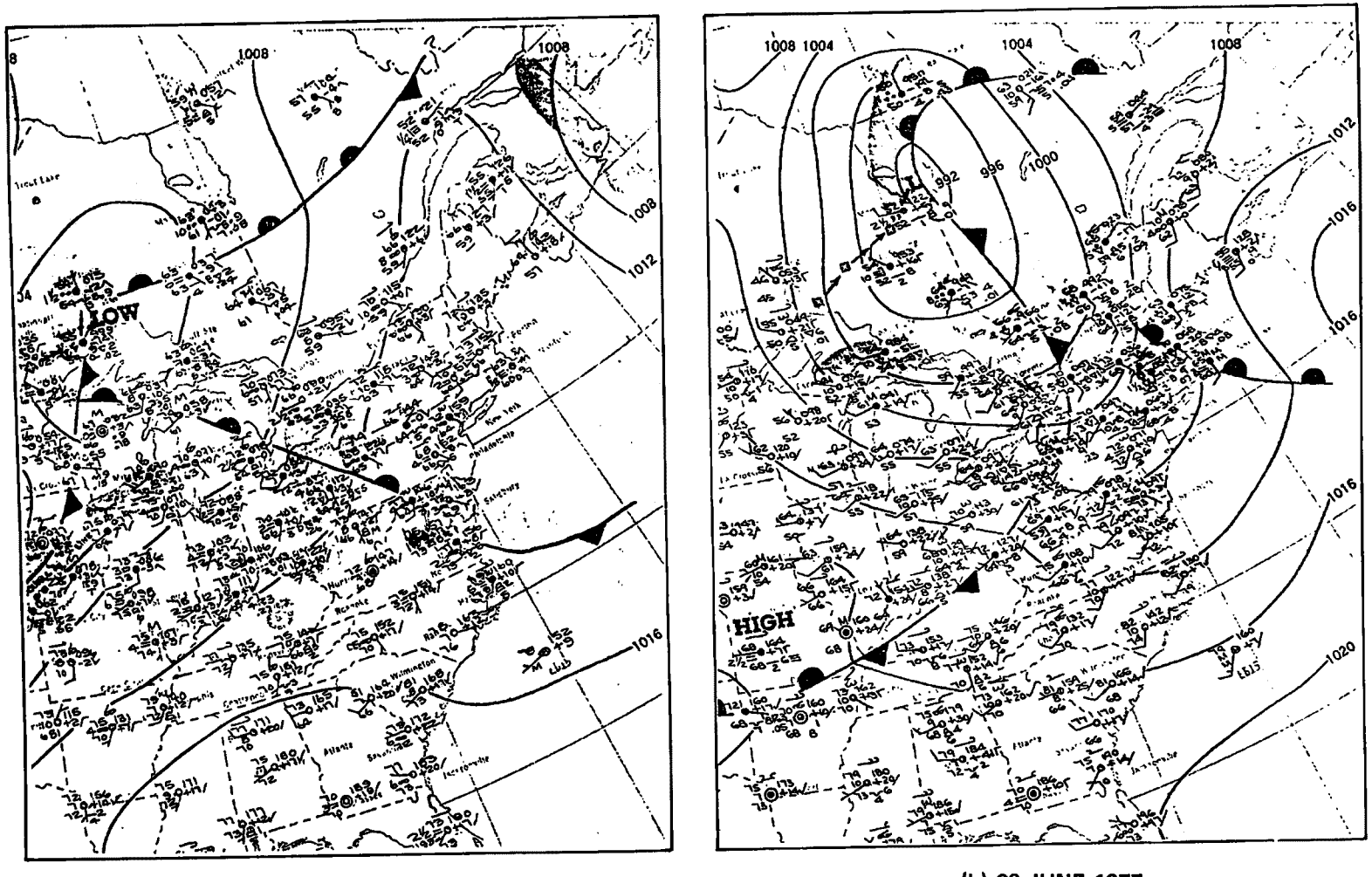


FIGURE 29 TIME HISTORIES OF OZONE CONCENTRATIONS IN NORTHERN NEW ENGLAND, 28-29 JUNE 1977



(a) 28 JUNE 1977

(b) 29 JUNE 1977

FIGURE 30 WEATHER MAPS FOR 28-29 JUNE 1977

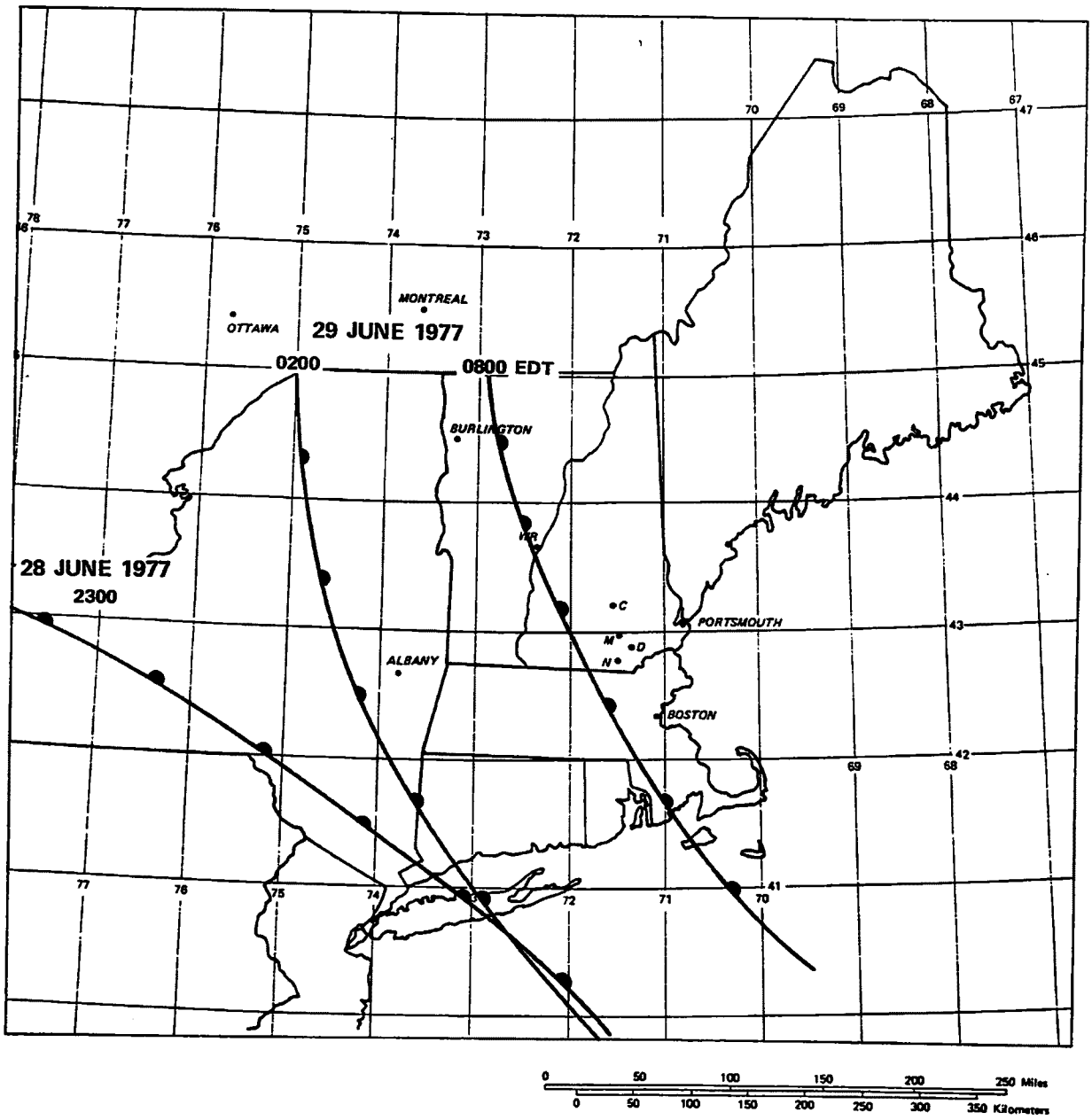


FIGURE 31 FRONTAL POSITIONS IN NORTHERN NEW ENGLAND, 28–29 JUNE 1977

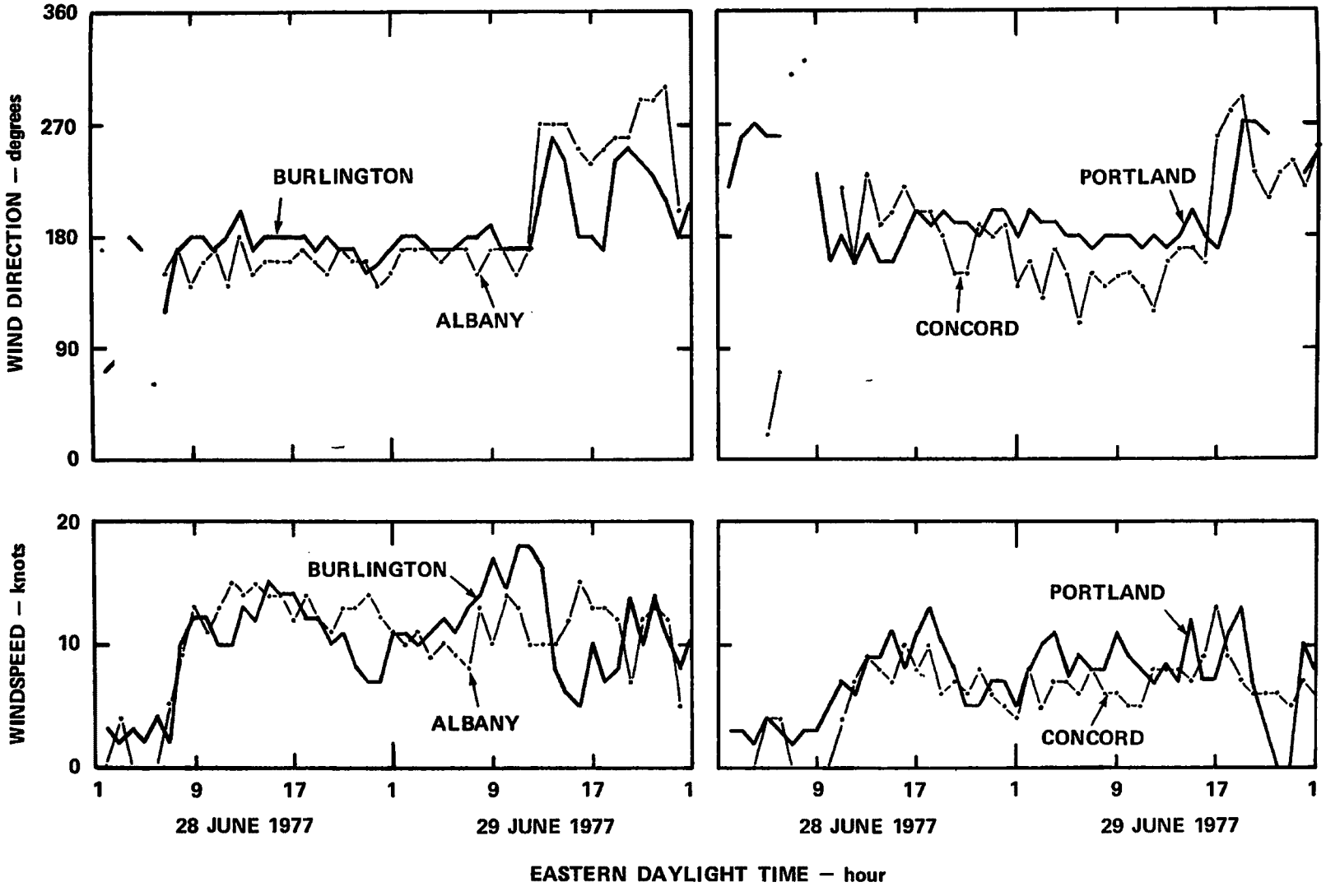


FIGURE 32 TIME HISTORIES OF WINDS, 28-29 JUNE 1977

taking place. Certainly, conditions for the previous 12 hours had been conducive to formation and transport of ozone from the large metropolitan areas to the south. Concentrations began to fall below the standard during the early morning hours of 29 June 1977, which probably meant that the supply of ozone aloft had been depleted. The depletion of ozone could have come about from the accumulated effects of destruction or because the ozone produced during the day had been advected beyond the study area. National Weather Service analyses show that the cold front did not pass the Burlington area until about 1200 EDT on the 29th, and Concord and Portland until about 1700 EDT.

The increased afternoon concentrations associated with the usual diurnal cycle were considerably suppressed on the 29th, but Keene did experience a short period of violations around 1500 on the 29th. However, both local and remote sources of ozone were likely to have been reduced once the front had passed, since it was accompanied by an increase in cloud cover and a shift in wind direction well away from source areas to the south.

All the features discussed earlier appeared to be present in this example. With the reasonably high wind speeds that were observed, it is probable that most of the ozone concentrations were the product of precursors advected from remote sources, rather than local production.

ii *15-16 June 1976*

This was a period when violations of the standard began around noon (15 June 1976) and remained high until about 0400 EDT the next morning. Figure 33 shows the ozone concentrations at sites with data during this period; the notable exception to the nighttime violations was Portland.

The daily weather maps (Figure 34) show the changes of meteorological influence, beginning with the south-southeasterly winds caused by a high-pressure system to the southeast, and continuing on the 16th in the warm sector ahead of the advancing cold front that passed through the area early on the 17th. The surface wind data in Figure 35 show fairly steady southerly wind directions at Burlington throughout the 15th and 16th. Directions at Concord and Portland were a little more variable, tending more to the SW on the 15th and more to the S on the 16th. Wind speeds were reasonably high (8 to 15 knots) on the 15th, dropping slightly during the early morning hours of the 16th, but then picking up sharply again toward noon.

Again the prime conditions required for high nighttime ozone concentrations were met; on 15 June 1976 there was a period of time suitable for the production and transport of ozone, and vertical mixing was present, as indicated by wind speeds that remained fairly high at night. Concentrations decreased after midnight at all sites but Burlington and Portland. The extended period of low concentrations at Portland, on the 15th was probably related to the offshore wind direction. As the direction became more southerly (and developed an onshore component) on the 16th, concentrations began to rise, and there was a period when concentrations exceeded 80 ppb around 1400 EDT. The importance of offshore and onshore winds will be discussed later in greater detail in connection with the sea breeze. The decrease in concentrations from 1900 on the 16th was consistent between all the sites and is probably the result of the formation of a stable layer at the ground in the early evening.

As with the previous example, the observations point to more remote sources of ozone than to any ozone that was locally produced.

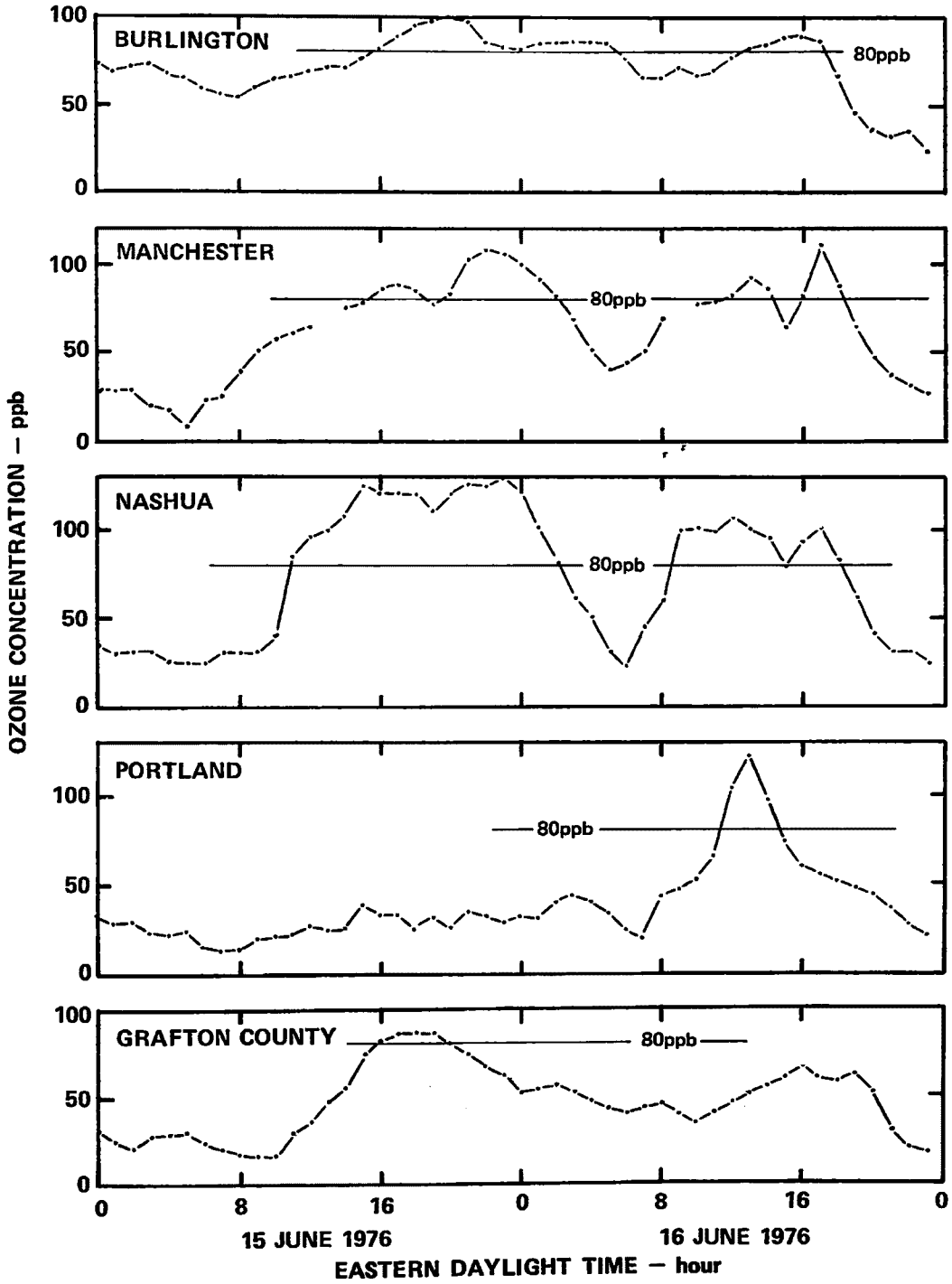
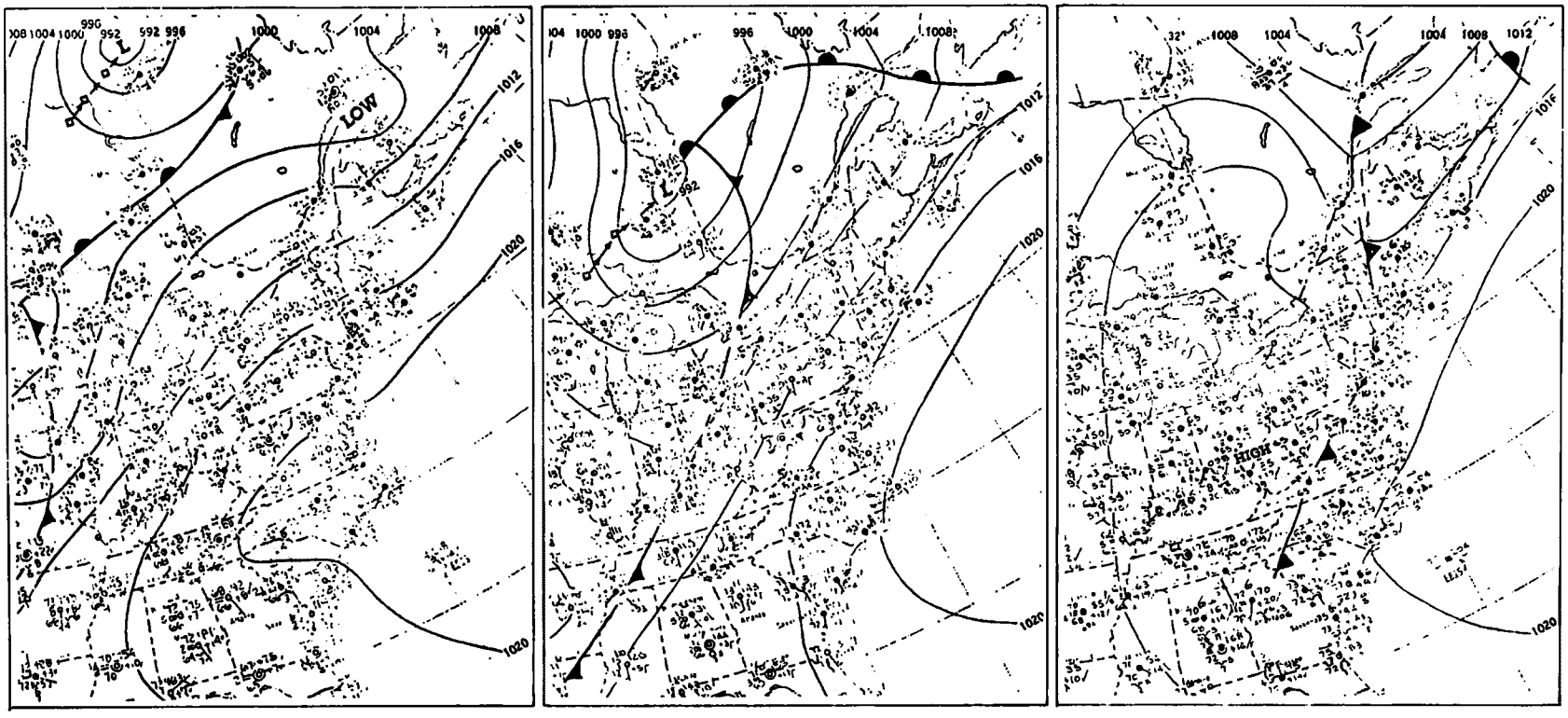


FIGURE 33 TIME HISTORIES OF OZONE CONCENTRATIONS AT NORTHERN NEW ENGLAND SITES, 15-16 JUNE 1976



(a) 15 JUNE 1976 (b) 16 JUNE 1976 (c) 17 JUNE 1976

FIGURE 34 WEATHER MAPS FOR 15-17 JUNE 1976

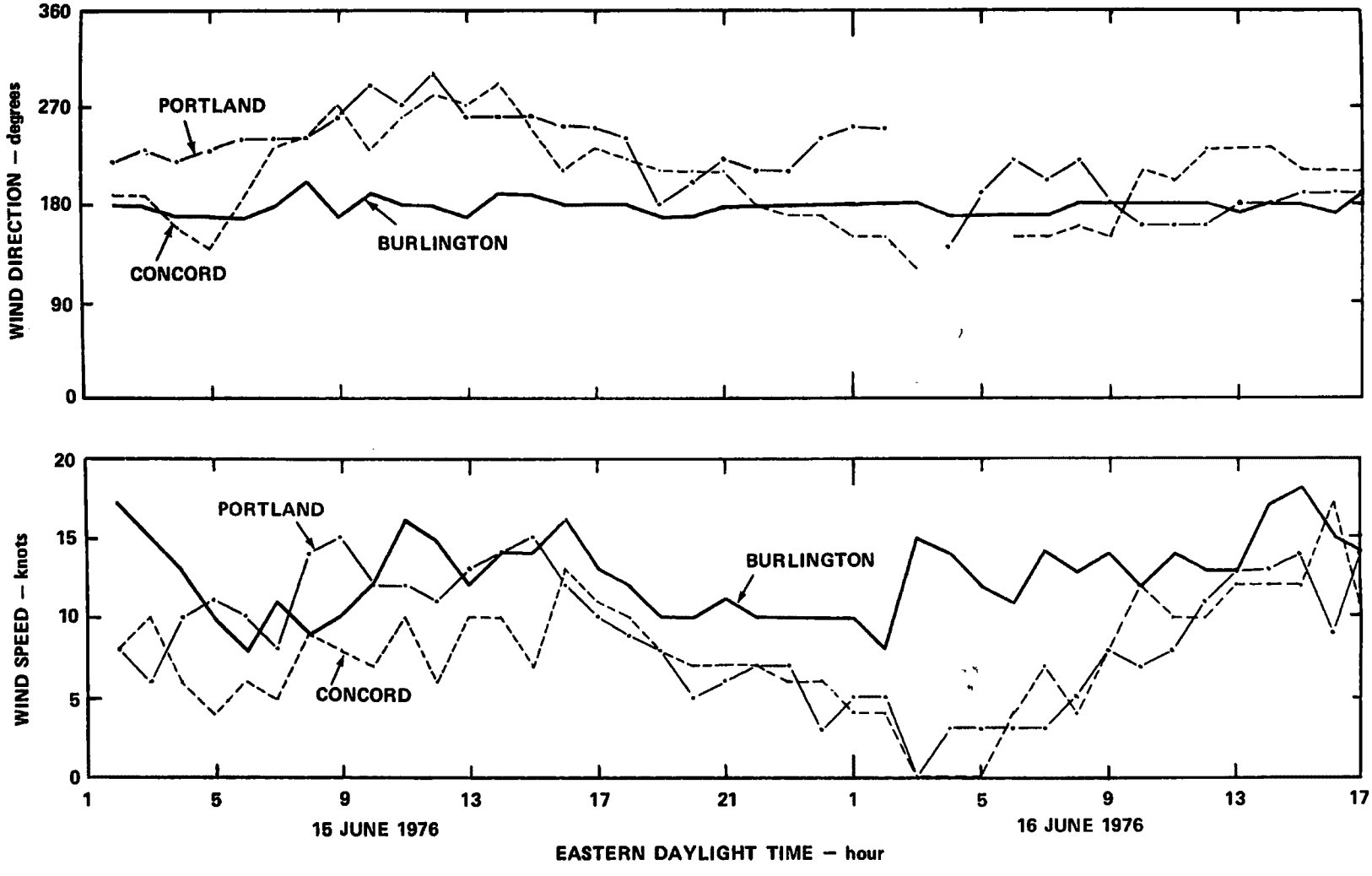


FIGURE 35 TIME HISTORIES OF WINDS, 15-16 JUNE 1976

b. *Sea-Breeze Effects*

Many of the processes discussed in the preceding sections have been of a fairly large scale, often involving transport over distances of 100 km or more. In this section, one of the smaller-scale phenomena will be discussed-- the effects of the sea breeze circulation at coastal locations. Unfortunately, data suitable for a comprehensive analysis of the effects as they are observed in the Northern New England States are few. However, the phenomenon has been studied in detail in other shore locations and those studies can serve by analogy to identify the important factors that may be operative in Northern New England.

Figure 36 (from Lyons and Cole, 1976) describes schematically the behavior of pollutants in the vicinity of a shorelne. The top half of the figure shows the behavior at about the time of the morning rush hour. The precursor pollutants are carried out over the nearby ocean, but have been separated from the surface by a very stable layer. This stable layer effectively inhibits mixing and prevents the precursors, or the ozone formed from them, from being mixed to the surface. The insolation and photochemical processes continue and the concentrations of ozone build. At the same time, the land is heating relative to the water. This produces a thermally induced landward circulation.

The air returning to the land in the afternoon is laden wih precursors and the ozone that has formed from them. According to Lyons and Cole (1976) the air is intercepted by a thermal internal boundary layer (TIBL) as it moves inland. More and more ozone is mixed downward as the air moves inland; eventually all the ozone is mixed into the lower layer. This process causes the highest concentrations to be found some distance inland from the shore. Lyons and Cole (1976) suggest that the maximum occurs a few kilometers inland. The effects of increased ozone entrainment will be modified by ozone destruction when the city is at the shore. The city's emissions of NO will remove much of the ozone near the shore and perhaps for a limited distance farther inland. This will accentuate the inland maximum.

It should be understood that the description above and especially the schematic diagrams in Figure 36 deal only with the components at right angles to the shoreline. There may also be motion parallel to the shore, so that the precursor emissions may leave the city, pass over the water, and return onshore at some other place. Lyons and Cole explained some observed ozone concentrations in southern Wisconsin as having been derived from emissions originating in Chicago.

The question arises, does the mechanism above, which was used to describe conditions on the western shore of Lake Michigan, also apply on the Northern New England Coast. Zeller et al. (1977) observed similar effects in the Boston region. Another important finding of their research was that the ozone "plume" from Boston was observable for long downwind distances. Concentrations in excess of 80 ppb were found aloft as far as 200 km downwind. In principle, this plume might be brought onshore somewhere downwind and mixed groundward if the conditions were right. Ludwig and Shelar (1977) have pointed out that winds from the southwest are frequently associated with high ozone concentrations in southern New England, so transport to the north-northeast along the coast, with subsequent onshore sea breeze flow, could produce high ozone concentrations at locations near the coast. It needs to be shown that high ozone concentrations are associated with onshore flow, especially when the air is moving from a southerly direction. It also needs to be demonstrated that high ozone concentrations can be transported to the coastal areas of New Hampshire and Maine.

We have examined ozone observations and wind direction measurements from a special study conducted during the latter part of July and most of August, 1974 (Londergan and

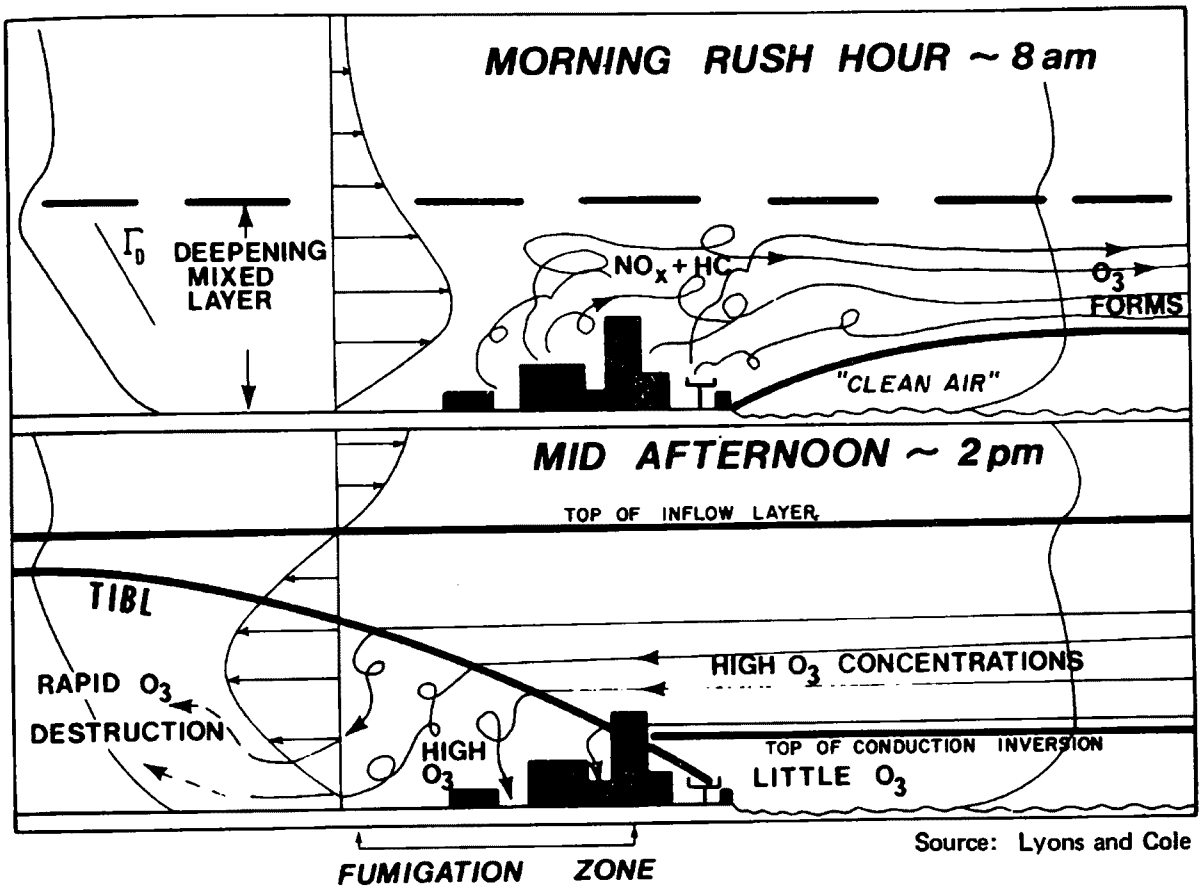


FIGURE 36 SCHEMATIC DEPICTION OF SUMMER SEA BREEZE CIRCULATION

Polgar, 1975), and while there is some evidence of a sea breeze effect, it is not wholly conclusive. On five days during the month of operations, ozone concentrations in excess of 80 ppb were observed at one or more of three stations that were monitoring ozone in the vicinity of Portland, Maine. A total of nine hours were involved. During eight of those hours, an onshore wind with a southerly component was observed. In each of the cases there had also been a period during the preceding morning when offshore winds were observed.

A similar analysis was performed using the routine Portland wind and ozone data for 1976. There were 16 afternoons or early evenings during which ozone concentrations were greater than 80 ppb. In all but one of the cases, the winds were onshore (from 40 degrees to 200 degrees) with a southerly component during most of the period of violation. In fact, about 85 percent of the 80 hours involved fell in the onshore flow category. Of the 15 days when the afternoon ozone violations occurred with onshore flow, 14 had had offshore flow earlier in the day.

Spicer et al. (1977) have presented data showing conclusively that ozone at high concentrations can be transported to an area where the sea breeze could advect it to shore. Figure 37 was taken from their report. It shows the ozone concentrations during the afternoon of 24 July 1975 at an altitude of about 300 m (1000 feet). According to the authors, the origins of the high ozone concentraions observed off the coast of Maine were emissions from Philadel-

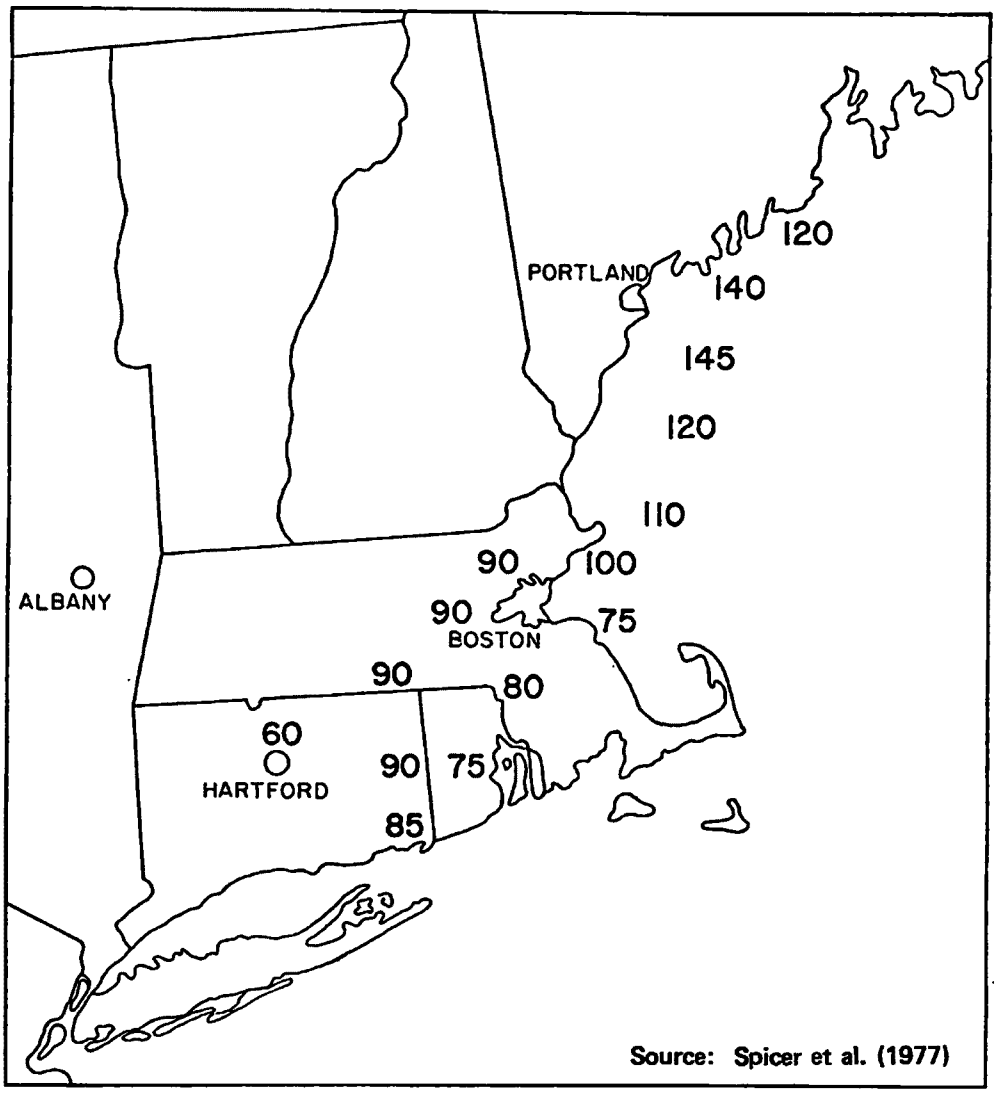


FIGURE 37 OZONE CONCENTRATIONS AT AN ALTITUDE OF 300 m, 24 JULY 1975

phia and New York on the preceding day. These earlier emissions and the ozone that arose from them were augmented by later emissions and more ozone from the Boston area on the morning of the day the observations were made.

It has not been possible to draw detailed wind fields and ozone concentration patterns for any specific cases, due to the lack of data. Therefore, it is not possible to show the sea breeze effects as conclusively as Lyons and Cole (1976) and Zeller et al. (1977) were able to do. However, it can be said with confidence that the winds at Portland are such that a majority of oxidant standards violations could involve sea breeze effects, but this does not necessarily mean that they actually do. It has also been shown that it is possible to transport large amounts of ozone at low altitudes over water to the coast of Maine where it would be in a position to be moved inland. Again, only the potential has been demonstrated. Although unproven, it appears quite probable that transport over water and sea breeze effects account for at least some violations in coastal Maine and New Hampshire.

c. *Diurnal Patterns of NAAQS Violations*

The mechanisms associated with high nighttime ozone concentrations and with sea breeze effects have at least one very important thing in common. They both involve ozone that is isolated from the surface in or above a stable layer. In the nighttime cases, the stable layer is produced by the radiative cooling of the surface after sundown. Sea breeze effects involve passage over cold water where the air also becomes very stable by being cooled from below.

The trapping of ozone aloft in a stable layer is very important for two reasons. The first of these is the isolation from surface destruction, which serves to "hermetically" seal off the ozone and preserve it. This effect could be offset if the ozone-rich air were mixed with cleaner air from above so that the concentrations were substantially diluted. However, the inhibition of vertical mixing in the stable layer that isolated the ozone from surface destruction can also reduce dilution by vertical mixing with air above.

The two phenomena differ in the time of day during which they are most pronounced. The sea breeze effect is a daytime phenomenon--the sea will be cooler than the overlying air, and for closely related reasons the air will flow onshore almost exclusively during the daytime hours. When the air remains over land it can be stabilized by radiative cooling of the underlying surface, which occurs only during the late afternoon and nighttime hours. Thus, we would expect high ozone concentraions to be more frequent at night at inland sites than at coastal locations. Figure 38 shows that such is the case.

Figure 38 displays the relative frequency of occurrence of ozone concentrations of 80 ppb or greater at different times of day. The data from three inland sites--Burlington, Manchester, and Nashua--were grouped together as were those from two coastal sites--Portland and Portsmouth. As discussed in Appendix A, these sites have all been ranked as having comparable levels of local urban influence, so the differences are believed to represent the coastal versus inland effects. Both sets of sites show the greatest frequency of high ozone concentrations during the afternoon hours. However, the frequency drops more rapidly and to appreciably lower levels with the onset of night at the coastal sites as compared to those inland.

As one might expect, the diurnal effect is more pronounced at the coastal sites where the photochemical processes, the typical mixing patterns, and the sea breeze effects all work together to emphasize afternoon ozone maxima. At inland sites the sea breeze is missing and the occurrences of high nighttime ozone concentrations due to long-range transport and nighttime mixing assume greater relative importance.

It should be noted that an island site or a site on a sharp point of land may behave much differently than ordinary coastal sites. The monitor on a point or island will often be in the midst of the general flow and will not have to depend on the sea breeze to bring transported ozone onshore. Furthermore, the sea might be warmer than the overlying air at night, so there would be greater vertical mixing than over land. High concentrations at night might be more frequent on a point than at an onshore site and the hypothesized daytime stable layer at the surface of the sea would reduce the afternoon frequency of high concentrations over the ocean. According to Mr. David Dixon of the Maine Department of Environmental Protection, Cape Elizabeth observed nighttime concentrations in excess of 80 ppb more frequently in 1977 than are shown for the coastal sites in Figure 38 and afternoon frequencies were less at the Cape Elizabeth site than the onshore sites. These more recent data are consistent with the hypothesized over water transport mechanism.

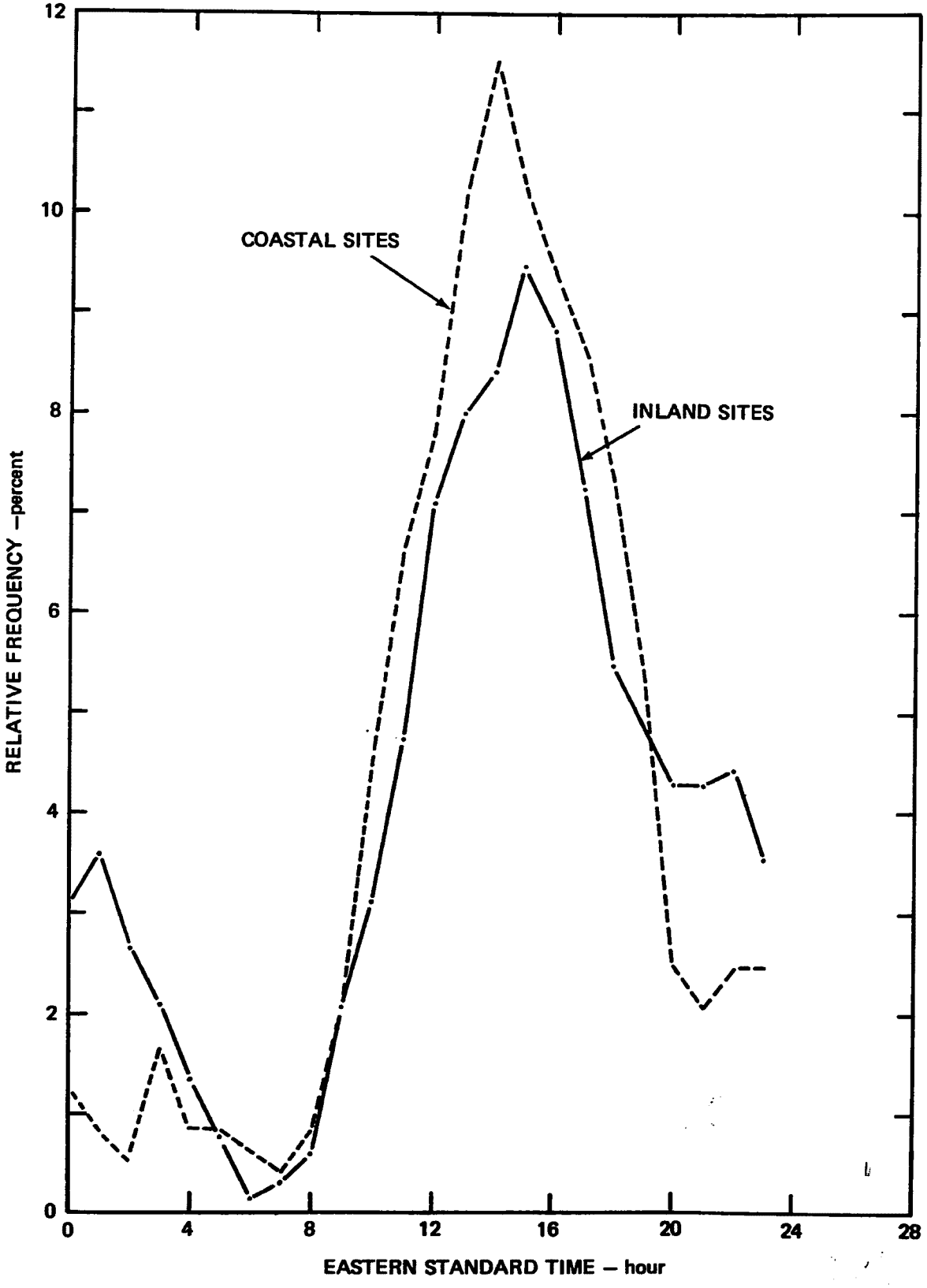


FIGURE 38 RELATIVE FREQUENCIES OF NAAQS VIOLATIONS AT DIFFERENT TIMES OF DAY FOR SELECTED COASTAL AND INLAND SITES

C. *Weekday Versus Weekend Ozone Concentrations*

1. *General*

Although nature has its cycles, those cycles may differ enough from the cycles of human activity so that they can be used to differentiate between natural and anthropogenic causes of high ozone. Daily and annual cycles would seem to be poor choices because both man and nature exhibit patterns of behavior with 24 hour and 365 day periods. However, man's habit of reduced weekend activity is not imitated by nature, so differences among the average patterns of pollutant behavior among weekdays, Saturdays, and Sundays are likely to reflect man's influence.

In the case of the photochemical oxidants, the effects of man's activities are somewhat paradoxical. Oxidant concentrations can be decreased or increased by anthropogenic emissions, especially NO. The immediate effect of NO is to destroy ozone, so the commonly observed "weekend effect" (see, e.g., Cleveland et al., 1974) in cities is to produce significantly lower ozone concentrations on weekdays than on weekends. Eventually, the same emissions that initially reduce ozone concentrations will result in increased concentrations somewhere downwind.

The behavior described in the preceding paragraph suggests that areas without important emissions might exhibit a reverse weekend effect if they were appreciably affected by ozone produced from imported anthropogenic emissions. However, such effects might be difficult to demonstrate statistically. The "weekend effect" at a site surrounded by emissions is independent of wind direction. However, the only cases that will contribute to the differences between weekdays and weekends at a remote site are those that occur when the monitor is in the urban plume. One is faced with the problem that the population of cases that demonstrate the effect is embedded in a larger, more homogeneous population of cases with no urban influence. Thus, it is much more difficult to use weekday/weekend differences to show that the major influences at a site are from some remote area than it is to use the effect to show that there are important local sources.

2. *Observations*

Mean hourly ozone concentrations were plotted for each day of the week at selected sites, for broad seasonal periods. These are shown in Figures 39 through 41. Marked differences are apparent at Manchester and Burlington. The differences show that Saturdays and Sundays had somewhat higher concentrations than Mondays through Fridays for most of the 24-hour period. Other sites, for example Nashua, tend to show the reverse to be true. The initial observations lend some weight to the arguments outlined earlier. Areas having relatively large local emissions of HC and NO_x the precursors to photochemical production of ozone, seem to experience higher ozone concentrations on weekends than weekdays. This would be due to the scavenging effect HC and NO_x have on ozone.

The observed differences between weekdays and weekends have been tested for statistical significance using the t-distribution. Differences between (1) Sundays versus Mondays through Fridays, (2) Saturdays versus Mondays through Fridays, and (3) Sundays versus Saturdays were tested at each site for two main periods-- summer (March through September) and winter (October through February). The results of the tests for both the daily mean and the daily maximum of the hourly-averaged ozone concentrations are shown in Tables 7 and 8. Although statistical significance was rare, the patterns of the results, particularly the tendencies

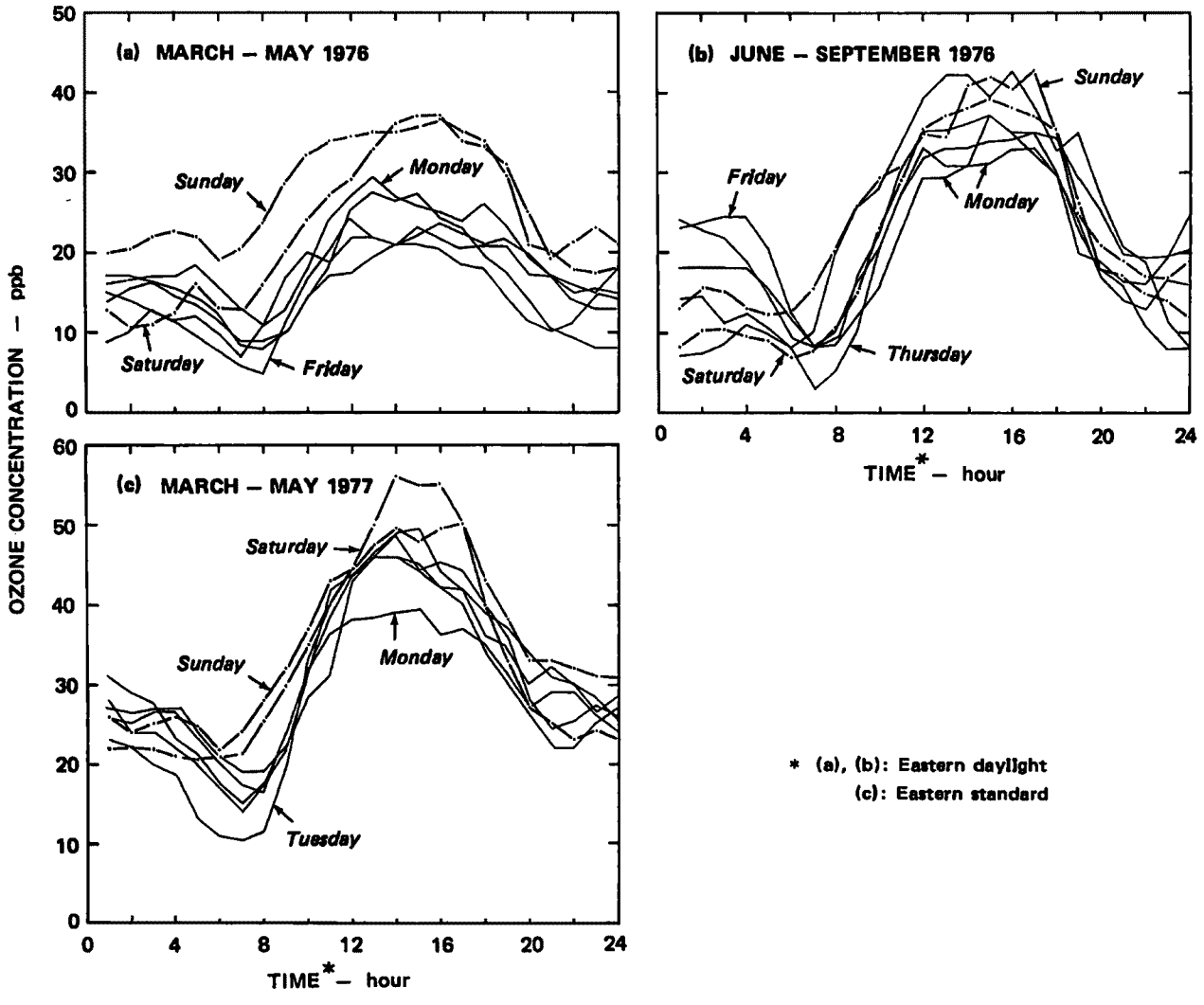


FIGURE 39 DIURNAL VARIATIONS OF AVERAGE OZONE CONCENTRATIONS FOR EACH DAY OF THE WEEK AT MANCHESTER, N. H.

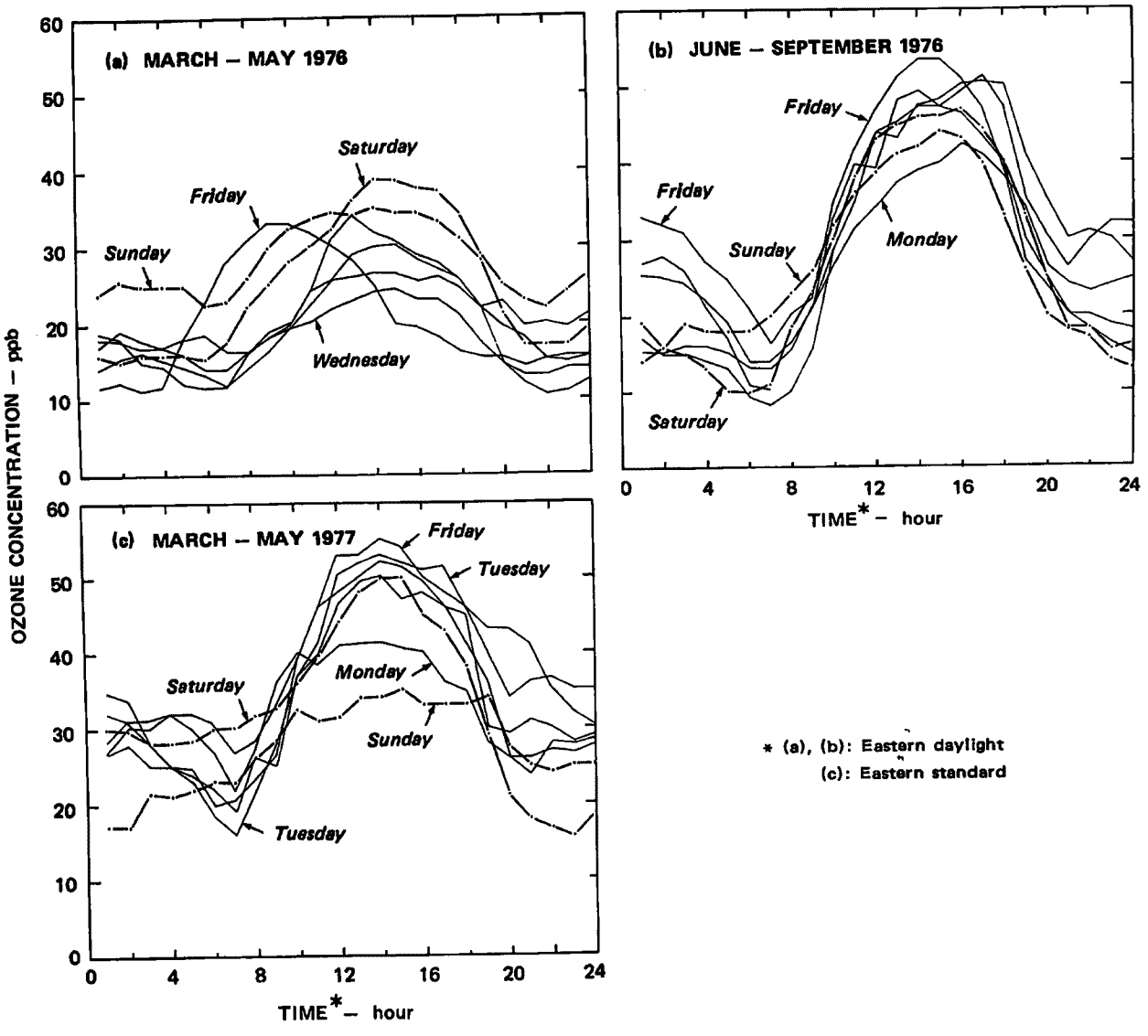


FIGURE 40 DIURNAL VARIATIONS OF AVERAGE OZONE CONCENTRATIONS FOR EACH DAY OF THE WEEK AT NASHUA, N. H.

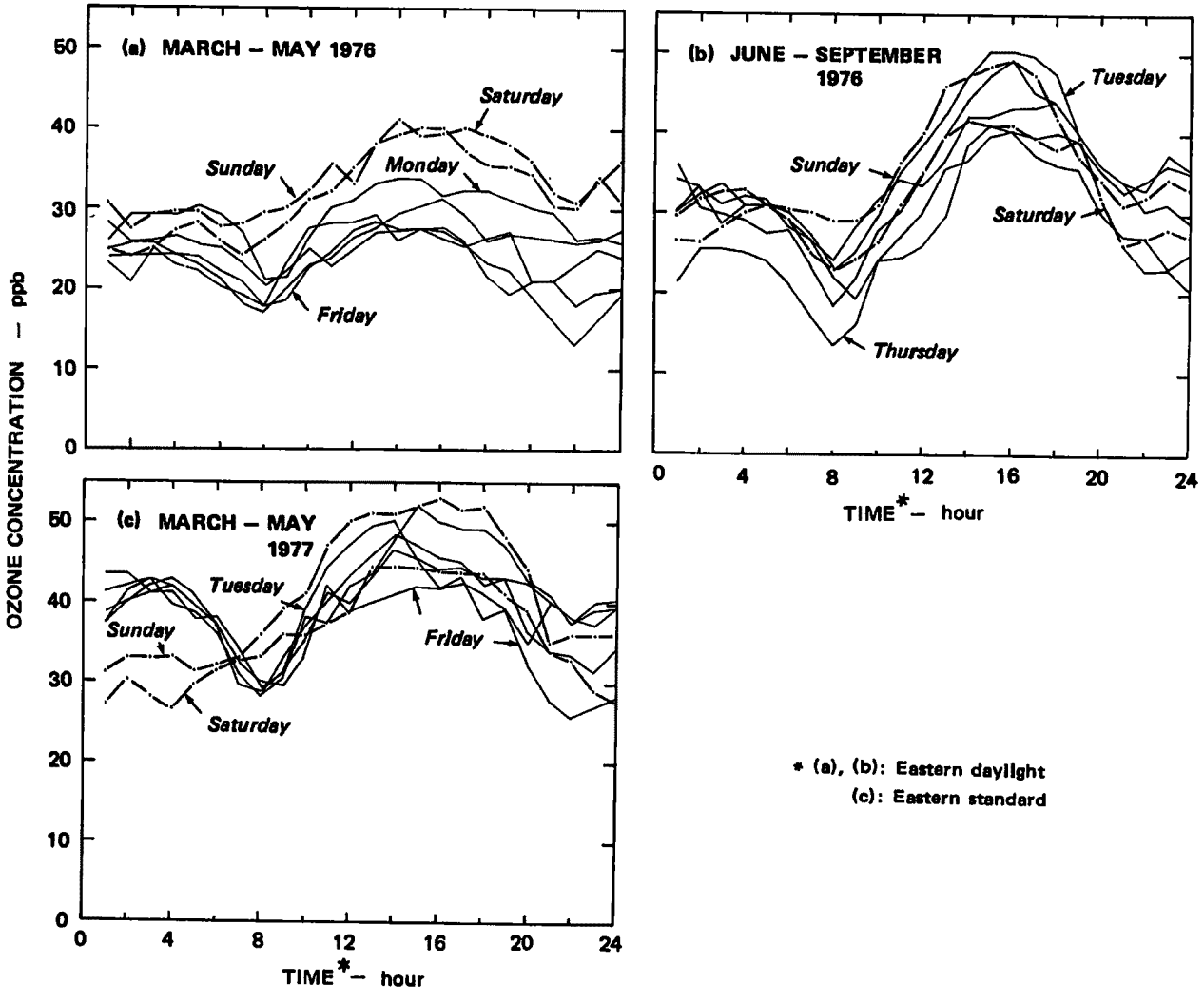


FIGURE 41 DIURNAL VARIATIONS OF AVERAGE OZONE CONCENTRATIONS FOR EACH DAY OF THE WEEK AT BURLINGTON, VERMONT

Table 7

DAILY MEAN OZONE CONCENTRATIONS--WEEKDAYS AND WEEKENDS

Site	Day of Week	"Winter" Mean	"Winter" Difference	"Winter" Significance	"Summer" Mean	"Summer" Difference	"Summer" Significance	March - May 1976 Mean	March - May 1976 Difference	March - May 1976 Significance	March - May 1977 Mean	March - May 1977 Difference	March - May 1977 Significance
Manchester	Sunday	6.5	0.8		25.8	5.4	1%	25.6	11.6	0.1%	30.6	2.3	
	Weekdays	5.7			20.4			14.0			28.3		
	Saturday	6.3	0.6		25.0	4.6	1%	22.1	8.1	0.1%	32.4	4.1	
	Weekdays	5.7			20.4			14.0			28.3		
	Sunday	6.5	0.2		25.8	0.8		25.6	3.5		30.6	2.3	
	Saturday	6.3			25.0			22.1			28.3		
Nashua	Sunday	6.7	-0.1		22.0	-1.7		26.2	8.9	0.1%	17.5	-10.9	
	Weekdays	6.8			23.7			17.3			28.4		
	Saturday	9.6	2.8		23.2	-0.5		24.6	7.3	1%	18.0	-10.4	
	Weekdays	6.8			23.7			17.3			28.4		
	Sunday	6.7	-2.9		22.0	-1.2		26.2	1.6		17.5	-0.5	
	Saturday	9.6			23.2			24.6			18.0		
Burlington	Sunday	19.1	2.0		34.8	5.5	1%	31.9	8.7	5%	38.7	0.4	
	Weekdays	17.1			29.3			23.2			38.3		
	Saturday	17.8	0.7		31.7	2.4		29.4	6.2		34.9	-3.4	
	Weekdays	17.1			29.3			23.2			38.3		
	Sunday	19.1	1.3		34.8	3.1		31.9	2.5		38.7	3.8	
	Saturday	17.8			31.7			29.4			34.9		
Portland	Sunday	13.5	3.1	5%	22.6	1.3		31.3	10.7	0.1%			
	Weekdays	10.4			21.3			20.6					
	Saturday	11.1	.7		24.1	2.8		26.4	5.8				
	Weekdays	10.4			21.3			20.6					
	Sunday	13.5	2.4		22.6	-1.5		31.3	4.9				
	Saturday	11.1			24.1			26.4					
Berlin	Sunday	6.9	-0.6		7.7	0.1		9.1	2.4		31.1	0.4	
	Weekdays	7.5			7.6			6.7			30.7		
	Saturday	6.5	-1.0		7.0	-0.6		7.1	0.4		27.5	-3.2	
	Weekdays	7.5			7.6			6.7			30.7		
	Sunday	6.9	0.4		7.7	0.7		9.1	2.0		31.1	3.6	
	Saturday	6.5			7.0			7.1			27.5		

Table 7 (Concluded)

Site	Day of Week	"Winter" Mean	"Winter" Difference	"Winter" Significance	"Summer" Mean	"Summer" Difference	"Summer" Significance	March - May 1976 Mean	March - May 1976 Difference	March - May 1976 Significance	March - May 1977 Mean	March - May 1977 Difference	March - May 1977 Significance
Grafton County	Sunday				13.4	-1.6							
	Weekday				15.0								
	Saturday				11.3	-3.7							
	Weekdays				15.0								
	Sunday				13.4	2.1							
	Saturday				11.3								
Deerfield	Sunday				21.6	1.9							
	Weekdays				19.7								
	Saturday				22.1	2.4							
	Weekdays				19.7								
	Sunday				21.6	-0.5							
	Saturday				22.1								
Keene	Sunday				26.9	-.2							
	Weekdays				27.1								
	Saturday				31.2	4.1							
	Weekdays				27.1								
	Sunday				26.9	-4.3							
	Saturday				31.2								
Portsmouth	Sunday				33.4	0.6					33.7	-0.1	
	Weekdays				32.8						33.8		
	Saturday				30.8	-2.0					28.3	-5.5	
	Weekdays				32.8						33.8		
	Sunday				33.4	2.6					33.7	5.4	
	Saturday				30.8						28.3		
White River Junction	Sunday	21.8	-5.0		32.8	3.2					36.7	4.3	
	Weekdays	26.8			29.6						32.2		
	Saturday	23.4	-3.4		30.5	0.9					31.4	-0.8	
	Weekdays	26.8			29.6						32.2		
	Sunday	21.8	-1.6		32.8	2.3					36.7	5.3	
	Saturday	23.4			30.5						31.4		

Table 8

AVERAGE DAILY MAXIMUM OZONE CONCENTRATION--WEEKDAYS AND WEEKENDS

Site	Day of Week	"Winter" Mean	"Winter" Difference	"Winter" Significance	"Summer" Mean	"Summer" Difference	"Summer" Significance	March - May 1976 Mean	March - May 1976 Difference	March - May 1976 Significance	March - May 1977 Mean	March - May 1977 Difference	March - May 1977 Significance
Manchester	Sunday	17.8	2.6		46.2	4.4		39.6	11.5		53.0	-0.2	
	Weekdays	15.2			41.8			28.1			55.2		
	Saturday	17.1	1.9		46.0	4.2		38.3	10.2		55.4	2.2	
	Weekdays	15.2			41.8			28.1			53.2		
	Sunday	17.8	0.7		46.2	0.2		39.6	1.3		53.0	-2.4	
	Saturday	17.1			46.0			38.3			55.4		
Nashua	Sunday	15.1	-1.5		40.6	-5.4		38.0	6.8		41.0	-14.0	
	Weekdays	16.6			46.0			31.2			55.0		
	Saturday	22.8	6.2		39.0	-7.0		39.0	7.8		28.9	-26.1	
	Weekdays	16.6			46.0			31.2			55.0		
	Sunday	15.1	-7.7		40.6	1.6		38.0	-1.0		41.0	12.1	
	Saturday	22.8			39.0			39.0			28.9		
Berlin	Sunday	14.0	-3.2		14.7	2.3		16.1	0.6		47.6	-3.0	
	Weekdays	17.2			12.4			15.5			50.6		
	Saturday	13.7	-3.5		15.5	3.1		17.7	1.6		42.1	-8.5	
	Weekdays	17.2			12.4			15.5			50.6		
	Sunday	14.0	0.3		14.7	-0.8		16.1	-1.6		47.6	5.5	
	Saturday	13.7			15.5			17.7			42.1		
Portland	Sunday	31.5	9.2	0.1%	37.0	-4.2		43.9	8.1				
	Weekdays	22.3			41.2			35.8					
	Saturday	24.1	1.8		45.0	3.8		44.8	9.0				
	Weekdays	22.3			41.2			35.8					
	Sunday	31.5	7.5	1%	37.0	-8.0		43.9	-0.9				
	Saturday	24.1			45.0			44.8					
Burlington	Sunday	30.3	3.3		51.0	4.4		44.0	8.4		58.3	2.0	
	Weekdays	27.0			46.6			35.6			56.3		
	Saturday	28.6	1.6		49.0	2.4		44.7	9.1		51.1	-5.2	
	Weekdays	27.0			46.6			35.6			56.3		
	Sunday	30.3	1.7		51.0	2.0		44.0	-0.7		58.3	7.2	
	Saturday	28.6			49.0			44.7			51.1		

Table 8 (Concluded)

Site	Day of Week	"Winter" Mean	"Winter" Difference	"Winter" Significance	"Summer" Mean	"Summer" Difference	"Summer" Significance	March - May 1976 Mean	March - May 1976 Difference	March - May 1976 Significance	March - May 1977 Mean	March - May 1977 Difference	March - May 1977 Significance
White River Junction	Sunday Weekdays	35.1 39.9	-4.8		51.7 55.1	-3.4					56.4 58.6	-2.2	
	Saturday Weekdays	38.7 39.9	-1.2		53.2 55.1	-1.9					53.8 58.6	-4.8	
	Sunday Saturday	35.1 38.7	-3.6		51.7 53.2	-1.5					56.4 53.8	2.6	
Grafton County	Sunday Weekdays				23.2 27.4	-4.1							
	Saturday Weekdays				24.5 27.4	-2.9							
	Sunday Saturday				23.2 24.5	-1.2							
Keene	Sunday Weekdays				44.0 46.9	-2.9							
	Saturday Weekdays				48.4 46.9	1.5							
	Sunday Saturday				44.0 48.4	-4.4							
Portsmouth	Sunday Weekdays				57.3 57.7	-0.4					54.5 57.8	-3.3	
	Saturday Weekdays				55.9 57.7	-1.8					50.4 57.8	-7.4	
	Sunday Saturday				57.3 55.9	1.4					54.5 50.4	4.1	
Deerfield	Sunday Weekdays				34.8 37.8	-3.0							
	Saturday Weekdays				38.6 37.8	0.8							
	Sunday Saturday				34.8 38.6	-3.8							

for Saturdays and Sundays to have greater or lesser ozone concentrations than Mondays through Fridays, seems to be at least consistent with much of the reasoning above. The following points may be extracted from Tables 7 and 8:

(1) Statistically significant differences were found at sites in the main urban centers--Burlington, Manchester, Portland. During the summer period, differences between mean daily values of Sunday and those of Monday through Friday were significant for Manchester and Burlington; also, the difference between means for Saturday versus Monday through Friday was significant at Manchester.

(2) Portland was the only site to show significant differences of both mean and maximum values during the winter period.

(3) t-test probabilities for most of the other sites were high, particularly for the summer months. Though differences were small, Sundays and Saturdays tended to have lower mean concentrations than Mondays through Fridays. The differences were most pronounced at Nashua, Berlin, and the Grafton County sites.

(4) The differences between t-test probabilities for daily mean and maximum hourly concentrations at each site are difficult to generalize. However, the significance of maximum hourly differences was greater than that of daily mean values during the winter months.

In addition to the broad summer/winter analyses, differences were tested for the March through May period of both 1976 and 1977. This is the period of year when natural affects should be a maximum and when anthropogenic effects should be increasing. The results for these months (also given in Tables 7 and 8) reflect the effects of reducing the sample size, especially for the period March through May 1976, which was characterized by a number of high ozone periods produced by unusual synoptic conditions, that were unevenly distributed among the days of the week. Tables 7 and 8 show that at all the sites with data during the period March through May 1976, daily mean and maximum hourly ozone concentrations on Saturdays and Sundays were greater than those for Mondays through Fridays. The effects were widespread. The differences observed at both Berlin and, more spectacularly, at Nashua were quite different from those observed during other time periods.

The March through May 1977 results shown in Tables 7 and 8 are more in line with the results for the longer-period analyses-- i.e., Burlington and Manchester show a "weekend" effect (though not significant) but Nashua and Berlin show a tendency toward the reverse of the usual urban weekend effect.

It appears that in some of the small subsamples of data, that certain synoptic meteorological patterns were not distributed randomly among the days of the week. Given the influence that synoptic events can have on ozone concentration, this could easily mask any 7-day cycles associated with human activity. The longer the period available for analysis, the better "average" conditions may be approximated. Thus the results for sites with small data sets (Derry, Keene, Portsmouth) should be interpreted with great caution.

V SUMMARY AND CONCLUSIONS

A. *Local Versus Imported Oxidants*

The evidence seems to leave little doubt that ozone produced from emissions generated outside the three Northern New England states, and subsequently transported into those states, represents a very significant part of their air quality problems. The general areas responsible for the contributed emissions are identifiable, but solid quantitative estimates of the local versus the imported contributions cannot yet be made. However, even if quantitative estimates were available, their usefulness in the formulation of control strategies would be quite limited by uncertainties about the future actions of neighbor states and the evolving status of photochemical air quality models.

The trajectory analyses and the wind analyses both suggest that the southern parts of Vermont, New Hampshire, and possibly Maine are often affected by emissions from the large urban areas toward the southwest. Conditions associated with photochemical production of ozone often include winds blowing from the southwest. Another general area from which emissions seem to come during periods when the NAAQS are violated is the region more to the west of the Northern New England States-- i.e., the industrial areas around Lakes Ontario and Erie. The northern parts of Vermont and New Hampshire are affected by these areas more frequently during periods of high ozone concentrations than they are by the more southerly source areas. Trajectory analysis of air arriving at Burlington, Vermont suggests that Montreal and perhaps the area north of Lake Huron can also contribute.

There were no ozone data from the northern parts of Maine, so it was not possible to identify periods of high concentration and to construct trajectories. The analysis of the wind directions and patterns associated with ozone concentrations in other parts of the Northeastern United States suggests that Montreal and the industrial areas around Lakes Ontario and Erie are the most likely areas to contribute to any air quality problems that might be found in northern Maine, if that region actually has any problems. This association is made because the data show that the westerly and southwesterly winds are most commonly associated with violations of the NAAQS for oxidant in other parts of the three Northern New England States.

The analysis of sea breeze effects suggested that coastal waters of Northern New England may serve as an effective avenue for the transport of ozone. The air is cooled from below as it passes over the sea surface, causing it to become more stable in the lower layers. This, in turn, inhibits dilution and isolates the ozone from destructive processes at the surface. During the afternoon, the preserved ozone that has been transported along the coast from its areas of origin is brought inland by the sea breeze and mixed to the surface by the turbulence within the thermally induced internal boundary layer over land areas near the coast. The data have shown this mechanism to be possible, but the data are not adequate to determine its importance. However, considering what is known about the winds and weather patterns that go with high oxidant concentrations in the Northeast, it seems likely that over-water transport and sea breeze advection are very important factors in the determination of the air quality of the coastal areas of Northern New England.

Some local effects are evident in the data from a few of the sites. The average weekend ozone concentrations at some of the sites are significantly greater than average values during the week. This is the result of the scavenging of ozone by local emissions of NO. The site descriptions given in Appendix A indicate that this localized effect is consistent with the degree of urban influence on the stations. However, there is little to suggest that these urban

influences will extend very far. In the next section, the extent of the urban influence is explored, because of its impact on control policies.

B. *Implications for Control Strategies*

1. *General*

A control strategy requires the specification of what is to be controlled, how much it should be controlled, and where and when it should be controlled. What is to be controlled and how much it should be controlled are dependent on what pollutants are already present. A highly simplified modeling approach has recently been introduced by the OAQPS (1977b, 1978) to describe the behavior of photochemical pollutants. The Empirical Kinetic Modeling Approach (EKMA) provides a useful tool for evaluating the impact of possible control strategies in the Northern parts of New England. It is especially useful to the analysis of local contributions in the more urbanized areas such as Portland, Maine and the Southern New Hampshire counties where the concentrations of hydrocarbon and NO_x emitters are the greatest.

The basic tool of the EKMA is an isopleth chart relating the sensitivity of ozone concentrations to changes in precursor concentrations. The report (OAQPS, 1977b) recommends that a separate isopleth chart be devised for each urban area of interest so that local differences in hydrocarbon mix and meteorological factors are incorporated into the system. However, when the appropriate measurements are not available, as they are not for locations in Northern New England, then a standardized graph like that in Figure 42 is used. Examination of that graph shows that concentrations of ozone produced from a mixture of hydrocarbons and oxides of nitrogen are sensitive to the relative amounts of those two classes of pollutants that are present. It is apparent that hydrocarbon controls are likely to be more effective for those mixtures of hydrocarbons and NO_x represented by the upper-left half of the diagram. When NO_x concentrations are low, and the lower-right half of the figure is used, then NO_x controls are likely to be much more effective than hydrocarbon controls. The next section examines the question of where high NO_x concentrations are likely to be found, and hence where hydrocarbon control strategies will be most effective.

2. *The Extent of Urban Influence on Oxides of Nitrogen Concentration*

Some studies have indicated that the ozone concentrations in rural regions are more influenced by the upwind anthropogenic emissions of oxides of nitrogen than by hydrocarbon emissions (e.g., Meyer et al., 1976; Ludwig et al., 1977a). Singh et al. (1977) suggested that the photochemical production of ozone in remote areas was limited by the availability of NO_x. The empirical evidence and the relationships displayed in Figure 42 underly this suggested explanation. Figure 8, which was discussed earlier, shows schematically how the concentrations of ozone might increase in remote areas if some oxides of nitrogen were introduced. If the assessment of these studies is accurate, then the extent to which NO_x from urban areas reaches into the surrounding countryside might serve as a guideline for estimating the extent of urban influence on ozone concentrations.

The EPA's Office of Air Quality Planning and Standards (OAQPS, 1977a) has recognized the importance of NO_x to the photochemical production of ozone in non-urban areas. They have examined the aerial extent to which urban areas cause measurable concentrations (defined as 7 ppb) of oxides of nitrogen. Figure 43, based on an illustration in the OAQPS

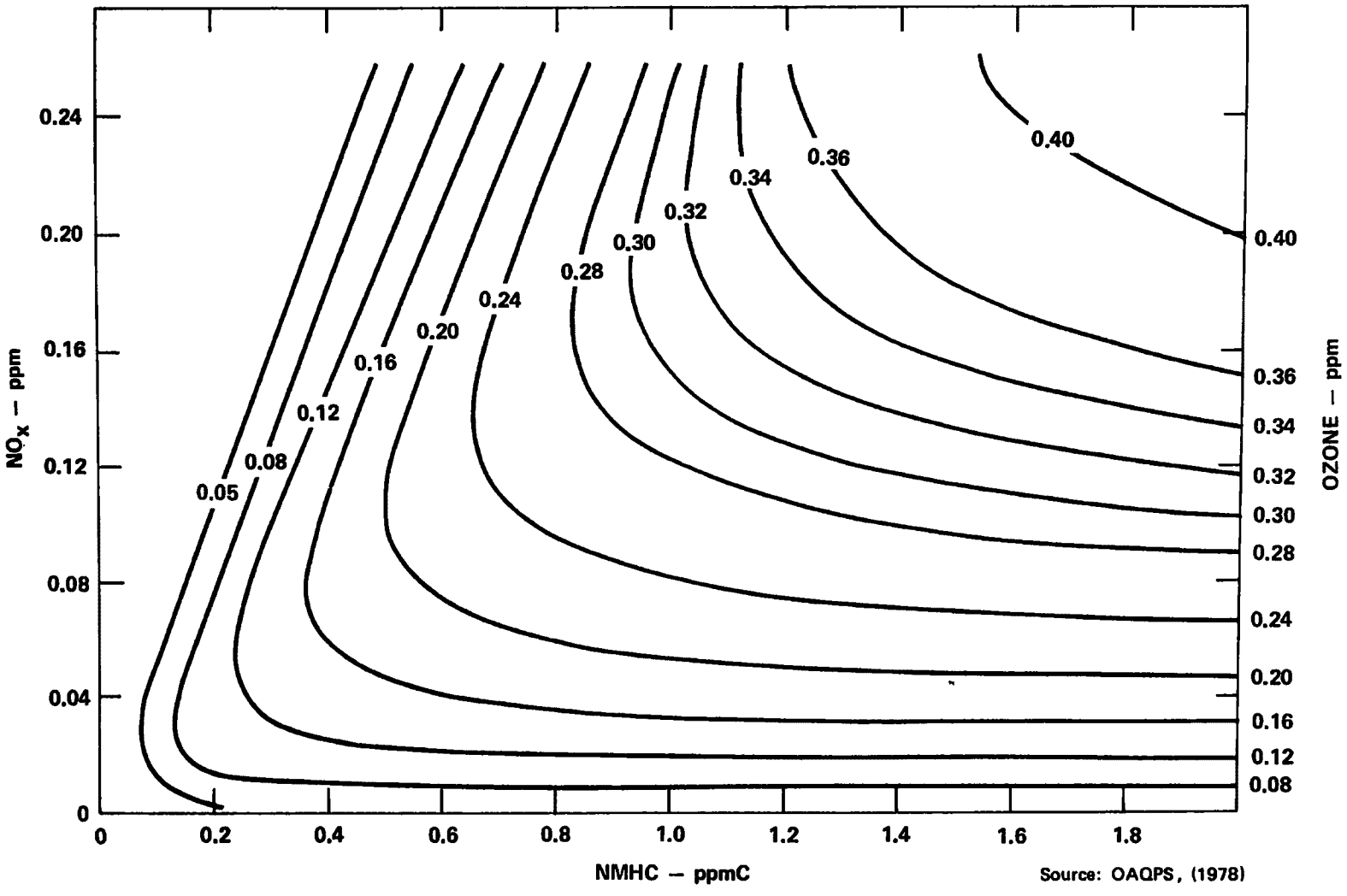


FIGURE 42 SENSITIVITY OF MAXIMUM AFTERNOON CONCENTRATIONS TO MORNING PRECURSOR LEVELS MEASURED UPWIND

(1977a) report, relates population of an urban area to its radius of influence. Within the radius defined by Figure 43, widespread hydrocarbon control strategies are likely to be effective in the reduction of ozone concentrations. Figure 44, also derived from the OAQPS (1977a) report, shows the areas in the U.S. that are influenced by urban NO_x emissions. It is evident that, based on the criteria used by OAQPS, there are not any large areas outside the cities and towns of northern New England where NO_x concentrations are likely to be appreciable.

Some caution should be exercised in the interpretation of Figures 43 and 44. They provide only an estimate of the regions within which hydrocarbon emission controls might be most effective in reducing photochemical oxidant production. The areas do not really have sharp boundaries. The relationship between population and concentration is uncertain and the the 7 ppb limit on NO_x concentration is arbitrary. Finally, the ozone that is produced from emissions within the designated areas may be transported well beyond those areas. This is an important point. It means that ozone standard violations can occur in the unshaded areas, but the control of such violations will have to be carefully considered. It may require limitations of hydrocarbon emissions within one or more of the shaded areas or of oxides of nitrogen and hydrocarbon emissions outside those areas.

3. *The Relative Importance of Transported and Locally Generated Ozone*

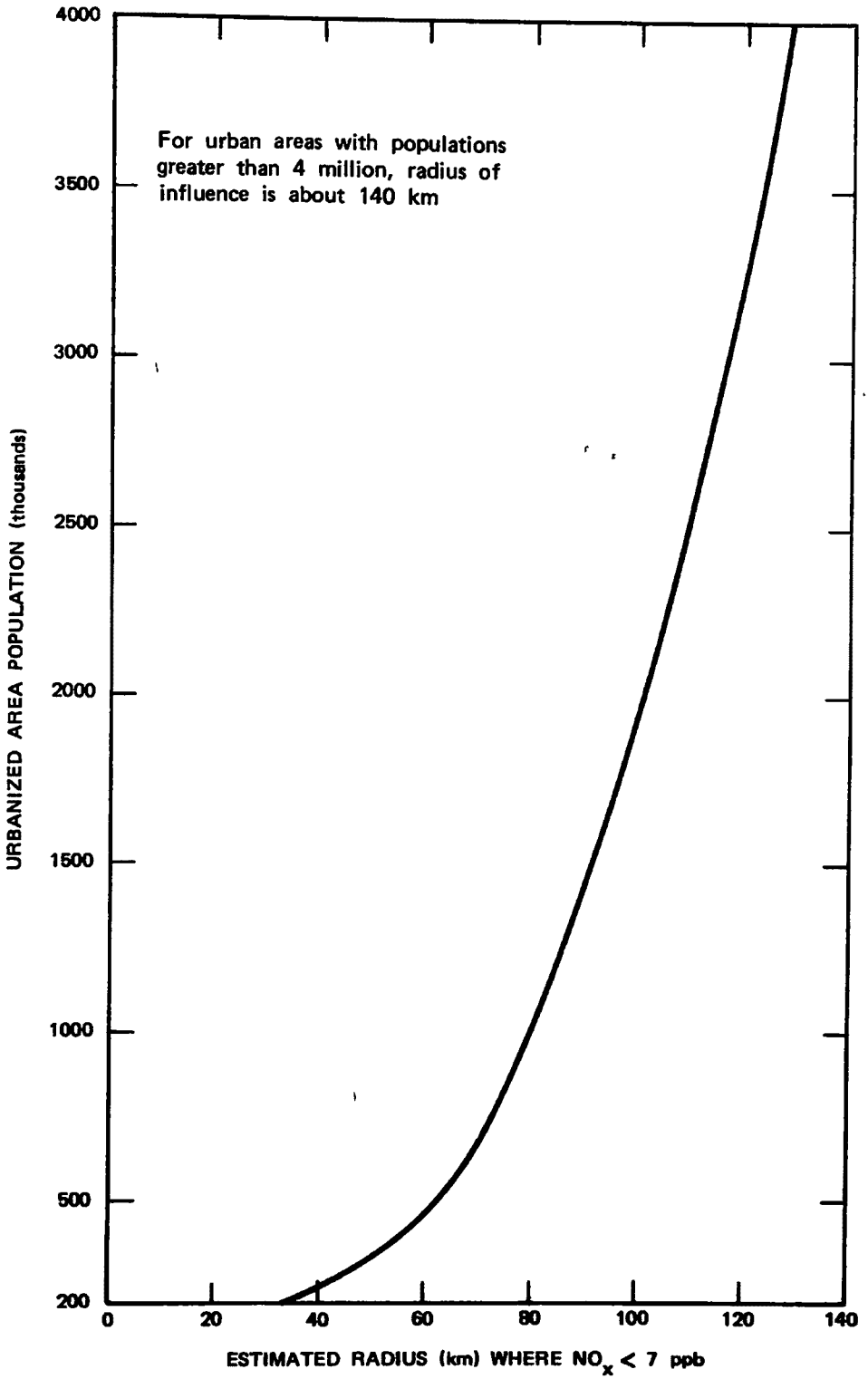
Calculations have been made with the EKMA that indicate that locally generated ozone concentrations are not increased by imported ozone in a linear fashion. In general, the amount of increase attributable to imported ozone will be half the imported concentrations or less, but the degree to which the transported ozone contributes depends on what meteorological and air quality conditions prevail. Table 9, from the OAQAPS (1977b) report, shows qualitatively how the additivity of the transported ozone depends on other factors. The various factors in the table are listed in decreasing order of importance.

The first factor in Table 9 is a meteorological one and may vary from locale to locale within Northern New England, but in general the dilution rates should be fairly high. Holzworth (1972) shows that summer afternoon mixing depths tend to be three or four times those in the morning for the Northern New England states. If the change from the morning height to the afternoon height occurs over a period of about 9 hours, then the average dilution rate is 13 percent per hour for a total change by a factor of 3. Thus, relatively high additivity would be expected in Northern New England on that basis.

Even the largest urban areas of Northern New England are relatively small, so the second factor listed in Table 9 also points toward greater influence from imported ozone. This is also true for the fourth factor listed in the table because air parcels leave small cities very quickly except under very stagnant conditions. Once the air parcel has left the city, the contribution from later emissions decreases dramatically.

A few data are available for Portland, Maine showing the average ratios of NMHC/NO_x for local sources and for the air transported into the area. According to the table given by OAQPS (1978), based on data from Londergan and Polgar (1975), the average ratio was 11.1 when the monitor was downwind of the source and about 31 when it was upwind. This factor should minimize the effects of transported ozone, unless of course severe hydrocarbon control measures reduced the ratio. A reduction of the ratio would tend to make the imported ozone fraction more significant.

In summary, it appears that in the vicinity of the urban areas of Northern New England (e.g., Portland and Portsmouth) about half the transported ozone would be additive to any



Source: OAQPS, 1977a

FIGURE 43 ESTIMATED RADIUS AT WHICH NO_x CONCENTRATIONS FALL BELOW 7 ppb, AS A FUNCTION OF METROPOLITAN POPULATION

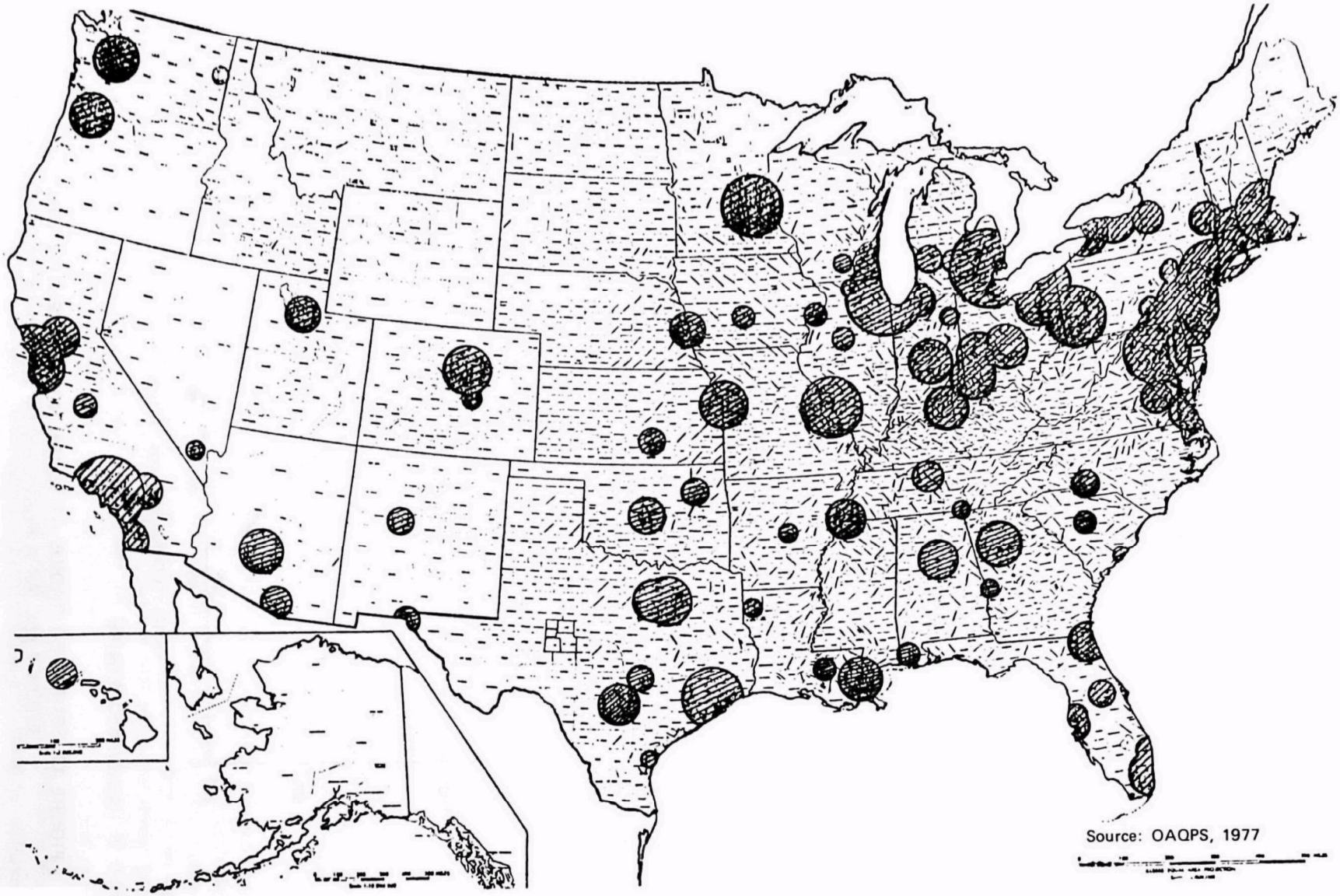


FIGURE 44 AREAS APPROPRIATE FOR HYDROCARBON EMISSION CONTROLS ACCORDING TO OAQPS (1977a)

Table 9

QUALITATIVE IMPACT OF VARIOUS FACTORS ON THE ADDITIVITY OF TRANSPORTED OZONE TO MAXIMUM OZONE CONCENTRATIONS IN URBAN AREAS*

Factor	Factor Value	Additivity
Dilution Rate (i.e., the extent and rate at which the diurnal mixing depth increases)	Relatively High (e.g., >13%/hour)	Relatively high (> 0.45)
Quantities of locally emitted precursors	Relatively Low (e.g., small city ~200,000)	Relatively high (> 0.45)
NMHC/NO_x Ratio	Relatively Low (e.g., < 6:1)	Relatively high (> 0.45)
Importance of post 9 a.m. emissions (This reflects both diurnal emission patterns and the larger atmospheric dilution capacity which generally occurs during the mid-morning and afternoon.)	Relatively High (e.g., significant NO emissions in the afternoon such as would occur if an air parcel remained within the city limits in the afternoon during a stagnation period)	Relatively low (< 0.45)

*Source: OAQAPS (1977b).

that might be generated locally. In the more remote regions such as areas in Vermont, the contribution would be relatively greater. Presumably, in an area free of local influences, nearly the entire transported amount would be observed, although some reduction would take place because of dilution and destruction at the surface.

4. *An Example of How the EKMA Might be Used to Devise Control Strategies in Northern New England*

Data summaries that were received as this final report was being written indicate that the second highest concentration in the southeastern parts of the region of interest was around 200 ppb--225 ppb at Cape Elizabeth near Portland, Maine and at Portsmouth, N.H.; and 160 ppb at Portland itself. For purposes of illustration we might consider the case of Portland with its 160 ppb concentration. If we assume that imported ozone amounted to about what was observed on the day illustrated earlier in Figure 37--say, 140 ppb. Only half of this--70 ppb--would be contributing to the 160 ppb observed in the area, leaving about 90 ppb from local causes.

As noted earlier, the average NMHC/NO_x ratio that has been observed in the Portland area is about 11. It should be noted that the value of 11 for the NMHNO_x ratio is based on very few observations and better information would be required to provide a more reliable basis for the development of appropriate control strategies. According to Figure 42, morning NMHC and NO_x concentrations of about 220 ppbC and 20 ppb, respectively, would have an NMHC/NO_x ratio of 11 and would lead to the production of about 90 ppb ozone concentrations.

How much would the morning NMHC concentrations have to be reduced to achieve standards? Since the contribution from upwind sources would be greater than the 80 ppb NAAQS even if all local emissions were stopped, it must be assumed that the controls applied in upwind areas can reduce the ozone concentrations received in the Northern New England states to some value nearer the general background of about 40 ppb. Let us assume that upwind controls reduce imported ozone to 50 ppb, of which 25 ppb is additive to the locally generated ozone. This means that the locally generated ozone must be reduced from 90 ppb to about 55 ppb. If this were done through hydrocarbon controls alone, it would require a 55 percent reduction in hydrocarbon emissions, to about 45 percent of the current amounts. If hydrocarbons and NO emissions were reduced in the same proportions, keeping the NMHC/NO_x ratio the same, then each would have to be at about 55 to 60 percent of its current level.

If we had used the 225 ppb ozone value that was observed in Portsmouth (and at Cape Elizabeth), the requirements for reduced emissions would have been more severe. Assuming that Portsmouth also has an NMHC/ NO_x emissions ratio of 11 and that imported ozone might be slightly more concentrated, say 180 ppb (of which 90 ppb is additive) because Portsmouth is closer to urban source areas, then the local production of ozone would be about 135 ppb. According to Figure 42, the corresponding NMHC and NO_x concentrations (assuming the same NMHC/ NO_x ratio of 11) would be about 400 ppbC and 36 ppb, respectively. If we again assume that imported ozone can be reduced to 50 ppb, of which 25 ppb would be additive, then the reduction of the local contribution from 135 ppb to 55 ppb (as would be required to meet an 80 ppb standard) would mean a reduction of NMHC emissions to about 20 to 25 percent of current levels. If the standard were raised to 100 ppb as has been considered, then NMHC emissions would still have to be reduced to about 30 percent of current levels.

The preceding cases are intended to serve as examples that illustrate how the EKMA might be applied and to show that much of the information that is required for even so simple

an approach as the EKMA is still not available. Although the examples use what are believed to be reasonable numbers, they do not provide an adequate basis for control strategy development. Control strategies deserve more than "educated estimates" for their formulation. The most important missing elements are: (1) ozone measurements free of local interferences, (2) reliable measurements of the imported ozone contributions, (3) good NMHC and NO_x measurements during episode conditions and, (4) reliable forecasts of the control measures that will be applied elsewhere and their effectiveness in reducing the imported ozone contributions.

How the reductions in emissions might be achieved is beyond the scope of this report. The approaches usually considered include mobile source controls (directly through exhaust gas limitations or indirectly through reduced traffic), vapor recovery systems at gas stations, controls of vapor loss at bulk storage and processing plants, and so forth. To give some idea of the magnitude of NMHC reductions available, the Federal motor vehicle emission control program should reduce the total emissions in Vermont by 41 percent by 1987 according to Wishinski (1977). Control of oxides of nitrogen is much more difficult with presently available technology.

It should be noted that in the rural areas the NMHC/NO_x ratios are apt to be very high, and any increases in NO_x emissions could lead to rather large increases in ozone concentrations, as indicated by Figures 8 and 42. Thus, while controls may not be necessary, the most serious consideration should be given to the possible consequences of any introduction of new sources of oxides of nitrogen.

C. *Final Remarks and Recommendations*

When the research reported here was begun, the use of EKMA was not foreseen. It certainly was not anticipated when the data that have been used in this report were collected. Had it been, there could have been more emphasis on measurements that would define the relative contributions of those urban areas within the three northern New England states.

Now that the data requirements for control strategy formulation are better defined, future data collections can be made to suit the recognized needs. For example, the existence now of monitoring stations at both Portland and Cape Elizabeth should aid future data analysts in defining the local contributions of Portland. According to Tudor (1978), much more extensive monitorng of ozone will be conducted throughout Maine during the summer of 1978. This will help define conditions in those areas that are farthest from the major sources. It may help define the extent to which transport of ozone to and from Canada is a problem. A good network in Maine would also provide the coverage necessary to describe the effects of weather fronts and nighttime transport in better detail.

In our opinion the most pressing remaining needs are for data that could be used to quantify the over-water transport mechanism and for better descriptions of the sea breeze effects. These would require another airborne monitoring program, but it would not have to be nearly as large as that conducted in Southern New England during 1975, if the effort focused on an investigation of coastal transport and sea breeze effects.

The existing data have provided the basis for reasonable explanations of many of the observed phenomena. They have also provided hypotheses than can be tested with the data soon to be collected. Finally, they have helped to define where shortcomings are likely to remain.

APPENDIX A

MONITORING SITE CHARACTERISTICS

APPENDIX A

MONITORING SITE CHARACTERISTICS

Introduction

The descriptions of monitoring stations that follow were provided by Norman Beloin of EPA Region I. During the course of these studies, we attempted to rank the various stations according to the degree to which they were influenced by urban emissions. Four criteria were used: population, nearness to the downtown area, nearness to a street, and traffic on the nearest street. The rankings for the individual criteria and the overall rankings are summarized in Table A-1.

Table A-1

RANKING OF LOCAL URBAN INFLUENCE AT MONITORING SITES

	Population	Distance from Road	Traffic	Distance from Town Center	Overall
Portland	2	3	1	2	1
Burlington	4	1	2½	4	2
Portsmouth	5	4	5	2	3
Manchester	1	5½	5	5	4
Nashua	3	2	7	8	5
Berlin	7	5½	2½	6½	6
Keene	6	7	5	6½	7
White River Jct.	8	8	8	2	8
Deerfield	9	9	9	9	9
Fraconia Notch	10	10	10	10	10

Station Descriptions

BURLINGTON, VERMONT. The probe is located 15 feet above the ground at a mobile trailer site within 20 feet of a two lane surface street. The traffic is two-way, with moderate to heavy travel. The site is within a downtown area and 60 to 70 feet away from a stop light at which there is substantial queuing during commuter hours.

MANCHESTER, NEW HAMPSHIRE. The probe is located on the roof of a fire station, (three stories high), which is one block from the central business district. The nearest road is 80 to 90 feet away and is a two way street with moderate traffic.

NASHUA, NEW HAMPSHIRE. The probe is located on the roof of a four-story building that is located one and a half blocks away from the central business district. The surrounding area is mostly residential, with some commerical buildings and only light traffic.

PORTLAND, MAINE. The probe is located on a 4-story building 10 feet from the main street of the central business district (Congress Street). This is very much of a "downtown site" with a heavily travelled roadway network. Furthermore, Portland is a coastal city located on a hill and this site is located on the top of the hill.

BERLIN, N.H. The monitoring is done from a trailer on the bank of the river at the bottom of a narrow valley, 250 to 500 m deep. The largest pulp mill in New England is located about 800m up the valley. A paper mill is down the valley from this site.

PORTSMOUTH, N.H. The site is being relocated. It has been in a trailer in the center of town, about 4 to 5 m high and about 15 m from the road.

DEERFIELD, N.H. This site was used for special studies in 1976. The site is rural, located behind a school building with a parking lot.

KEENE, N.H. This is a downtown site about a block from the center of town. It is on the roof of a two-story building. It is about 25m back from a road with moderate traffic.

FRACONIA NOTCH (CANNON MOUNTAIN -- GRAFTON COUNTY), VT. This site is about 1200 m above sea level in the summit house at the top of the Gondola lift. It is a rural mountain site. It has suffered moisture problems.

WHITE RIVER JUNCTION, VT. this is an acceptable site whose center-city location may cause a reduction in measured ozone concentrations.

APPENDIX B

SUMMARY OF HOURS WHEN NATIONAL AMBIENT AIR QUALITY STANDARD FOR OZONE WAS VIOLATED

APPENDIX B

SUMMARY OF HOURS WHEN NATIONAL

AMBIENT AIR QUALITY STANDARD FOR OZONE WAS VIOLATED

This appendix lists all the hours when ozone concentrations above 80 ppb were observed at one of the Northern New England stations. the observed concentrations are given in ppb. The data were obtained from the SAROAD tapes provided by EPA Region 1. No data were available for dates subsquent to 30 June 1977 or before 1 January 1976. As noted in the text of the report, there were substantial gaps in the data sets from several of the stations. It should be noted that 1977 New Hampshire data were reported using Eastern Standard Time. Other states used Eastern Daylight Time (EDT), as did New Hampshire in 1976.

Time (EDT)

Site	Date	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Portland, Maine	11 May 76													82											
	14 May 76														82										
	29 May 76															88	86								
	10 June 76												92	100	112	118	170	146	114	92					
	16 June 76												104	122	98										
	29 June 76															82	102	94	94						
	6 July 76														100	108	124	102	84	84		84	84	84	
	7 July 76											96	108	136	120	84									
	11 July 76											106	120	122	108	108	108	108	102	86					
	16 July 76																		92	84					
	4 August 76																	88	90						
	5 August 76												94	120	140	94	88	82							
	6 August 76			82																					
	12 August 76													86	82	161	120	110	115	103	98	85			
	26 August 76															104	108	115	114	100	100	92	98	84	
	27 August 76			94	86	82																			
	1 September 76													92	92	100	90	90	92						
	19 September 76																	94	92						

Time*

Site	Date	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Manchester, N.H.	15 June 76																88	90	87		85	104	110	108	101
	16 June 76	92	81										82	92	88		84	111	89						
	20 June 76																126	88							
	28 June 76																82								
	30 June 76															140	125		150	112		100			
	7 July 76									92	95	95													
	8 July 76				88																				
	11 July 76									91	95	100		118	112	107	102	90							
	23 July 76														88	86									
	5 August 76																		84						
	12 August 76																								88
	22 August 76													82	95										
	26 August 76																	101							
	11 March 77												90	98	99	89									
	12 March 77												89	107	116	109									
	30 March 77																83	88							
	12 April 77												82		81										
	13 April 77											86		85											
	21 April 77												81	83	81										
	22 April 77											81	81												
	1 May 77												83	82		88	90	81		100	92	95	96	91	89
	2 May 77	84																							
	17 May 77											88	88	87	100	100	102	101	90		102	101	92	93	108
	18 May 77	92	100	94	100																				
	21 May 77											85	110	130	127	140	140	105							

*1976 dates use Eastern Daylight Time (EDT); 1977 dates use Eastern Standard Time (EST).

Time (EST)

Site	Date	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Manchester, N.H. (cont.)	22 May 1977										86		95	90	90	93	108	96			82	82	95	90	
	24 May 1977											92	91	86											
	28 May 1977													86											
	14 June 1977															98	112	94							
	17 June 1977																	98	120	120	96	82			
	24 June 1977											88				87	91	112	121	101	85				
	25 June 1977												81												
	28 June 1977											81		85	88	95	140	116	119	103	89	90	97	88	

Time (EDT)

Site	Date	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Nashua, N.H.	19 Apr 76											85	120	85						100	100	90			
	14 May 76										81	85	95	100	100	110	110	100	90	90					
	10 June 76																						85		
	11 June 76										85	85	85	85	85										
	15 June 76											85	95	100	110	125	120	120	120	110	120	125	125	130	120
	16 June 76	100								100	100	100	105	100	95		90	100							
	18 June 76												95	105	110	125	110	90							
	28 June 76														90	105	105	105	110	125	125	120	90		
	29 June 76														95	95	90	90							
	6 July 76																85						85		
	7 July 76	90	85							90	125		105	85											
	16 July 76												90	95	95	95	90								
	20 July 76													85	85		85	100	110	135	135	120	90		
	23 July 76														85										
	27 July 76													85		90	90	105	105	105	110	105	100	95	
	5 August 76															85	90	95	85	100	90	90	85	85	
	12 August 76																115	95				125	145	125	105
	13 August 76	85														90	90								
	22 August 76															95									
	26 August 76															85	110	115							
	1 September 76														95	100	95	90	90						

Time (EST)

Site	Date	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Nashua, N.H.	12 March 77												100	105	100	90									
	12 April 77									95	100	100	100	100	95	90	85								
	13 April 77											85	95	90	85										
	25 April 77														85										
	1 May 77																		100	95	100	100	100	95	90
	2 May 77	85																							
	4 May 77													90											
	5 May 77										85	95	100	105	100	100	100	90							
	6 May 77										85	115	115	110	105	95	90	100	125	115	90				
	16 May 77															85									
	17 May 77								85	95	105	105	110	110	110	120	130	125	120	120	115	115	110	110	115
	18 May 77	125	120	120				90	90	95	95														
	20 May 77													85											
	24 May 77											105	110	105	100	100	105	95	85						
	25 May 77											85	85												
	26 May 77												85	90	90	90	90	90	95		85	85		90	110
	27 May 77	100		105	100	95	95	100	120	130	135	140	140	150	140	140	135	135	130	130	145	120	105	90	
	28 May 77									90	130	170	170	170	185	160	150	145	100						
	30 May 77														85	85	85								
	31 May 77																	85							
	17 June 77																	90	95						
	24 June 77															85		90	100	90					
	28 June 77													85	85	95	100	95				85	85		

Time*

Site	Date	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Portsmouth, N.H.	29 March 77														85										
	30 March 77												85	90	90		85	85							
	12 April 77											85	85												
	13 April 77													85	90										
	21 April 77												85	95	100	100	95								
	22 April 77											100	100	100	100	95	85								
	1 May 77													85	90	95	100	95	85					90	85
	17 May 77											95	100	105	110	115	120	115	105	85			95	90	90
	18 May 77	90	85																						
	20 May 77													90	110	110	100	85							
	22 May 77										95	110	120	125	125	115	120	140	120	115	100	85	85		85
	23 May 77										100	110	105	105	105	100	105	110	110						
	24 May 77										105	120	135	135	150	200	230	230	180	165	110	85			
	25 May 77									85	105	110	110	110	105	100	95	90							
	31 May 77												105	110	105										
	10 June 77			90	90	85						85													
	14 June 77										90	95	95												
	18 June 77										85		85	85	85	115	140	110							
	24 June 77											85	85	150	130										
	30 June 77								85	90	98	95	95	100	100	95	95	90							
Berlin, N.H.	24 May 77											82													
Deerfield, N.H.	11 July 76														90	82									
	20 July 76																					91	81		
	22 August 76															90									

*1976 dates use EDT; 1977 dates use EST

Time*

Site	Date	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Grafton County (Fraconia Notch) N.H.	29 May 76						82	94	96	90	84	90	95	96	92	91	86	87	85	81				81	
	6 June 76															85	85								
	8 June 76									82															
	10 June 76														83	81	85	85	85						
	15 June 76																	85	85	85					
	22 August 76																		83						
Keene, N.H.	22 May 77														82	83	81								
	17 June 77																		107	102	101	98	84		
	25 June 77	81	85	94	102	95	84	84		82		85	102	121	109	93									
	28 June 77								89	87	90	87	84	92	103	127	133	135	154	147	118	105	120	110	93
White River Jct., Vt.	12 April 77										90	94	94		88	86	84								
	13 April 77											87	100	102	102	92	83	81							
	20 April 77												85	87	89	89									
	21 April 77												95	105	95	94	92	88							
	22 April 77												91												
	5 May 77													85			81								
	6 May 77														81	87	89	82	84	83					
	17 May 77											102	119	129	128	125	123	99	87						
	18 May 77										88	87	88	89	89										
	21 May 77													93	97	98	101	104	102	96	108	128	118	108	94
	22 May 77	82										84	94	96	83		81	87	86	83					
	23 May 77													83											
	24 May 77											82	93	99	98	96									
	17 June 77																			91	100	108	108	87	81

*Keene, N.H. data are EST; others use EDT.

Time (EDT)

Site	Date	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Burlington, Vt.	29 May 76											86	99	97	89	85							90		
	10 June 76																						82	88	92
	11 June 76	90	87	86	86	84																			
	13 June 76															83	82					81			
	14 June 76																82	83	88	87	85				
	15 June 76																82	89	95	98	100	98	87	83	83
	16 June 76	85	85	86	87	87								82	83	89	90	87							
	19 June 76	84	100	82																					
	7 July 76													95	98	89									
	11 July 76												83	86	86	85									
	14 September 76	-												84	87	90						83	88	88	94
	15 September 76	89																							
	21 April 77														100	102	104	102	96	98	102	95	94	88	94
	22 April 77	85	81																						
	1 May 77																	84	86	88	83			88	98
	2 May 77	96	91	83																					
	17 May 77											85	92	94	82					88	96	88	93	102	104
	18 May 77	98	102	95	85											"									
	21 May 77													82	84	82						90			90
	22 May 77	110	113	104	91	84					85	91	100	103	104	104	101	104	108	94		94	94		
	23 May 77		84																	84				82	
	24 May 77																84								
	17 June 77															85	90	92	88	87	94	102	83		
	26 June 77																			82					
	28 June 77										85	92	97	95	98	100	105	112	110	107	112	119	108	89	105
	29 June 77	101	92	91	83																				

REFERENCES

Chameides, W.L., and D.H. Stedman, 1976: Ozone Formation from NO_x in "Clean Air" Env. Sci. and Tech., 10, 150-154.

Cleveland, W. S., et al., 1974: Sunday and Workday Variations in Photochemical Air Pollutants in New Jersey and New York. Science, 186, 1037-1038.

Cleveland, W. S., B. Kleiner, J. E. McRae and J. L. Warner, 1976: Photochemical Air Pollution: Transport from the New York City Area into Connecticut and Massachusetts. Science, 191, 179-181.

Crutzen, P. J., 1971: Ozone Production Rates in an Oxygen-Hydrogen-Nitrogen Oxide Atmosphere. J. Geophys. Res., 76, 7311-7327.

Danielsen, E. F. and 1964: Report on Project Springfield. Report DASA-1517, Defense Atomic Support Agency, Washington, D.C.

Danielsen, E. F. and V. A. Mohnen, 1976: Project Dust Storm Report: Ozone Measurements and Meteorological Analyses of Tropopause Folding. Proc. the Non-urban Tropospheric Composition Symposium, Hollywood, Florida, November 10-12, pp 17.1-17.13.

Federal Register, 1971: Volume 36, Part 50--National Primary and Secondary Ambient Air Quality Standards, pp. 22384-22397.

Fishman, J. and D. J. Crutzen, 1976: A Numerical Investigation of Tropospheric Photochemistry Using a One-Dimensional Model. Proc. The Non-Urban Tropospheric Composition Symposium, Hollywood, Florida, November 10-12, pp. 23.1-23.15.

Heffter, J. L. and A. D. Taylor, 1975: A Regional-Continental Scale Transport, Diffusion and Deposition Model, Part I: Trajectory Model. NOAA Tech. Memo ERL ARL-50, pp. 1-16.

Holzworth, G. C., 1972: Mixing Heights, Wind Speeds, and Potential for Urban Air Pollution through the Contiguous United States, Pub No. AP-101, EPA Office of Air Programs.

Lamb, R., 1976: A Case of Study of Stratospheric Ozone Affecting Ground-Level Oxidant Concentrations (unpublished manuscript; SAI, San Rafael, California)

Londergan, R. J. and L. G. Polgar, 1975: Measurement Program for Ambient 03, NO_x and NMHC at Portland, Maine--Summer, 1974. Report, EPA Contract 68-02-1382, Task Order 2, The Research Corp. of New England, Wethersfield, Connecticut.

Ludwig, F. L., E. Reiter, E. Shelar, and W. B. Johnson, 1977a: The Relation of Oxidant Levels to Precursor Emissions and Meteorological Features, Part 1: Analysis of Findings. EPA Report No. 450/3-77-022a, Final Report, EPA Contract 68-02-2089, SRI International, Menlo Park, CA.

Ludwig, F. L., P. B. Simmon, R. L. Mancuso, and J. H. S. Kealoha, 1977b: The Relation of Oxidant Levels to Precursor Emissions and Meteorological Features, Part 3:

Appendices. EPA Report No. 450/3-77-022, Final Report, Contract 68-02-2084. SRI International, Menlo Park, CA.

Ludwig, F. L., and E. Shelar, 1977: Ozone in the Northeastern United States. EPA Report No. 901/9-76-007, Final Report, EPA Contract 68-02-2352. Stanford Research Institute, Menlo Park, CA.

Ludwig, F. L. and E. Shelar, 1978a: Site Selection for the Monitoring of Photochemical Air Pollutants, EPA Report No. 450/3-78-013, Final Report, EPA Contract 68-02-2028, SRI International, Menlo Park, CA.

Ludwig, F. L. and E. Shelar, 1978b: Effects of Weather Fronts on Ozone Transport, in "Air Quality and Atmospheric Ozone". edited by A. L. Morris and R.C. Barras, American Soc. Test. and Materials Doc. No. STP 653, 389-406.

Lyons, W. A. and H. S. Cole, 1976: Photochemical Oxidant Transport: Mesoscale Lake Breeze and Synoptic-Scale Aspects, J. Appl. Meteorol., 15, 733-743.

Meyer, E. L., W. P. Freas, J. E. Summerhays, and P. L. Youngblood, 1976: The Use of Trajectory Analysis for Determining Empirical Relationships Among Ambient Ozone Levels and Meteorological and Emissions Variables. Proc. of Int. Conf. on Photochem. Oxidant Pollution and its Control, Raleigh, NC, September 12-17, 1976.

Mohnen, V. A., 1977: International Conference on Oxidants 1976--Analysis of Evidence and Viewpoints. Part III. The Issue of Stratospheric Ozone Intrusion. EPA Report No. 600/3-77-115, pp. 7-66.

National Oceanic and Atmospheric Administration, 1976, 1977: Daily Weather Map Series.

OAQPS, 1977a: Effectiveness of Hydrocarbon Emission Control Programs as a Function of Geographic Location, Unpublished Report. U.S. EPA Office of Air Quality Planning and Standards.

OAQPS, 1977. Uses, Limitations and Technical Basis of Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors. EPA Report No. 450/2-77-021a. U.S. EPA Office of Air Quality Planning and Standards.

OAQPS, 1978: Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors. Supporting Documentation, EPA Report No. 450/2-77-021b, U.S. EPA Office of Air Qualty Planning and Standards.

Reiter, E. R., 1975: Stratospheric-Tropospheric Exchange Processes. Rev of Geophys. and Space Phys., 13, 459-474.

Reiter, E., 1977: International Conference on Oxidants, 1976--Analysis of Evidence and Viewpoints, Part III, The Issue of Stratospheric Ozone Intrusion. EPA Report No. 600/3-77-115.

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

Singh, H. B., F. L. Ludwig and W. B. Johnson, 1977: Ozone in Clean Remote Atmospheres, Final Report for Coordinating Research Council, Stanford Research Institute, Menlo Park, CA.

Singh, H. B., F. L. Ludwig and W. B. Johnson, 1978: Tropospheric Ozone: Concentrations and Variations in Clean Remote Atmospheres. Atmos. Environ., in press.

Spicer, C. W., J. L. Gemma and P. R. Sticksel, 1977: Ozone: Transport Considerations and Predictive Models for Southern New England. Draft Report, EPA Contract 68-02-2241, Battelle, Columbus, Ohio,

Tudor, D., 1978: Status Report on Maine's Air Quality. Presented at Workshop on Air Pollution in Maine; Augusta, Maine June 1, 1978. Sponsored by Maine League of Women Voters.

Weinstock, B., and T. Y. Chang, 1976: Methane and Nonurban Ozone. Presented at the APCA meeting in Portland, Oregon, June 29.

Went, F. W., 1960: Organic Matter in the Atmosphere and its Possible Relation to Petroleum Formations. Proc. National Academy of Science, Vol. 46, 211.

Wishinski, P., 1977: Report Establishing a Data Base for Photochemical Oxidants (0_3) and Preliminary Analysis of Data. State of Vermont Air Program.

Zeller, K., R. B. Evans, C. K. Fitzsimmons, and G. W. Siple, 1977: Mesoscale Analysis of Ozone Measurements in the Boston Environs. J. Geophys. Res., 82, 5879-5888.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

Readily available meteorological and air quality data were analyzed to determine the extent to which ozone concentrations in the Northern New England states of Maine, New Hampshire, and Vermont are influenced by causes external to those states. It is concluded on the basis of air trajectory and wind analysis that ozone generated from precursor emissions to the southwest or west is transported into the southern parts of Vermont, New Hampshire, and Maine. In the northern parts of New Hampshire and Vermont, violations of the ozone standard are more frequently associated with air that has come from the areas around Lakes Erie and Ontario. Although the Northern New England states are influenced by ozone transported from elsewhere, some control measures might still be required within the area even if the external sources were controlled and concentrations entering the region were reduced to levels near the tropospheric background.

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