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Northeast Corridor Regional Modeling Project

Ozone and Precursor Transport in New York City and Boston During The 1980 Field Program

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NORTHEAST CORRIDOR REGIONAL MODELING PROJECT

Ozone and Precursor Transport in New York City and Boston During the 1980 Field Program

by

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CONTENTS

FIGURES

TABLES

ACKNOWLEDGEMENTS

This report was prepared by EPA from the report "Analysis and Interpretation of Ambient Measurements in New York and Boston from the 1980 Northeast Corridor Regional Modeling Project" submitted by Battelle's Columbus and Pacific Northwest Laboratories under Contract 68-03-2958. Additional analyses conducted by EPA to supplement the original submittal have been included in this report. The assistance of various EPA staff in reviewing the report, and the final typing by Zada Nelson, Carol Bradsher and Carole Mask, are greatly appreciated.

EXECUTIVE SUMMARY

This report describes the results of a 1-1/2 year study to analyze portions of the data base obtained during the 1980 Northeast Corridor Regional Modeling Project (NECRMP). The NECRMP data base was obtained primarily for the application of urban and regional scale photochemical models to the Northeast, including the major Corridor cities: Washington, DC; Baltimore; Philadelphia; New York City; and Boston. Although the NECRMP data base provides data primarily for model application, the extensive data base is also suitable for interpreting the meteorological and chemical processes which influence O_3 formation and transport.

The 1980 NECRMP data collection program involved extensive air quality and meteorology measurements at the surface and aloft. Surface based measurements available from selected sites in the Northeast Corridor include O_3, NO/NO_x, NMOC, wind speed, wind direction, temperature, solar radiation, and hydrocarbon species. In addition, upper air meteorological measurements were obtained by rawinsonde soundings, sodar, and pilot balloon observations. Instrumented aircraft were operated in the New York and Boston areas to obtain measurements aloft of O_3, NO/NO_x, b_{scat}, temperature, and relative humidity. The protocol for aircraft monitoring flights required vertical profiling of the atmosphere upwind of the city in the mornings and mapping of the urban O_3 plumes in the afternoon. Surface based measurements were made throughout the summer, while aircraft monitoring was limited to the period from mid-July through mid-August.

The present study focuses on 20 days of the 1980 NECRMP data base. These case study days were divided between New York City (12 days) and Boston (8 days) and were selected to provide for analyses of the following three meteorological situations:

- moderate wind speeds with wind directions conducive to interurban transport between Corridor cities;
- moderate wind speeds with wind directions from sectors for which interurban transport is unlikely; and
- weak flows and stagnating or near stagnating conditions.

The interpretive effort was designed to address a number of questions and issues relating to O_3 formation and transport in the Northeast Corridor. These include:

1. Do concentrations of O_3 and precursors tranported into New York City and Boston differ during along-Corridor and non-Corridor transport regimes?
2. What is the diurnal variation of O_3 and precursors in air parcels leading to the maximum ozone concentration in the urban plume?
3. What is the average transport time and distance to maximum O_3 in the urban plume? What is the typical downwind distance to maximum NO_2 in the urban plume?
4. What is the typical downwind distance to where NO_x in the urban plume becomes indistinguishable from background concentrations?
5. Can mid-morning surface O_3 measurements be used to estimate early morning upwind O_3 aloft?
6. Can mid-day aircraft measurements of O_3 be used to estimate surface concentrations for areas between measurement sites?
7. Does O_3 aloft, initially isolated from the effects of surface emissions and scavenging, change substantially prior to the dissipation of the nocturnal inversion when pollutants aloft are mixed to the surface?
8. Is there evidence in the data of O_3 plumes from medium size cities such as Bridgeport, New Haven, and Hartford, CT or Providence, RI?

A summary of the study and the important findings pertinent to these questions are presented below.

1. Do concentrations of O_3 and precursors transported into New York City and Boston differ during along-Corridor and non-Corridor transport regimes?

The transport of O_3 and precursors into New York City and Boston was examined for the surface layer and for layers aloft. Although the analysis was to have categorized each day according to one of three flow regimes, intepretation of trajectories and pollutant measurements indicates that more than one type of flow regime occurred on about half of the case study days. On such days the direction of transport was rather complex and varied with time and altitude. Typically, overnight transport in the surface layer was along the Corridor, whereas aloft, above the nocturnal inversion, transport was from areas west of the Corridor.

Measurements at the surface and aloft were partitioned and averaged by flow regime with the following results. For New York City, morning precursor concentrations transported into the urban area at the surface were twice as high with along-Corridor transport than when transport was from outside the Corridor. Aloft, precursor concentrations, particularly NMOC, were also much higher when transport was along the Corridor. The analysis indicates that high morning precursor concentrations transported into the New York area with along-Corridor flow were attributable to overnight emissions in the Philadelphia area. During mid-afternoon the impact of the Philadelphia O_3 plume was typically observed at one or more monitoring sites on the upwind (southwest) fringe of New York City.

In Boston, there was little difference in surface precursor concentrations during along-Corridor versus non-Corridor transport regimes. However, the concentration of NMOC aloft during along-Corridor transport was triple the magnitude of aloft concentrations when transport was from outside the Corridor. Average O_3 aloft transported into Boston during the morning was also higher with along-Corridor flow (100 ppb versus 76 ppb). The impact of the New York City O_3 plume on portions of the Boston area was observed during the evening across the upwind (southwest) fringe of Boston on days when transport was along the Corridor.

2. What is the temporal pattern of O_3 and precursors in the air parcel containing the maximum ozone concentration in the urban plume?

Mesoscale trajectories and surface measurements were used to determine the temporal pattern of O_3, NO, NO_2, and NMOC in the air parcel which contained the maximum O_3 observed within the urban plume on each study day. In New York City, the concentration of O_3 decreased as the air parcel traveled from upwind rural and suburban locations into the urban area in the morning, then increased rapidly later in the morning as the air parcel departed the city and the rate of photochemical reactions increased. In almost every case, the maximum O_3 concentration in the plume occurred between 1300 and 1500 EST. (In general, after 1500 EST, UV intensity decreases, and the rate of dilution overcomes the rate of O_3 production such that the air parcel O_3 concentration also begins to decrease.) The concentrations of NO, NO_2, and NMOC generally increased as the air parcel approached the city in the morning. After leaving the city, the nitrogen oxide concentration fell, most likely due to dilution and chemical conversion to HNO_3, PAN, and particulate nitrate.

Unfortunately, there were insufficient NMOC sites to judge the temporal pattern downwind beyond the urban area. Hourly concentrations of O_3, NO, NO_2, and NMOC are provided for ten of the case study days in Section 4.1.2. (Analyses pertaining to the temporal pattern of O_3 and precursors in the Boston plume were very limited since the plume was transported offshore on all but one case study day).

3. What is the average transport time and distance to maximum O_3 in the urban plume? What is the typical downwind distance to maximum NO_2 in the urban plume?

Surface measurements of O_3, NO/NO_2, and NMOC were examined in conjunction with mesoscale trajectories to determine the maximum pollutant concentrations formed in air parcels crossing the urban centers of New York City and Boston during the morning when precursor emissions are greatest. For New York City, the results indicate that the highest O_3 concentrations were associated with air parcels crossing the city at approximately 0800 EST. On the average, air parcels crossing the city at 0600 EST yielded maximum O_3 of 152 ppb at 1300 EST, parcels crossing at 0800 EST generated an O_3 maximum of 219 ppb at 1400 EST, and those crossing at 1000 EST showed a maximum O_3 concentration of 211 ppb occurring at 1500 EST. (Only one day was analyzed for Boston since the urban plume was transported offshore on the other case study days.)

The data base was analyzed to determine the distance and travel time from the center of both New York City and Boston to the location of the peak O_3 concentration in the urban plume. For New York City, the average downwind distance to maximum O_3 measured at the surface was 93 km, with an average transport time of just over 5 hours. The average distance and travel time to peak O_3 aloft was 110 km and 6.5 hours, respectively. In the Boston area, aircraft data provided the most useful information relative to this question

since the urban plume was transported over the ocean on all but one case study day. The aircraft data indicate that the average distance to the O_3 maximum aloft was 81 km, with a range of 61 to 107 km. The average transport time to peak O_3 was 4 hours.

The analysis indicates that maximum surface concentrations of NO and NO_2 are found within or shortly downwind of the urban center. For most cases studied, the highest concentrations of NO and NO_2 were associated with the air parcels crossing the city at 0800 EST. Aloft, the distance to maximum NO_2 downwind during mid-day ranged from 23 to 48 km in New York City and 34 to 110 km in Boston. Estimated transport time to maximum NO_2 was 1 to 3 hours for both urban areas.

4. What is the typical downwind distance to where NO_x in the urban plume becomes indistinguishable from background concentrations?

For three days in Boston and two days in New York City, the distance from the urban area to the point where the urban plume NO_x concentration aloft became indistinguishable from the air mass background NO_x concentrations were estimated. This distance ranged from 85 to 165 km. The estimated travel time to background NO_x ranged from 5.5 to 12 hours.

5. Can mid-morning surface O_3 measurements be used to estimate early morning upwind O_3 aloft?

Measurements of O_3 at the surface and aloft, and sodar-derived mixing heights were analyzed to determine whether mid-morning surface O_3 measurements during the period when the nocturnal inversion is dissipating can yield information on O_3 concentrations aloft prior to inversion break-up. The analysis indicates that average surface O_3 concentrations upwind (3-hour average centered around the time of inversion dissipation) do represent early morning O_3 concentrations aloft on many study days. However, there were also a number

of cases when such an assumption would lead to significant underestimation (or overestimation) of the early morning levels aloft. In these cases, it appears that O_3 aloft transported into the city had actually increased (or decreased) between the time of the early morning aircraft measurements and the time of inversion dissipation. This may have been due to reactions among O_3 and transported precursors or to spatial variations in O_3 aloft transported across the urban area. Thus, using surface data for estimating early morning concentrations aloft should be done with caution, particularly in situations where urban areas are in fairly close proximity or high concentrations of transported precursors are expected.

6. Can mid-day aircraft measurements of O_3 be used to estimate surface concentrations between measurement sites?

Afternoon surface O_3 measurements were compared to mid-boundary layer ($\sim$ 800m) aircraft measurements made in the vicinity of surface monitoring stations. The results indicate that, in locations where the atmosphere appears to be well mixed, the surface and aircraft data agree within 10 to 15 ppb. However, large differences were observed between surface and aircraft data in most comparisons near the edge of urban plumes, and in conjunction with the internal boundary layer produced by sea breeze wind flows. These differences were the result of strong vertical and horizontal concentration gradients associated with such features. It is concluded that aircraft data should be used with caution for estimating surface concentrations in areas subject to sea breeze circulations or other mesoscale meteorological flows, and in areas of large gradients at the edge of urban plumes. However, mid-day aircraft data can provide a reasonable estimate of area-wide surface O_3 concentrations away from the preceding complex situations.

7. Does O_3 aloft, initially isolated from the effects of surface emissions and scavenging, change substantially prior to the dissipation of the nocturnal inversion when pollutants aloft are mixed to the surface?

Temporal variations in O_3 concentrations aloft, in air parcels isolated from boundary layer influences (e.g., emissions, scavenging, etc.) were investigated using aircraft pollutant and meteorological measurements. The results indicate that, in most of the cases examined, O_3 concentrations aloft were fairly stable (within ± 5 ppb) between early morning (0500/0600 EST) and mid-morning (1000/1100 EST) measurements within an air parcel. However, O_3 production was evident in those air parcels containing comparatively high air mass NO_x concentrations and probably other O_3 precursors, as indicated by the aerosol content and estimated track of the air parcel relative to upwind urban areas.

8. Is there evidence in the data of O_3 plumes from medium size cities such as Bridgeport, New Haven, and Hartford, CT or Providence, RI?

The surface and aircraft data were examined in an attempt to identify O_3 plumes from other smaller Corridor cities, such as Bridgeport, New Haven, and Hartford, CT, and Providence, RI. In general, it was difficult to define O_3 plumes from such cities due to the relatively high air mass O_3 levels, the complexity of airflow patterns, and the frequent incursions of urban plumes from the major Corridor cities. Also, since the monitoring program was not directed toward investigating these cities, comparatively little data were available for this type of analysis. However, on two occasions, there was evidence of the Providence O_3 plume from the Boston area aircraft data. In the clearest example, O_3 in the Providence plume was 20 to 30 ppb higher than the air mass O_3 concentration upwind of both cities.

SECTION 1

INTRODUCTION

Investigations since the mid-1970s have demonstrated that ozone (O_3) is a pervasive contaminant of air over the northeastern United States.[1-5] Studies have shown that ambient concentrations exceeding the 0.12 ppm (120 ppb) National Ambient Air Quality Standard (NAAQS) level for O_3 are observed in many parts of the Northeast, and concentrations up to 300 ppb have been observed downwind of cities in this highly urbanized corridor. Also, ozone concentrations exceeding the NAAQS are frequently observed over a large portion of the region, and field study results have shown that both interurban and long distance transport of O_3 and its precursors should be considered in designing control strategies.

In order to devise effective and equitable strategies for reducing the concentration of O_3 in the Northeast, the Environmental Protection Agency (EPA) has been conducting a major long-term program with both field measurement and modeling components. The field measurement programs associated with the Northeast Corridor Regional Modeling Project (NECRMP) were designed to develop a data base for regional/urban model verification/application, as well as to improve understanding of the chemical and meteorological phenomena resulting in high regional O_3 concentrations. The major urban data collection program of NECRMP was conducted during the summer of 1980. The purpose of that effort was to obtain a data base for the application of the Airshed[6] urban photochemical model to Northeast Corridor cities, including Washington, DC, Baltimore, New York City, and Boston. Regional monitoring studies were also conducted during

1980 as part of NECRMP. Although NECRMP was designed primarily to provide data for model application, the extensive data base is also suitable for interpretation of meteorological and chemical processes which influence O_3 formation and transport.

This report describes the results of a program designed to address a number of questions and issues relating to O_3 formation and transport in the New York City to Boston portion of the Northeast Corridor. These questions/ issues include:

1. Do concentrations of O_3 and precursors transported into New York City and Boston differ during along-Corridor and non-Corridor transport regimes?

2. What is the diurnal variation of O_3 and precursors in air parcels leading to the maximum O_3 concentration in the urban plume?

3. What is the average transport time and distance to maximum O_3 in the urban plume? What is the typical downwind distance to maximum NO_2 in the urban plume?

4. What is the typical downwind distance to where NO_x in the urban plume becomes indistinguishable from background concentrations?

5. Can mid-morning surface O_3 measurements be used to estimate early morning upwind O_3 aloft?

6. Can mid-day aircraft measurements of O_3 be used to estimate surface concentrations in areas between measurement sites?

7. Does O_3 aloft, initially isolated from the effects of surface emissions and scavenging, change substantially prior to the dissipation of the nocturnal inversion when pollutants aloft are mixed to the surface?

8. Is there evidence in the data of O_3 plumes from medium size cities such as Bridgeport, New Haven, and Hartford, CT or Providence, RI?

SECTION 2

PROGRAM SCOPE

The 1980 NECRMP urban measurement programs in New York and Boston included extensive air quality and meteorological measurements at the surface and aloft. Surface-based measurements available from sites in the Northeast Corridor include O_3, nitric oxide/nitrogen dioxide/oxides of nitrogen ($NO/NO_2/NO_x$), nonmethane organic compounds (NMOC), wind speed, wind direction, temperature, solar radiation, and hydrocarbon species. In addition, 30-minute average mixing heights were derived from monostatic sodar, and temperature and/or winds above the surface were obtained by rawinsonde soundings and pilot balloon observations (pibals). Measurements made aloft by instrumented aircraft in the New York and Boston areas include O_3, NO/NO_x, light scattering coefficient (b_{scat}), temperature, and relative humidity. Surface-based measurements were made throughout the summer, while aircraft monitoring was limited to the period from mid-July through mid-August. A map of the study area is shown in Figure 1 along with the location of surface monitoring sites included in this analysis.

The present study was designed to analyze 20 days of the 1980 NECRMP data base. These case study days were selected to provide for analysis of the following three meteorological situations:

(1) moderate wind speeds with wind directions conducive to interurban transport between Corridor cities;

(2) moderate wind speeds with wind direction from sectors for which interurban transport is unlikely; and

(3) weak flows and stagnation or near stagnation conditions.

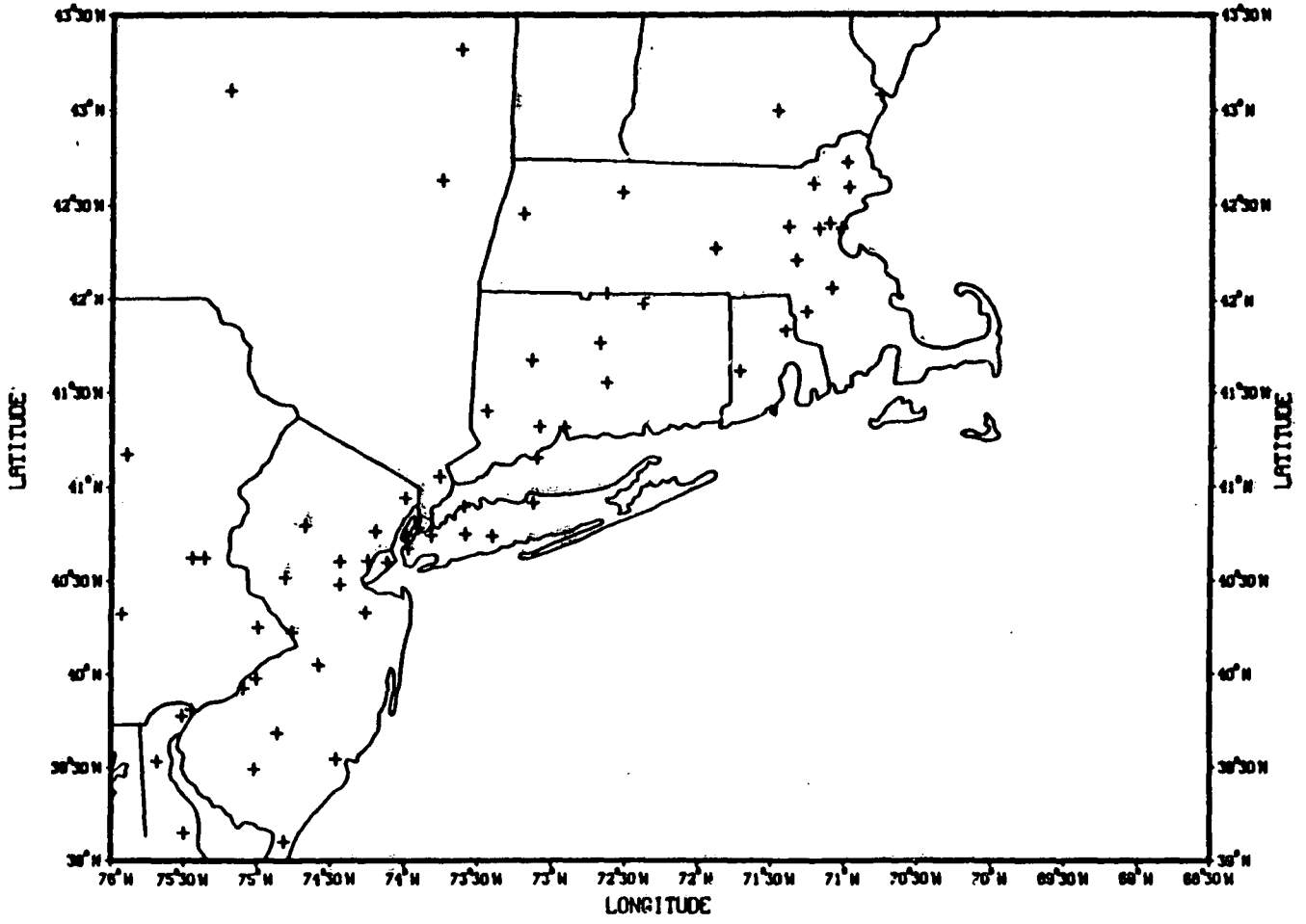

Figure 1. The study region and the location of monitoring stations included in this study.

The scope and organization of this report are linked directly to the Statement of Work for Contract 68-03-2958, "Analysis and Interpretation of Ambient Measurements in New York and Boston from the 1980 Northeast Corridor Regional Modeling Project," conducted by Battelle's Columbus and Pacific Northwest Laboratories.

2.1 Selection of Case Study Days

At the start of the program, 20 days were selected for analysis out of the approximately 3 months of the 1980 NECRMP field program. These study days were divided between New York City and Boston, and it was desired to select days on which the airflow fit certain criteria. These criteria were listed earlier and basically describe days on which interurban transport is (1) likely, (2) unlikely, or (3) days of near stagnation. The data base for the entire NECRMP study was screened to identify candidate study days meeting the airflow criteria. Hourly surface wind speed, wind direction, and O_3 concentration data were used, together with pertinent aircraft and upper air wind measurements, to provide a preliminary classification of the candidate days into the three airflow categories. From the list of candidate days meeting the airflow criteria, final study days were selected using additional criteria including the availability of aircraft data, completeness of the surface data set, level of pollutant concentrations, etc. The New York area was the focus of 12 days and Boston was the focus of 8 days. The study days are listed in Table 1.

Table 1. Case Study Days Selected for Analysis

New York Area

June 24	Tue.	July 21*	Mon.	August 6*	Wed.
June 25	Wed.	July 22*	Tue.	August 8*	Fri.
July 16*	Wed.	July 24*	Thu.	August 26	Tue.
July 18*	Fri.	July 31*	Thu.	August 28	Thu.

Boston Area

June 24	Tue.	August 1*	Fri.
July 15*	Tue.	August 5*	Tue.
July 16*	Wed.	August 6*	Wed.
July 17*	Thu.	August 8*	Fri.

*Aircraft data available.

SECTION 3

DEFINITION OF AIR FLOW ON STUDY DAYS

3.1 Synoptic-Scale Trajectories

Synoptic-scale trajectories were used in this analysis to determine the probable upwind source areas of O_3 transported into New York City and Boston, and the general downwind direction of urban plume transport. Forward and backward trajectories were prepared for five cities in the Northeast Corridor: Boston; New York City; Philadelphia; Baltimore; and Washington, DC.

These trajectories were computed using the ATAD trajectory model developed by Heffter et al.[7] The trajectory calculations were made from 6-hour and 12-hour National Weather Service (NWS) upper air wind data averaged through the layer from 500 to 1500m. Trajectories were computed in 3-hour increments, backward and forward for 48 hours, from all five cities. In addition, forward trajectories using wind data through the layer from 200 to 1000m were computed for New York City, Philadelphia, and Washington, DC. The start/end time for the forward/backward synoptic trajectories was 0700 EST.

3.2 Mesoscale Trajectories

Mesoscale forward and backward trajectories were computed for points within the New York City and Boston urban areas. Used in the computation were 6-hour and 12-hour NWS upper air wind data, along with data from

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*A revised version of this model is now available from Heffter.[8] However, because the trajectories in this analysis were computed for a fixed layer and were not used to specify space/timem source/receptor relationships it is unlikely that using trajectories computed with the revised model would alter the conclusions of the study.

the special rawinsonde soundings and pibal observations obtained as part of the 1980 NECRMP ambient monitoring program. The pibal observations were hourly, whereas the rawinsonde soundings were conducted at various times between 0500-1500 EST. The winds were averaged over the appropriate layers and interpolated hourly between measurement times to fill in missing data. These data, in turn, were used to produce gridded wind fields covering the area of interest. The interpolation and trajectory computation techniques are based on procedures described by McNaughton, et al.[9]

Mesoscale trajectories were computed starting at 0600, 0800, and 1000 EST from each of three locations in the New York urban area and two locations in Boston. Forward trajectories were computed hourly for 10 hours and the backward trajectories for 5 hours for these locations and start times.

The back trajectories ending at 0600, 0800, and 1000 EST were used to represent the flow above the nocturnal surface layer, upwind of the urban area. The layer chosen for these trajectories was 250m to 1000m. The lower limit of 250m was selected to avoid the effects of wind shear near the ground during the early morning hours. For the forward trajectories, wind measurements were averaged within the layer from 50m to the top of the boundary layer. An estimate of the depth of the boundary layer on an hourly basis for each day was developed from the available temperature soundings. These estimates represent the overland, convectively induced mixing heights in the area of interest. For cases of a morning, surface based stable layer, a mixing height of 250m was used.

SECTION 4

INTERPRETATION OF POLLUTANT AND METEOROLOGICAL MEASUREMENTS

4.1 Pollutant Concentrations in the Urban Plume

Several characteristics of the New York City and Boston urban plumes were examined as part of this task. These include the travel time and downwind distance to peak concentrations of O_3, NO, and NO_2 and the travel time and downwind distance to where NO_x in the urban plume diminished to the estimated air mass background concentration. In addition, the data were examined for evidence of O_3 plumes from several medium size cities between New York City and Boston.

4.1.1 Maximum Pollutant Concentrations from Morning Emissions

The objective of this task was to identify the maximum concentrations of O_3, NO, and NO_2 associated with air parcels crossing the urbanized portions of New York City and Boston during the morning when precursor emissions are at a maximum. The analysis procedure included the use of mesoscale trajectories to estimate the downwind track of air parcels initially over the city at each of three morning time periods: 0600; 0800; and 1000 EST. Isopleth maps of O_3 concentrations for various times during the day were used to confirm the path of the urban plume. Time histories of O_3 concentration within each of the three air parcels were estimated from surface monitoring data in the vicinity of the trajectory track using the procedure shown in Figure 2. In this figure, the intersection of the heavy lines with the O_3 diurnal profiles represents the O_3 concentration in the air parcel that had crossed the city at 0600, 0800, or 1000 EST as noted.

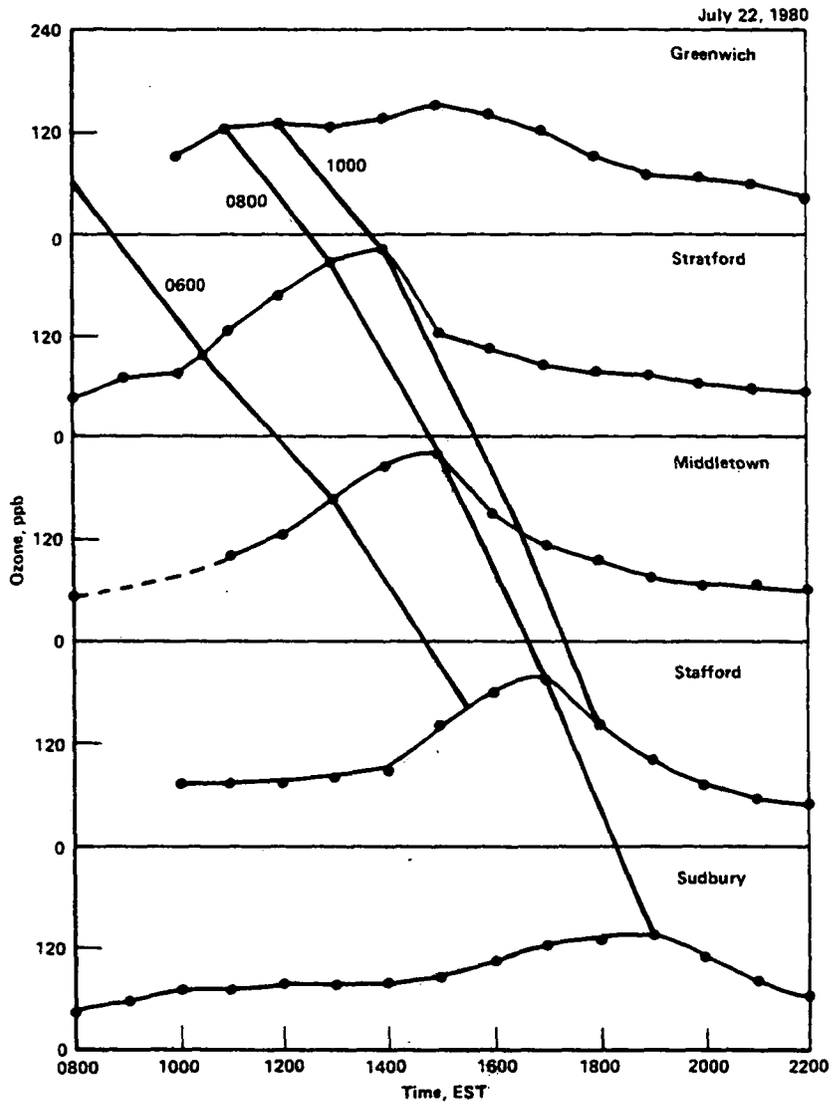

Figure 2. Time lines of air parcels crossing the New York City urban area at 0600, 0800, and 1000 EST and diurnal ozone concentrations at sites in the vicinity of parcel tracks on July 22, 1980.

As indicated in the example in Figure 2, the air parcels containing morning emissions from New York City on July 22, 1980 were transported northeastward across Connecticut during the day and approached the Boston area by evening. The maximum measured O_3 concentrations were 169 ppb, 227 ppb, and 226 ppb along the 0600, 0800, and 1000 EST trajectories, respectively. All of these values occurred in Connecticut.

Of the 20 case study days, 10 were excluded from this task because the wind flow on those days transported the urban plume out over the Atlantic Ocean away from surface monitoring sites. The maximum O_3 concentration estimated from morning emissions on the remaining 10 case study days are provided in Table 2. Also shown in this table are the maximum concentrations of NO and NO_2, along with times and locations of these maxima. Unfortunately, the coverage available for NO and NO_2 is not nearly as comprehensive as for O_3, due to the much smaller number of stations which monitored these pollutants. In any case, it is clear from Table 2 that both NO and NO_2 typically reach their peak values within or shortly downwind of the urban area. Even though NO_2 is being produced in the air parcels during the first hours of transport, the rate of production is apparently overwhelmed by the rate of dilution. In most cases, the highest concentrations of NO and NO_2 are associated with the 0800 EST air parcel.

Inspection of the O_3 data in Table 2 reveals that the highest O_3 maxima are associated with air parcels departing the city at 0800 EST. The concentrations of O_3 precursors in air leaving the city at 0600 EST are not as high initially and are no doubt reduced even more than the later parcels by dilution prior to the onset of extensive photochemical reaction. The

Table 2. Maximum Pollutant Concentrations Generated in Air Parcels Crossing New York City and Boston at Selected Times

Date	Time of Air Parcel Departure, EST	Max. O_3 ppb	Time EST	Location	Max. NO ppb	Time EST	Location	Max. NO_2 ppb	Time EST	Location
6-24-80	0600	140	1500	Kent Co., RI	051	0600	Manhattan, NY	070	0600	Manhattan, NY
	0800	220	1530	Middletown, CT	037	0800	Manhattan, NY	117	0800	Manhattan, NY
	1000	230	1430	Stratford, CT	005	1000	Manhattan, NY	068	1000	Manhattan, NY
6-25-80	0600	160	1400	Middletown, CT	038	0600	Manhattan, NY	059	0600	Manhattan, NY
	0800	275	1300	Stratford, CT	--	--	--	--	--	--
	1000	180	1430	Stratford, CT	005	1000	Manhattan, NY	063	1000	Manhattan, NY
7-15-80	0600	160	1600	Georgetown, MA	061	0600	Manhattan, NY	073	0600	Manhattan, NY
	0800	190	1500	Worcester, MA	025	0800	Manhattan, NY	076	0800	Manhattan, NY
	1000	145	1700	Worcester, MA	009	1000	Manhattan, NY	059	1000	Manhattan, NY
7-16-80	0600	180	1200	Middletown, MA	068	0700	Queens, NY	079	0700	Queens, NY
	0800	230	1400	Middletown, MA	006	0800	Manhattan, NY	095	1000	Glen Cove, NY
	1000	290	1400	New Haven, CT	011	1000	Manhattan, NY	074	1000	Manhattan, NY
7-21-80	0600	175	1600	Kent Co., RI	040	0700	Queens, NY	100	0700	Queens, NY
	0800	240	1300	Stony Brook, NY	016	0800	Manhattan, NY	095	0800	Manhattan, NY
	1000	303	1500	Stratford, CT	011	1000	Manhattan, NY	078	1000	Manhattan, NY
7-22-80	0600	170	1300	Middletown, CT	030	0600	Manhattan, NY	082	0600	Manhattan, NY
	0800	220	1500	Middletown, CT	026	0800	Manhattan, NY	062	0800	Manhattan, NY
	1000	225	1400	Stratford, CT	004	1100	Queens, NY	069	1100	Queens, NY
8-1-80	0600	122	1200	Litchfield, CT	054	0600	Dumont, NJ	108	0600	Manhattan, NY
(New York Source)	0800	140	1300	Litchfield, CT	010	0800	Manhattan, NY	080	0800	Manhattan, NY
	1000	125	1500	Litchfield, CT	002	1000	Manhattan, NY	040	1000	Manhattan, NY
8-1-80	0600	110	1100	Portsmouth, NH	040	0600	East Boston, MA	100	0600	East Boston, MA
(Boston Source)	0800	145	1600	Gardiner, ME	005	0900	Danvers, MA	115	0800	East Boston, MA
	1000	125	1130	Sagamore Hill, MA	005	1000	East Boston, MA	035	1000	East Boston, MA
8-6-80	0600	125	1100	New Haven, CT	057	0600	Manhattan, NY	067	0600	Manhattan, NY
	0800	250	1300	Stratford, CT	039	0800	Manhattan, NY	085	0800	Manhattan, NY
	1000	190	1500	Stratford, CT	002	1100	Queens, NY	076	1100	Queens, NY
8-8-80	0600	140	1330	Kent Co., RI	065	0700	Queens, NY	097	0700	Queens, NY
	0800	205	1500	Kent Co., RI	039	0900	Queens, NY	105	0900	Queens, NY
	1000	215	1630	Kent Co., RI	003	1100	Queens, NY	075	1100	Queens, NY

reduced photochemical activity is due to the relatively low solar intensity at this early hour.

On the average, air parcels leaving New York City at 0600 EST yielded maximum O_3 of 152 ppb at 1300 EST, parcels departing at 0800 EST generated an O_3 maximum of 219 ppb at 1400 EST, and those leaving at 1000 EST showed a maximum O_3 concentration of 211 ppb, with the peak occurring at 1500 EST. The times of the maxima reflect the combined effects of reaction time, solar intensity, and dilution. Reduced solar intensity and continuing dilution in the late afternoon eventually overcome the effects of increased reaction time, so that the highest concentrations on a given day usually occur before 1600 EST.

On five of the 10 days analyzed (June 24 and 25, July 16 and 21, and August 6), the trajectories indicate a westerly flow in the New York area although the track of the surface O_3 plume was to the northeast across Connecticut into eastern Massachusetts, consistent with the low level wind flow. Examinations of surface and upper air wind observations in the area indicate that this situation may reflect the combined effects of the onshore sea breeze circulation near the coast, coupled with topographic channeling of the low level wind flow northward within the broad valley from New Haven to Hartford, CT. As a result of this flow regime, the New York City plume on these days was transported across Long Island Sound (and adjacent land areas of coastal Connecticut and Long Island), then northeastward into central Connecticut. Because the sea breeze flow is most pronounced within 400 to 500m of the surface it was apparently smoothed out in the mesoscale trajectory computations which included winds through a much deeper layer.

It should be noted that the diurnal profiles for sites along the urban plume track provide strong prima facie evidence for O_3 transport in urban plumes. In nearly every case, the peak O_3 concentration for each site occurs at progressively later times along the plume track. In several cases, the O_3 maxima for the sites farthest downwind of the urban center occurred in the late afternoon or evening after the sunlight intensity, the driving force behind O_3 production, had dropped off considerably, supporting the contention that transport is the prime contributor to the observed peak O_3 concentration.

4.1.2 Diurnal Pollutant Concentration Profiles in Urban Air Parcels

This task was aimed at determining the time history of O_3, NO, NO_2, and NMOC concentrations in air parcels which lead to the observed maximum O_3 in the urban plume. In order to determine the time history of the pollutant concentrations, the path of the air parcel leading to the maximum concentration was determined from trajectories and isopleth maps as in the previous task. With this information, monitoring stations in the vicinity of the air parcel track were selected to provide the pollutant concentrations within the plume at times prior to and after the observed maximum concentration.

As in the previous section, days were excluded from the analysis if the urban plume was carried out over the ocean or over a land area with few monitoring stations. This criterion resulted in the exclusion of most Boston study days and some of the New York cases. However, data from two additional days (July 15 and August 1) were included for the New York area to supplement the analysis. The summary of O_3 concentration time histories is given in Table 3. Data on NO, NO_2, and NMOC are also tabulated, but these data are limited by the fact that few of the monitoring sites for these pollutants are outside the urban area.

Table 3. Time, Position, and Concentration Profiles for Air Parcels Generating Ozone Maxima

Date	Time, EST	Location	O_3, ppb	NO, ppb	NO_2, ppb	NMHC, ppbC
6/24/80	0600	New Brunswick, NJ	006	029	058	630
	0700/0800	Linden/Bayonne, NJ	041	015	043	955
	0800/0900	New York City, NY	031	027	100	1890
	1130	Greenwich, CT	149	004	022	----
	1400	Stratford, CT	253	---	---	----
	1500	New Haven, CT	170	---	---	----
	1700	Middletown, CT	159	---	---	----
6/25/80	0500	New Brunswick, NJ	019	---	---	----
	0600/0700	Linden, NJ	033	012	040	420
	0700/0800	New York City, NY	027	032	072	1620
	1030	Greenwich, CT	119	005	022	----
	1300	Stratford, CT	276	---	---	----
	1600	Middletown, CT	165	---	---	----
7/15/80	0500	New Brunswick, NJ	017	010	032	120
	0600/0700	Linden/Bayonne, NJ	012	032	057	233
	0700/0800	New York City, NY	019	041	076	930
	0900	Glen Cove, NY	078	003	045	---
	1100	Stratford, CT	135	---	---	---
	1300	Middletown, CT	162	---	---	---
	1500	Worcester, MA	193	---	---	---
	1730	Georgetown, MA	142	---	---	---
7/16/80	0600	New Brunswick, NJ	004	041	056	690
	0800/0900	Linden/Bayonne, NJ	018	020	054	293
	0900/1000	New York City, NY	033	025	080	1125
	1100	Queens, NY	103	006	055	----
	1330	Stratford, CT	254	---	---	----
	1400	New Haven, CT	291	---	---	----
	1600	Middletown, CT	262	---	---	----
	1800	Kent Co., RI	112	---	---	----
7/21/80	0700	New Brunswick, NJ	032	013	031	300
	0800/0900	Linden/Bayonne, NJ	042	004	032	360
	0900/1000	New York City, NY	084	008	064	1620
	1100	Queens, NY	133	002	046	----
	1200	Glen Cove, NY	202	005	015	----
	1400	Stony Brook, NY	240	---	---	----
	1500	Stratford, CT	303	---	---	----
	1700	Middletown, CT	262	---	---	----
	1800	Kent County, RI	200	---	---	----

a Measurement below detectable limit of the instrument.

Table 3. Time, Position, and Concentration Profiles for Air Parcels Generating Ozone Maxima (continued)

Date	Time, EST	Location	O_3, ppb	NO, ppb	NO_2, ppb	NMHC, ppbC
7/22/80	0600	New Brunswick, NJ	005	032	043	630
	0600/0700	Linden/Bayonne, NJ	009	020	042	300
	0700/0800	New York City, NY	025	034	071	1298
	1000	Glen Cove, NY	064	008	061	----
	1100	Greenwich, CT	127	003	017	----
	1300	Stratford, CT	213	---	---	----
	1400	New Haven, CT	227	---	---	----
	1500	Middletown, CT	220	---	---	----
	1700	Stafford, CT	197	---	---	----
	1900	Sudbury, MA	134	---	---	----
8/1/80	0600	New Brunswick, NJ	004	036	050	810
(NEW YORK)	0600/0700	Linden/Bayonne, NJ	018	027	055	495
	0700/0800	New York City, NY	032	017	074	810
	0900	Dumont, NJ	049	013	075	----
	1000	White Plains, NY	062	---	---	----
	1200	Danbury, CT	120	---	---	----
	1300	Litchfield, CT	140	---	---	----
	1500	Agawam, MA	075	---	---	----
8/1/80	0700	Medfield, MA	058	007	006	----
(BOSTON)	0800	Boston, MA	073	LD[a]	115	0830
	1000	Sagamore Hill, MA	103	LD	023	----
	1200	Portsmouth, NH	127	---	---	----
	1400	Cape Elizabeth, ME	133	---	---	----
	1600	Gardiner, ME	143	---	---	----
	2000	Penobscot Co., ME	082	---	---	----
8/6/80	0500	New Brunswick, NJ	009	017	020	300
	0600/0700	Linden/Bayonne, NJ	017	014	038	975
	0700/0800	New York City, NY	021	030	077	2168
	0900	Queens College, NY	052	006	053	----
	1000	Glen Cove, NY	085	LD	051	----
	1300	Stratford, CT	249	---	---	----
	1400	New Haven, CT	168	---	---	----
8/8/80	0600	New Brunswick, NJ	003	038	037	----
	0700/0800	Linden/Bayonne, NJ	034	008	045	578
	0800/0900	New York City, NY	031	032	092	2068
	1030	Glen Cove, NY	084	---	---	----
	1200	Stony Brook, NY	143	---	---	----
	1300	Stratford, CT	246	---	---	----
	1600	Kent Co., RI	222	---	---	----
	1830	Easton, MA	095	---	---	----

[a]Measurement below detectable limit of the instrument.

In New York City, data from five urban sites were used to characterize O_3 and precursor concentrations in the air parcel as it passed within the urban area. Two-hour average concentrations were computed for two urban sites in New Jersey (Linden and Bayonne) and for three urban sites in New York (Manhattan, Astoria, and Brooklyn). These average values were used to partially account for a decrease in the reliability of the trajectories for estimating transport within the core of the urbanized area.

The data for July 22, 1980 were plotted as an example profile from the data given in Table 3. The time history plot is shown in Figure 3. This figure shows the concentrations of NO, NO_2, and O_3 in the air parcel which generated the highest surface concentration of O_3 on this day. The time of day is given along the bottom of the graph and the air parcel position along the top. This particular parcel crossed northern New Jersey before 0800 EST and the concentrations of NO and NO_2 increased as the air approached the metropolitan New York area. The NO reached a peak at 0800 EST directly over New York City, whereas NO_2 appears to have peaked at 0900 EST on the downwind fringe of the city. The level of NO_x dropped off rapidly after the parcel left the urban source area. In contrast, the O_3 concentration decreased slightly as the air parcel approached New York City in the morning but increased rapidly after leaving the city. The rapid rise in O_3 concentration occurred at the time the sodar data indicate a rapid rise in the boundary layer. Morning vertical O_3 profiles upwind of New York City indicate that the O_3 concentration above the surface based inversion averaged 56 ppb (650 to 1500m). Hence, photochemical reactions, rather than mixing of O_3 stored aloft overnight, must have been responsible for the majority of the O_3 generated on this day, although mixing

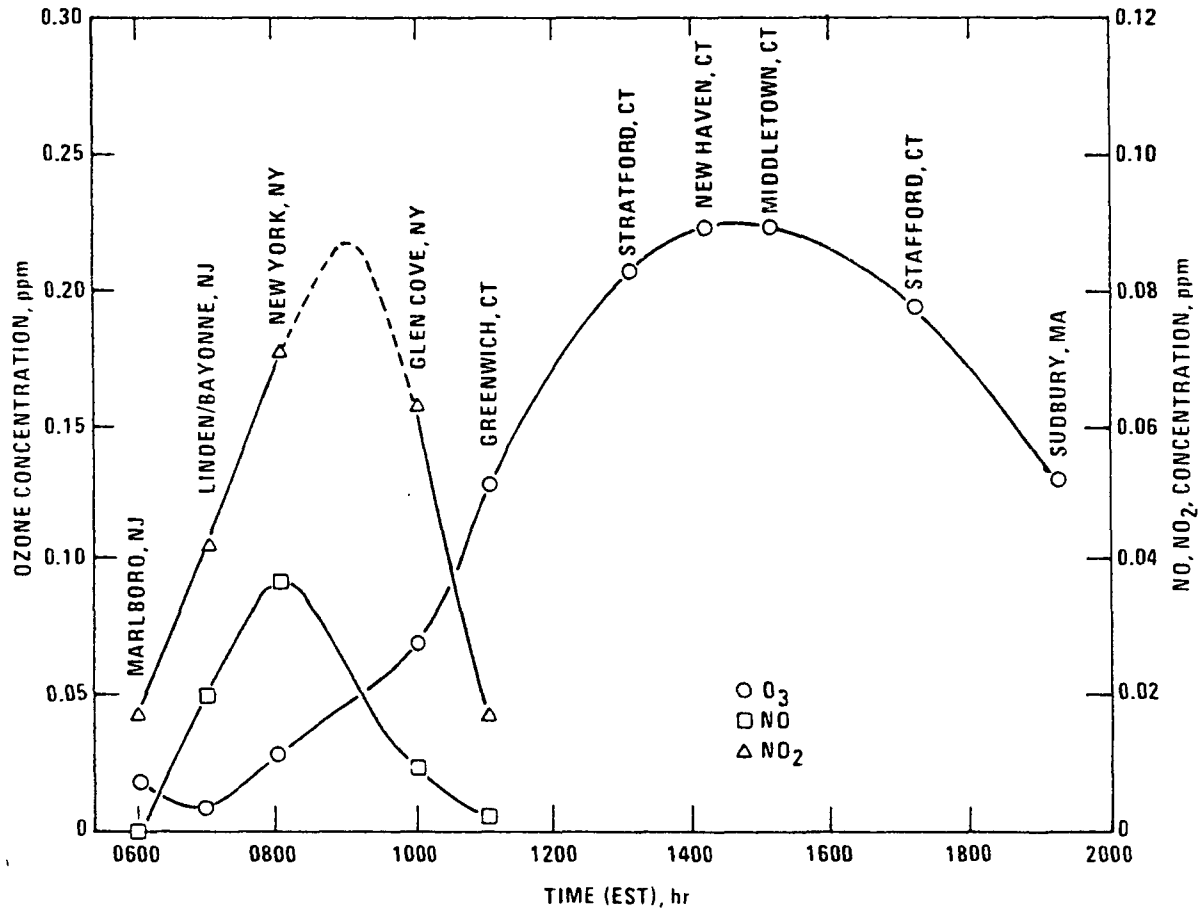

Figure 3. Time history of air parcel leading to maximum ozone on July 22, 1980.

of O_3 from aloft undoubtedly accelerated the photochemical reactions by increasing the rate of NO oxidation to NO_2. On this day the maximum measured O_3 concentration occurred at 1400 EST at New Haven, CT. As the air parcel continued to move downwind throughout the afternoon and into the evening, the O_3 concentration decreased. Nevertheless, this same parcel was apparently responsible for the maximum O_3 measured at Stafford, CT (1700 EST), and at Sudbury, MA (1900 EST).

In general, the data in Table 3 indicate that the concentration of O_3 decreased as the air parcel moved into the urban area in the morning, due to processes such as chemical scavenging reactions. Ozone then increased rapidly later in the morning as the air parcel left the city and the rate of photochemical reactions increased. In almost every case, the maximum O_3 concentration in the urban plume occurred between 1300 and 1500 EST. After 1500 EST, UV intensity generally decreases, and the rate of dilution overcomes the rate of O_3 production such that the air parcel O_3 concentration begins to decline slowly.

The concentrations of NO, NO_2, and NMOC generally increased as the air approached the city in the morning. After leaving the city, the NO_x fell, likely due to dilution and probable chemical conversion to HNO_3, PAN, and particulate nitrate. Unfortunately, there are insufficient NMOC data to evaluate the time history of hydrocarbon concentrations.

4.1.3 Transport Time and Distance to Peak O_3 and NO_2

To determine the distance and travel time from New York City and Boston to the peak O_3 and NO_2 concentrations measured in the urban plumes of

each city, information on the location of maximum O_3 prepared in the previous section was enhanced with O_3 and NO_2 meaurements aloft.

The times and distances to the maximum O_3 concentrations at the surface and aloft in the New York area are shown in Table 4. Because of the complex flow during stagnation conditions on August 26, 1980, the transport time was not computed. The surface data for three other days (July 18 and 31 and August 28) were also excluded from the analysis, because the northwest flow aloft on these days transported the plume out over the Atlantic Ocean. Recirculation of portions of the plume onshore in sea breeze flows later in the day made it difficult to estimate travel distance and transport time. The actual surface maximum may have occurred over the ocean.

Among the remaining days, the average downwind distance to maximum O_3 at the surface was 96 km, with a mean transport time of just over 5 hours. On the other hand, the average distance to peak O_3 aloft was 110 km, with a mean transport time of 6.5 hours. (Direct comparisons between the surface and aloft values are somewhat misleading, because different days were involved and day-to-day meteorology varied considerably.) In general, for the cases studied, one can characterize the transport time to O_3 maxima in the New York City plume as 5 to 7 hours, with a typical downwind distance of 100 km.

For Boston, two difficulties were encountered in defining the maximum O_3 concentration within the urban plume. First, transport from upwind sources was frequently responsible for the highest surface O_3 concentration in the Boston area. Second, on ocean transport days, when the plume was carried offshore, the highest concentration in the plume may not have been measured, even at coastal monitoring sites during sea breeze flows. These situations

Table 4. Times and Distances from New York City to Maximum Ozone

Date	Site	O_3 Max., ppb (Ground)	Time, EST	Distance km[c]	Transport Time, hours	O_3 Max. ppb, Aloft[d]	Time, EST	Distance, km[c]	Direction from City	Transport Time, hours	Location
6/24/80	Stratford, CT	253	1400	90	5-6	---	----	---	---	---	----
6/25/80	Stratford, CT	276	1300	90	5-6	---	----	---	---	---	----
7/16/80	New Haven, CT	291	1400	110	4-5	215[e]	1530	103	NE	4	near Derby, CT
7/18/80	a	---	----	---	---	249	1420	51	SE	6	south of Long Island
7/21/80	Stratford, CT	303	1500	90	5-6	---	----	---	---	---	----
7/22/80	New Haven, CT	227	1400	110	5-6	223[f]	1355	91	NE	5	near Bridgeport, CT
		---	----	---	---	220	1700	150	NE	7-8	near Middletown, CT
7/24/80	a	---	----	---	---	152[e]	1452	110	S	5-6	near Barnegat, NJ
7/31/80	a	---	----	---	---	269[e]	1627	124	ESE	7	south of Westhampton, LI
8/6/80	Stratford, CT	249	1300	90	5-6	352	1519	126	E	7	north of Riverhead, LI
8/8/80	Stratford, CT	246	1300	90	4-5	242	1322	121	NE	4	over Long Island Sound
8/26/80	Linden, NJ	188	1400	U[g]	---	---	----	---	---	---	----
	New Brunswick, NJ	188	1300	50	---	---	----	---	---	---	----
8/28/80	b	---	----	---	---	---	----	---	---	---	----

[a] Northwest air flow; maximum O_3 over Atlantic Ocean.
[b] Recirculation air flow; maximum O_3 may have occurred over Atlantic Ocean.
[c] Distance from Manhattan, NY.
[d] Measurement at 700-800m MSL unless otherwise noted.
[e] May not be maximum O_3; measurement listed was obtained on furthest downwind traverse of plume.
[f] Measurement at 200m MSL during spiral.
[g] Measurement at urban site.

were considered when interpreting the times and distances to maximum O_3 given in Table 5. For June 24, July 15, 16, 17, and August 6 and 8, the first site listed is upwind, but in fact measured the highest concentration in the Boston area. These values do not reflect the potential for O_3 generation by emissions in Boston. The second site is a coastal location. The O_3 concentrations listed for this site were measured during an onshore flow and thus provide a lower limit estimate of O_3 formed in the Boston plume (higher concentrations may have occurred offshore). On August 1 and 5 transport from upwind urban areas may have had a substantial contribution to maximum O_3 at surface sites. Thus, in the Boston area, aircraft data provide a more appropriate estimate of O_3 formation in the urban plume. The aircraft data in Table 5 show that the downwind distance to maximum O_3 in the Boston plume ranged from 61 to 107 km, with an average distance of 81 km. The mean transport time to peak O_3 was 4 hours.

The times and distances to O_3 maxima in the urban plumes of New York City and Boston are useful pieces of information for the development of control strategies, as well as for investigators who develop and test urban models for these cities. Additional information of particular usefulness to modelers relates to the transport time and distance to peak NO_2. The concentration of nitrogen oxides is especially sensitive to monitor locations, because NO and NO_2 are primary pollutants (i.e., emitted directly to the atmosphere). Nitrogen dioxide is also a secondary pollutant formed in the series of reactions leading to O_3 formation. In and around major urban areas, the peak NO_2 concentration is usually observed near or shortly downwind of the urban center, because surface monitoring stations are strongly influenced by

Table 5. Times and Distances from Boston to Maximum Ozone

Date	Site	O_3 Max., ppb (Ground)	Time, EST	Distance km	Transport Time, hours	O_3 Max. ppb, Aloft[c]	Time, EST	Distance, km	Direction from City	Transport Time, hours	Location
6/24/80	Medfield, MA	154	2100	(a)	(a)	---	----	---	--	---	----
	Cape Elizabeth, ME	097	1500	150	7-8	---	----	---	--	---	----
7/15/80	Worcester, MA	193	1500	(a)	(a)	208	1538	(a)	SW	(a)	near RI border
	Cape Elizabeth, ME	145	1400	150	4-5	170	1400	65	NE	2	over Atlantic Ocean
7/16/80	Easton, MA	127	1500	(a)	(a)	200	1700	(a)	SW	(a)	near RI border
	Cape Elizabeth, ME	127	1400	150	6	197	1542	107	NE	4	over Atlantic Ocean
7/17/80	Easton, MA	150	1700	(a)	(a)	151	1648	(a)	SW	(a)	near RI border
	Cape Elizabeth, ME	143	1700	150	5	133	1554	61	NE	4	over Atlantic Ocean
8/1/80	Georgetown, MA	143	1100	42[b]	2[b]	170[e]	1525	104	NE	6	over Atlantic Ocean
	Gardiner, ME	143	1700	222[b]	11[b]	---	----	---	--	---	----
8/5/80	Medfield, MA	159	1400	(d)	(d)	232	1548	66	NE	5	over Atlantic Ocean
8/6/80	Tewksbury, MA	115	1300	31	2	173	1448	68	NE	4	over Atlantic Ocean
8/8/80	Easton, MA	120	2000	(a)	(a)	156	1449	93	E	3-4	over Atlantic Ocean
	Cape Elizabeth, ME	112	1200	150	5-6	---	----	---	--	---	----

[a] Maximum O_3 occurred upwind from Boston and reflects daytime transport from upwind urban areas.
[b] Overnight transport aloft from upwind sources may have resulted in observed O_3 max.
[c] Measurement at 700-800m MSL unless otherwise noted.
[d] Convergent air flow west of Boston; peak may have contribution from Boston and Providence.
[e] May not be max. O_3; measurement listed was obtained on furthest downwind traverse of plume.

nearby emission sources. This phenomenon was demonstrated earlier in Tables 2 and 3, which show that the maximum surface NO_2 concentration is nearly always found within or on the downwind fringe of the urban area. In order to determine the time and distance required to generate peak NO_2 by chemical reaction, it is more appropriate to employ the aircraft monitoring data. These data are much less sensitive to local surface emissions and, consequently, are more representative of the chemical dynamics of photochemical air pollution. However, these data suffer from a lack of measurements close in to the urban area on several days. Table 6 lists the time, distance and transport time to maximum NO_2 concentration aloft in the afternoon for the New York study area. Maximum NO_2 concentrations aloft ranged from 30 to 87 ppb, and the downwind distance to peak NO_2 aloft ranged from 23 to 48 km. Transport times ranged from 1 to 3 hours. In addition, on July 31 and August 6 relatively high NO_2 concentrations were measured far downwind (33 ppb at 102 km and 68 ppb at 125 km, respectively). In both cases, high levels of O_3 were also present, and it is likely that a portion of the measured NO_2 was actually present in the form of nitric acid and peroxyacetyl nitrate.

The transport times and distances to maximum NO_2 aloft in the Boston area during the afternoon are also shown in Table 6. Peak NO_2 concentrations aloft were in the range from 17 to 49 ppb. The distances to peak NO_2 were in the range of 34 to 110 km, with transport times of 1 to 3 hours.

4.1.4 Downwind Distance to Background NO_x

The purpose of this task was to determine the downwind distance from the city to where the NO_x concentration in the urban plume becomes diluted

Table 6. Times and Distances to Maximum NO_2 Aloft in the New York City and Boston Urbam Plumes

Date	Time, EST	NO_2 Maximum, ppb	Distance from City, km	Transport Time, hours
NEW YORK				
7/18/80	1153	87	32	4.0
7/22/80	1205	76	37	2.0
7/24/80	1211	34	23	1.0
7/31/80	1204	30	40	3.0
8/6/80	1220	76	48	2.0
8/8/80	1218	75	41	1.5
BOSTON				
7/15/80	1339	20	34	1.0
7/16/80	1543	19	110	3.0
7/17/80	1459	17	62	2.0
8/1/80	1500	23	74	3.0
8/5/80	1401	49	36	2.0
8/6/80	1425	23	41	2.0
8/8/80	1335	18	53	1.5

to the point where it approaches the observed air mass background NO_x concentration. Unfortunately, there was insufficient spatial coverage of surface NO_x sites to permit assessment of this distance. However, aircraft data are better suited to this purpose and were used in this task. It is important, for purposes of this task, that fresh emissions of NO_x into the plume downwind of the city be excluded; otherwise, the NO_x concentration could actually increase with downwind distance. This criterion was met by using flights which pass primarily over the ocean, where such emissions are minimal. Two afternoon flights in the New York area and three in Boston met all of the criteria for this task and were used in the analysis. The urban plume NO_x concentrations from aircraft plume traverses were plotted versus downwind distance, and a straight line fitted through the points and extrapolated to the air mass background NO_x concentration observed outside the urban plumes. The results of this analysis are shown in Table 7.

The distance at which plume NO_x reaches the background concentrations (i.e., is indistinguishable from air mass background by the measurement method) is obviously dependent on a number of variables, foremost of which are dilution rate, reaction rates and wind speed. No direct measure of dilution or reaction rate is available, but the afternoon boundary layer transport speeds estimated from the trajectories are included in the table. As expected, the highest transport speeds are associated with the furthest distance to background NO_x. The travel time for NO_x to reach air mass background concentrations ranged from 5.5 to 12 hours, and the estimated travel distance was 85 to 165 km.

4.1.5 Plumes from Medium Size Cities Between New York City and Boston

Clearly defined O_3 plumes have frequently been observed downwind of major centers of population and industry on photochemically active days.

Table 7. Distance at Which NO_x in Plume Approaches Background Concentration

Date	City	Flight Number	Estimated Distance to Background NO_x, km	Transport Speed, $km\text{-}hr^{-1}$
7/18/80	New York	5	85	7.0
7/24/80	New York	15	165	20.0
7/24/80	Boston	18	100	18.2
8/5/80	Boston	31	95	12.5
8/6/80	Boston	32	100	18.0

The contribution of medium size cities to the downwind O_3 burden has been studied infrequently. Several medium size cities are sources of O_3 precursors in the Northeast Corridor, but observation of O_3 plumes from these cities is likely to be difficult, due to the generally high background levels of O_3 in the region. Nevertheless, important insight into O_3 formation and transport processes in the region may be gained by identification of plumes from smaller cities, and comparison of their plume characteristics with those from New York City and Boston.

It was difficult to define plumes from small cities using surface data, because the number and distribution of monitoring stations was nearly always insufficient for this purpose. Aircraft data are most appropriate for this task, since complete upwind and downwind traverses can be made over a relatively short time. Although a considerable number of aircraft flights were conducted during the monitoring program, no flights were designed specifically for small city plume mapping. As a consequence, this analysis is limited to those flights in which small city plumes were observed fortuitously.

The identification of O_3 plumes from smaller cities in the study region focused on Bridgeport, New Haven, Hartford, and Providence. Because no data were collected to address the issue of small city O_3 plumes specfically, all surface and aircraft data collected during NECRMP, were surveyed without limiting the analysis to the 20 study days. From this examination two possible cases of the Providence plume were identified in the data.

Case 1 ---

There is an indication of an O_3 plume from Providence, on July 18, 1980. An examination of surface O_3 concentrations indicates that the O_3 level at the

Kent County site is relatively high compared to surrounding sites. The time series of O_3 concentration and wind direction at Kent County is shown in Table 8. At this site, O_3 reached 95 ppb at 1800 EST, while the concentration remained less than 80 ppb at the surrounding stations (Attleboro, Providence, Hartford, and Middletown). Airflow on July 18 was generally from the northerly quadrant early in the day. However, the wind data in Table 8 indicate a shift to southerly flow after 1600 EST. These data suggest a recirculation of air during the day, such that Providence emissions were first transported offshore then back onshore toward the Kent County site. This indicates that the Providence plume was the primary cause of the elevated O_3 levels at the Kent County site. However, it could be argued that Boston area emissions provided a contribution even though the mesoscale trajectories for July 18 indicate that Boston's plume passed south of Cape Cod during the day.

If we assume that a plume from Providence caused the peak values at Kent County, then the increase in O_3 above the air mass concentration was 30 ppb, as judged by the concentrations at surrounding locations.

Case 2 ---

The second, and perhaps more definitive, case of the Providence plume is evident on July 24, 1980. On the afternoon of this day, the Boston plume was tracked to the south via aircraft. The zig-zag flight track is shown as a solid line on a map of the area in Figure 4. The O_3 concentration along traverses C-D and E-F is also plotted on the map. At the western-most edge of the traverse E-F, there is a peak in O_3 which appears as a shoulder on the major peak representing the Boston urban plume. The Boston plume is also

Table 8. Ozone and Wind Direction at Kent County, RI on July 18, 1980

Time, EST	Ozone, ppb	Wind Direction, Degrees
0800	45	340
0900	50	345
1000	58	350
1100	60	345
1200	60	50
1300	60	315
1400	60	335
1500	62	35
1600	85	100
1700	90	170
1800	95	210

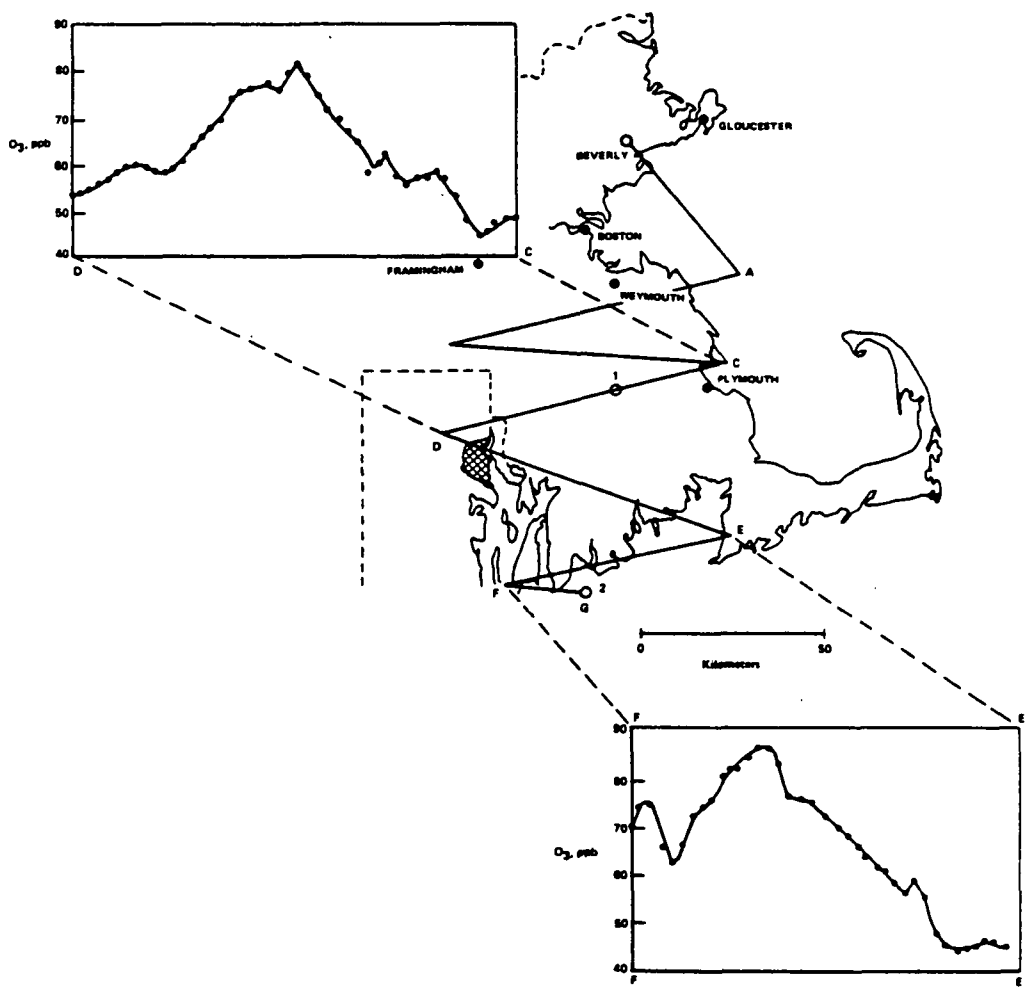

Figure 4. Flight track for Boston on the afternoon of July 24, 1980.

seen centered along traverse C-D but, in this case, there is no shoulder at the western edge. The two traverses show that O_3 concentrations upwind of Providence, and outside the Boston plume, are 55 to 60 ppb, while downwind in the Providence plume O_3 is 75 ppb. These concentrations are replotted in Figure 5 as shaded contours. This diagram shows even more clearly the distinction between the Boston and Providence plumes.

The mesoscale trajectories for 1000 EST on July 24, also shown in Figure 5, indicate the position of the Boston plume at 1400 EST. Comparison of the ozone plume with the trajectories suggests that the Boston plume center line and the trajectory track are in exact agreement. If we assume a parallel trajectory from Providence, the plume from this city would be expected in precisely the location where the shoulder was observed. The estimated O_3 for the Providence plume on July 24 was 15 to 20 ppb above the upwind concentration.

Examination of the NECRMP data did not reveal plumes from Hartford, New Haven, and Bridgeport, CT. The technical problems of identifying such plumes are compounded by the proximity of cities in this area and the complex meteorology introduced by the land/sea interface. The increase in O_3 in the two instances when a Providence plume was identified ranged from 15 to 30 ppb. This range can be compared with the increase in O_3 observed in the plume of a city of slightly smaller size in the Midwest. A study of the Springfield, IL plume on a photochemically active day in the summer of 1977 revealed an increase in O_3 of 30 ppb above the air mass O_3 concentration.[10] Thus, the contribution to the downwind O_3 burden of these two moderate size cities was similar under these particular meteorological conditions.

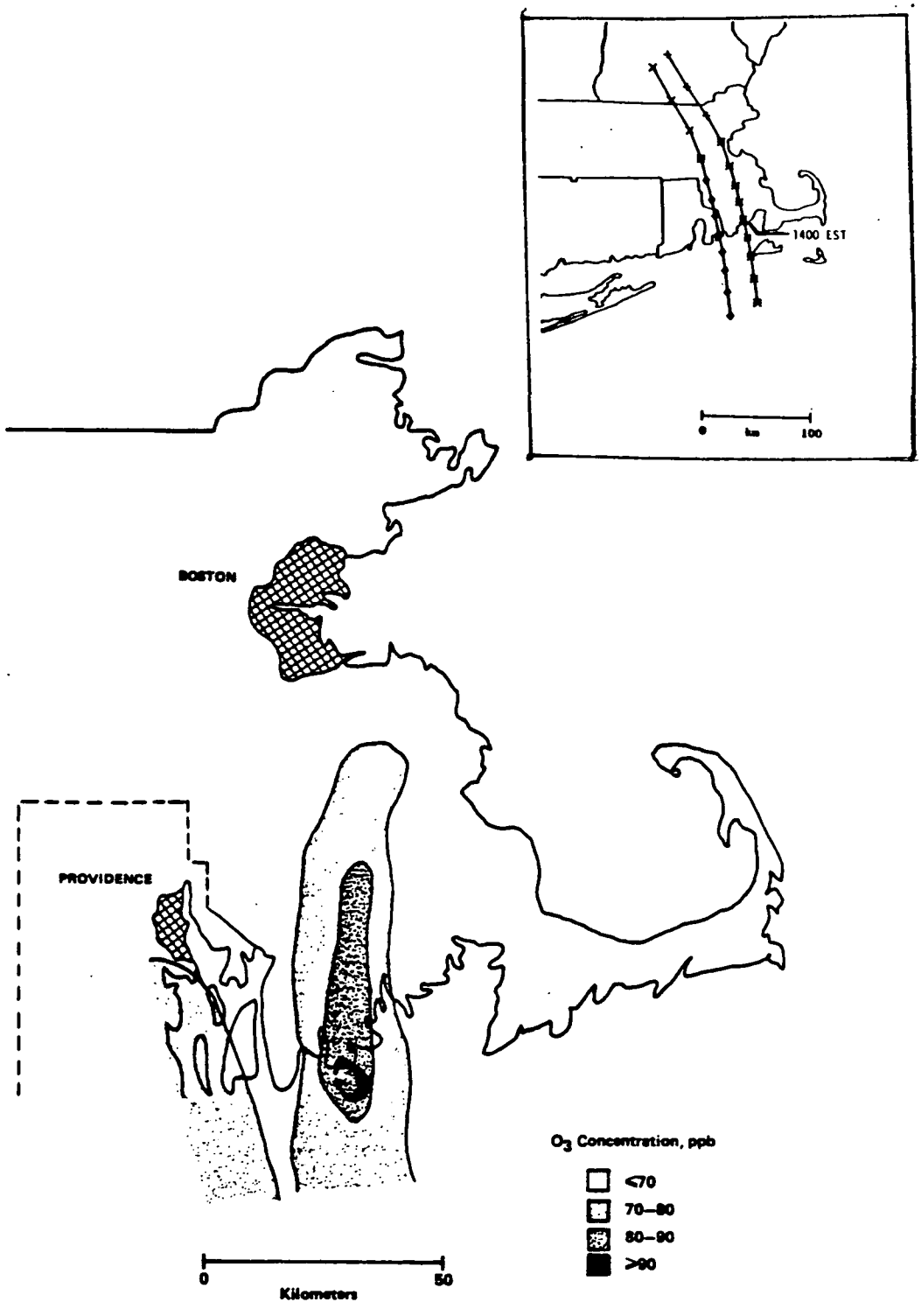

Figure 5. Ozone distribution aloft downwind of Boston on the afternoon of July 24, 1980.

4.2 Pollutant Transport

The objectives of this task were: (1) to quantify the concentrations of O_3 and its precursors transported into and across the New York City and Boston areas on the case study days; and (2) to identify the transport direction on each day and infer the probable source area of O_3 and precursors outside the New York City and Boston urban plumes. These objectives are addressed concurrently in this section.

For both New York City and Boston, surface and aircraft data were used to determine the concentrations of pollutants transported into and across the urban area during each case study day. Ozone measurements downwind of the urban area, but outside the urban plume were also examined to evaluate the homogeneity of air mass O_3 concentrations transported across the region. The probable source area for the observed transported concentrations was inferred by interpretation of synoptic and mesoscale trajectories, and the surface and upper air wind data.

4.2.1 Analysis Procedure

Analysis of pollutant concentrations upwind and downwind but outside the urban plume of New York City was conducted for the case study days: June 24, 25; July 16, 18, 21, 22, 24, 31; and August 6, 8, 26 and 28. In Boston, the analysis was conducted for June 24; July 15, 16, 17; and August 1, 5, 6, and 8. For these days, pollutant concentrations were examined for three specific time periods in order that temporal patterns of pollutant transport might be observed: morning (0600-1000 EST); mid-day (1200-1600 EST); and evening (1800-2200 EST). First, surface winds and the trajectories were interpreted to determine a boundary layer transport wind direction for each time period. The transport wind directions were used to identify surface

sites upwind or downwind outside the urban plume. For these sites, average concentrations of O_3, NO, NO_2, and NMOC were computed for each of the three time periods. Data were not averaged for the entire 4-hour period when large temporal concentration gradients were observed. Rather, an average range was computed for the time period.

The concentrations of O_3, NO, and NO_2 aloft were estimated from aircraft spiral and transect data collected during flights in the vicinity of each city. Upwind/downwind directions were determined from trajectories and upper air winds. The spirals were divided into two or three vertical segments depending on concentration gradients, and layer average concentrations were calculated for each pollutant. Since no afternoon upwind aircraft spirals were made in the New York area, measurements made during horizontal flights over northeastern New Jersey were used for estimating upwind concentrations aloft. The concentrations of O_3, NO, and NO_2 aloft downwind, but outside the urban plume, were obtained by computing a spatial average concentration for each pollutant from portions of downwind transects that were outside the plume.

4.2.2 Discussion of Ozone and Precursor Transport

This analysis was to have grouped each case study day into one of three distinct flow regimes: Corridor transport; transport from outside the Corridor; and near-stagnation/recirculation. The results, as summarized in in Table 9, indicate that more than one type of flow regime occurred on many of the days. Often, the direction of transport into New York City and Boston varied by time of day and/or altitude. For example, on four days,

Table 9. Transport Regimes on Case Study Days

Urban Area	Day	Flow Regime
New York City	6/24/80	Along-Corridor Transport
	6/25/80	Along-Corridor Transport
	7/16/80*	Along-Corridor Transport, except morning transport aloft from outside the Corridor
	7/18/80	Non-Corridor Transport
	7/21/80*	Along-Corridor Transport, except morning transport aloft from outside the Corridor
	7/22/80*	Along-Corridor Transport, except morning transport aloft from outside the Corridor
	7/24/80	Non-Corridor Transport
	7/31/80*	Non-Corridor Transport/ Recirculation Flow
	8/6/80	Non-Corridor Transport
	8/8/80*	Along-Corridor Transport, except morning transport aloft from outside the corridor
	8/26/80*	Near-Stagnation Conditions
	8/28/80*	Near-Stagnation Conditions
Boston	6/24/80*	Morning: Non-Corridor Transport Afternoon: Along-Corridor Transport
	7/15/80*	Along-Corridor Transport, except morning transport aloft from outside the Corridor
	7/17/80*	Morning: Non-Corridor Transport Afternoon: Along-Corridor Transport
	8/1/80	Along-Corridor Transport
	8/5/80*	Recirculation Flow
	8/6/80	Along-Corridor Transport
	8/8/80*	Morning: Non-Corridor Transport Afternoon: Along-Corridor Transport

*Flow regime varied with height and/or time on these days.

overnight transport into the New York area at the surface and aloft up to several hundred meters, was from along the Corridor. However, at higher altitudes up to 1500m transport was from the west, beyond the Corridor. On such days, a plume of high NO_2 and NMOC concentrations was observed during early morning in the layer of along-Corridor flow with much lower concentrations aloft in the layer transported from outside the Corridor. As the daytime boundary layer grew, pollutants from both layers were eventually entrained, and became mixed with precursors from surface emissions. Thus, on such days pollutants transported from source areas both within and beyond the Corridor participated in O_3 formation in the New York area.

The estimated concentrations of O_3, NO, NO_2, and NMOC transported into and across the New York and Boston areas are summarized by flow regime in Table 10. The vertical partitioning of pollutant concentrations aloft into different flow regimes was typically made at an altitude between 500 and 1000m. The partitioning on a particular day was based upon the vertical variation in wind direction, vertical gradients in pollutant concentrations, and the track of layer-averaged trajectories. Measurements from sites affected by recirculation flows (in which pollutants are transported back over areas that previously had been upwind), and days with near-stagnation conditions (when upwind/downwind areas are difficult to define) are not included in the table. Also excluded are (1) morning O_3 concentrations at the surface which may have been affected by variations in local scavenging affects, and (2) mid-day precursor concentrations which were low compared to early morning concentrations.

For New York City, the data indicate that morning precursor concentrations at the surface resulting from along-Corridor transport were about twice the concentration on days with transport from outside the Corridor.

Aloft, precursor concentrations, particularly NMOC, were also much higher in layers transported along the Corridor. These precursors appear to be the result of overnight emissions in the Philadelphia area or other portions of the Corridor upwind of New York City. Fairly large spatial and temporal variations in morning NO and NO_2 concentrations were observed among monitoring sites upwind of New York on most days, as indicated by the range in average concentrations for these pollutants given in Table 10. This likely reflects the combination of several factors including variations in the dispersion and transport of overnight emissions within and just above the nocturnal surface-based stable layer. (Spatial variations in NMOC could not be assessed since only one NMOC site was operated upwind of New York.)

Mid-day O_3 concentrations transported into New York City with along-Corridor flow were 15 to 30 ppb higher at the "close-in" upwind sites (i.e., sites over northern and central New Jersey 60 to 90 km from mid-Manhattan) than at other sites further upwind (beyond ~100km). The elevated O_3 concentrations at these "close-in" sites are likely the result of emissions in suburban areas on the fringe of the main Corridor cities. Also, on Corridor transport days, the direct impact of the Philadelphia O_3 plume was typically observed during mid-afternoon at one or more of these "close-in" upwind sites. However, as the Philadelphia plume traveled across the New York urban area surface O_3 concentrations declined due to reaction with fresh NO emissions.

In Boston, there was little difference in the magnitude of surface precursors during Corridor and non-Corridor transport regimes. Aloft, however, the concentration of NMOC during Corridor transport was three times the magnitude of NMOC when transport was from outside the Corridor. Also, incoming O_3 aloft

Table 10. Average Transported Ozone and Precursors for Corridor and Non-Corridor Flow Regimes

Transport Regime	Morning Precursors, ppb						Ozone, ppb		
	Surface[a]			Aloft			Morning Upwind Aloft	Mid-day	
	NO	NO_2	NMOC, ppbC	NO	NO_2	NMOC, ppbC		Outside Urban Upwind	Plume Downwind
New York City									
				Corridor Transport					
	LD[d]-021	014-034	567	LD-006	043	285	-	089-116	076-089
				Transport from Beyond Corridor					
	LD-013	LD-019	278	LD	LD-013	048	070[b]	074-084[b]	- [c]
Boston									
				Corridor Transport					
	LD-009	LD-009	219	LD	013	108	100	085-098	-
				Transport from Beyond Corridor					
	009	LD-008	285	LD	LD-012	036	076	-	-

[a] 0600-1000 EST

[b] Excludes measurements on July 24, 1980 which were unrepresentatively low compared to data for the other six days in this category. Morning upwind O_3 aloft was 035 ppb and mid-day O_3 was 040 - 049 ppb. Trajectories indicate 48 hour transport from Southeast Canada on this day.

[c] Only two days in this transport category with mid-day downwind data: July 24 with O_3 of 040 - 050 ppb, and August 6 with O_3 of 075 - 085 ppb.

[d] Concentration at or below the lower detectable limit of the monitor.

during the morning on Corridor transport days averaged 100 ppb, compared to 76 ppb when transport was from outside the Corridor. It is interesting to note that the average concentrations of surface NMOC, and the average concentration of O_3, NO, NO_2, and NMOC aloft are of similar magnitude upwind of New York City and Boston during transport from areas outside the Corridor. This suggests regional homogeneity in O_3 and precursors on the days when transport was not along the Corridor.

The impact of the New York City O_3 plume on the Boston area was observed at sites upwind of Boston and/or aloft during the late afternoon or evening on most Corridor transport days. The 1-hour maximum surface O_3 concentration upwind of Boston associated with boundary layer urban plume transport ranged from 120 ppb (August 8) to 193 ppb (July 15). Aloft, transported O_3 during the afternoon was as high as 200 ppb near the Massachusetts - Rhode Island border on July 16.

An example of daytime O_3 transport from the New York area to Boston is shown in Figure 6. The location of the New York City O_3 plume is clearly identified by the isopleths of surface O_3 measurements. The analysis indicates a rapid rise in O_3 between 1000 EST and 1100 EST along a 75 km wide band from the downwind edge of New York City across Long Island Sound and coastal Connecticut. By 1400 EST the plume extended into Rhode Island with the highest concentrations at ~100 km downwind of New York City. During the next several hours the area of high ozone within the plume progressed northeastward toward the Boston area. The highest concentrations at the surface decreased rapidly between 1600 EST and 1800 EST, but then remained fairly stable at ~140 ppb through 2200 EST. On this day, transport appears to have been responsible for the maximum O_3 concentration measured in the Boston area (154 ppb/2100 EST at Medfield, MA).

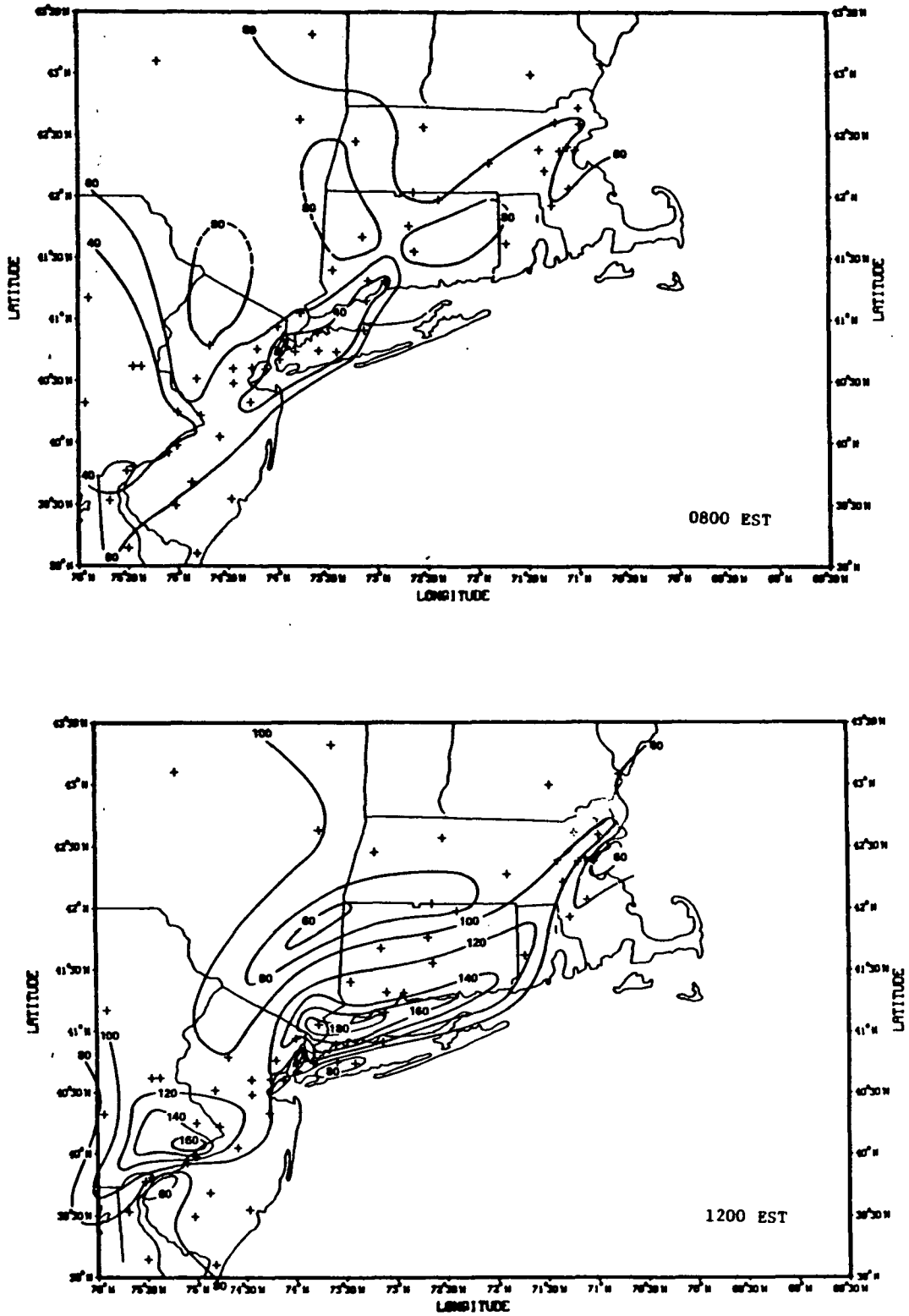

Figure 6. Surface ozone concentration isopleths (ppb), 0800 through 2200 EST, on June 24, 1980.

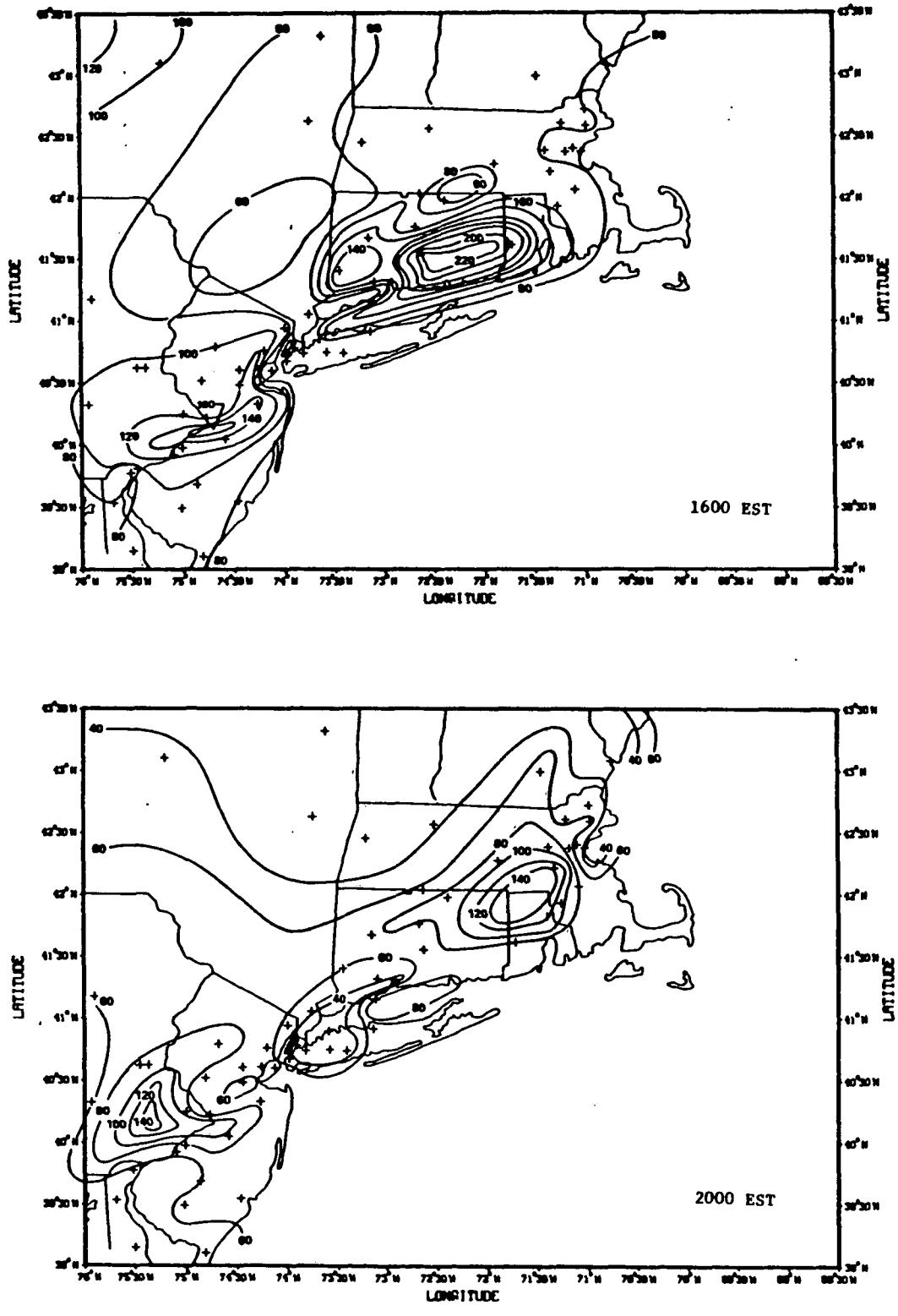

Figure 6 (continued). Surface ozone concentration isopleths (ppb), 0800 through 2200 EST, on June 24, 1980.

4.3 Temporal Changes in Ozone Above the Boundary Layer

The purpose of this task was to address the following question: To what extent do O_3 concentrations aloft increase between sunrise and mid-morning when O_3 aloft is entrained rapidly into the boundary layer during the dissipation of the nocturnal inversion?

Daytime O_3 concentrations within the boundary layer occur due to a combination of physical and chemical processes, including photochemical production, scavenging, transport, and entrainment from aloft. One of the key parameters for modeling boundary layer O_3 is the magnitude of O_3 aloft available for entrainment as the boundary layer grows in response to daytime thermal convection. In many cases, a lack of extensive measurements requires that assumptions be made regarding the temporal behavior of O_3 entrained into the boundary layer. It was the purpose of this task to investigate the temporal variation in O_3 concentrations aloft outside the boundary layer. Of interest was whether substantial production of O_3 aloft occurs during the day, as a result of reactions among transported O_3 and aged precursors. Because the monitoring program did not include experiments to specifically address this issue, the following analysis is restricted to using measurements obtained for other purposes. As a result, only a cursory investigation of this topic is possible, given the available data.

The analysis procedure was designed to identify groups of aircraft spirals which represent quasi-Lagrangian measurements aloft during the day. The temporal variation of O_3 aloft on a particular day was determined by comparing measurements from these selected spirals. Evaluating O_3 concentrations

in a quasi-Lagrangian manner, rather than comparing time changes in concentrations at a particular location, avoids the complicating influence of variations in O_3 aloft due to changes in transport.

All selected groups of spirals containing quasi-Lagrangian measurements in an air parcel were pairs of early morning (0500/0600 EST) upwind and mid-morning (0900/1000 EST) downwind spirals in Boston. For the spirals in each group, temperature, dew point temerature, O_3, b_{scat}, and NO_x measurements were used in defining the vertical bounds of specific layers which were isolated from the boundary layer during all spirals in the group. In most cases, the spirals resembled one of the six characteristic profile types identified by Ludwig [11] and shown in Figure 7. For types "a" and "b," O_3 concentrations were averaged from above the layer of depletion near the surface to the top of the spiral or an upper level inversion. For types "c" and "d," O_3 concentrations were averaged vertically, beginning above the large gradient at the top of the boundary layer to the top of the spiral or an upper level inversion. For types "e" and "f" (and other patterns with large O_3 gradients well above the boundary layer), the spirals were divided into several layers and the O_3 data averaged for each layer separately. The transition zones of large O_3 gradient were excluded from layer averages. In most cases, vertical bounds of the selected layers were associated with changes in the atmospheric stability. Discontinuities in the temperature/dew point temperature profiles which marked a change in stability were usually identifiable on successive spirals so that continuity of the layers was preserved. However, in some cases, the top of the spiral had to be used as the upper bounds for computing vertical averages when no stability discontinuity or pollutant gradient was observed near the maximum altitude of the spiral. Tracking O_3 concentrations within

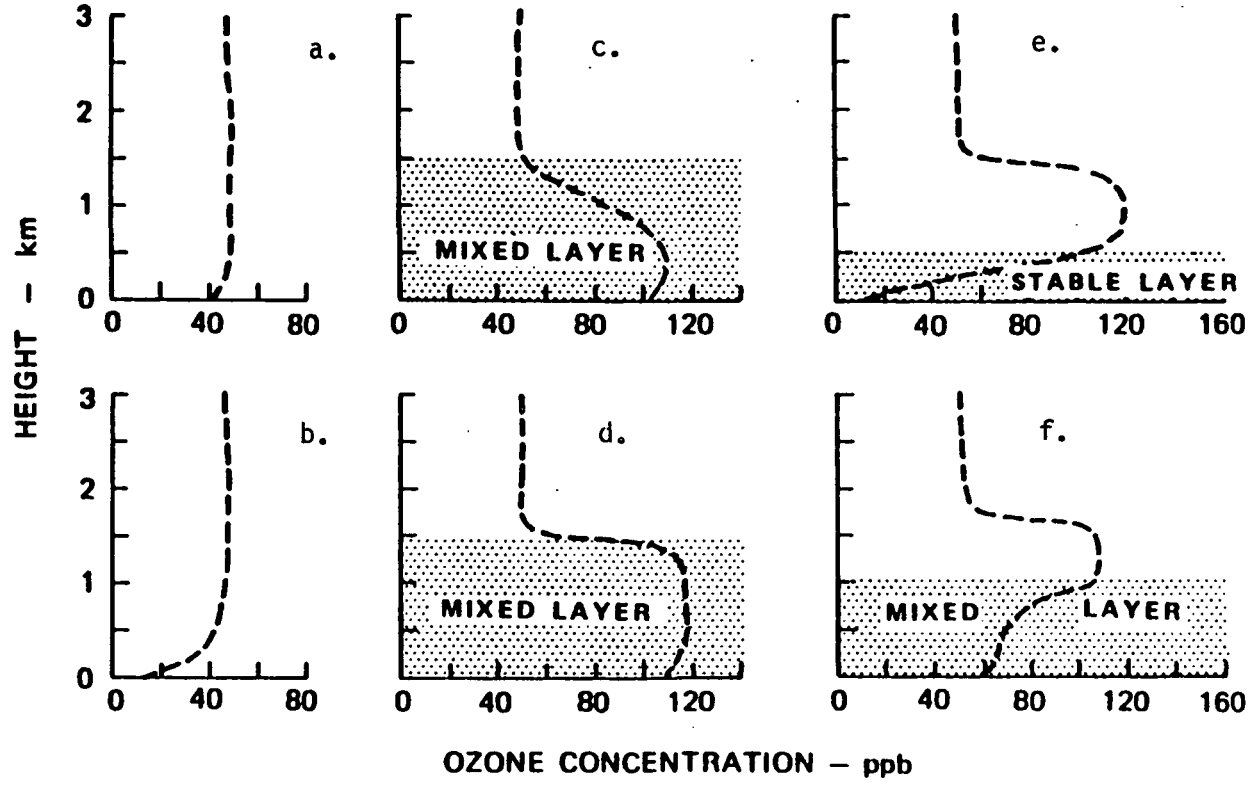

Figure 7. Characteristic ozone profile types identified by Ludwig.[11]

discrete, fairly homogeneous layers defined by stability discontinuities minimized the probability that other processes, such as vertical dilution and entrainment from the boundary layer, significantly affected O_3 concentrations aloft. Thus, any changes are most likely due to photochemical processes among the pollutants aloft.

As a result of following the above procedures, thirteen cases were identified for evaluating the formation of O_3 aloft above the boundary layer. The dates, times, dimensions, and O_3 concentrations in these layers are provided in Table 11. Also provided are the profile type, and the observed change in layer average O_3 (residual). It is evident from the data that the analyses included a wide range in initial O_3 concentrations (?6 to 99 ppb). Yet, only four cases (I, III, IV, and XI) stand out as having a measurable increase in O_3 concentration. In the remaining cases, O_3 varied by $\pm$ 5 ppb or less, which was within $\pm$ 10% of the initial concentration. Variations in this range could be due to uncertainties in the measurement system, rather than real fluctuations in O_3 concentration.

In order to investigate why O_3 increased in certain cases but remained unchanged in others, NO_x data were examined to see if the layers with apparent O_3 formation had higher NO_x levels. Although no NMOC measurements were available, b_{scat} data and back trajectories were used to infer whether the layers may have received precursors from major anthropogenic source areas during the previous two days. In addition, observations of sky cover and temperature were examined from the Boston National Weather Service station to determine whether local meteorological conditions may have hindered or enhanced O_3 formation. However, neither variations in temperature nor cloud cover could not explain the differences in O_3 concentrations aloft.

Table 11. Temporal Variations in Ozone Aloft

	Date	Time, EST	Flight/ Spiral #	O_3 Profile Type (Ludwig)	Dimension of Layer, m Bottom	Top	O_3 Concentration (ppb) Layer Average	Peak	ΔO_3 of Layer Average
City:	Boston			Lower Layers					
I	7/15/80	0545	4-1	e	485	1600	094	109	
		0915	5-1	e	500	1500	111	124	+017
II	7/16/80	0600	7-1	b	600	1500	093	101	
		0945	8-1	c	600	1500	095	102	+002
III	8/1/80	0500	26-1	e	300	800	086	105	
		0930	27-3	f	450	800	124	141	+038
IV	8/8/80	0530	33-1	b	450	1350	071	078	
		0945	34-1	c	450	1350	092	095	+021
V	8/14/80	0530	39-1	b	650	1500	039	044	
		0850	40-1	a	650	1500	036	041	-003
				Upper Layers					
VI	7/15/80	0545	4-1	e	1700	2040	068	072	
		0915	5-1	e	1660	2050	067	071	-001
VII	7/16/80	0600	7-1	b	1850	2120	078	079	
		0945	8-1	c	1840	2100	076	078	+002
VIII	7/17/80	0600	10-1	b	1000	1400	079	081	
		0945	11-1	a	1000	1400	081	086	+002
IX	7/24/80	0530	16-1	a	1000	2000	026	032	
		0930	17-1	a	1000	2000	024	033	-002
X	7/25/80	0530	19-1	b	1300	1900	046	048	
		0930	20-1	a	1300	1900	043	045	-003
XI	8/1/80	0500	26-1	e	1100	1500	048	050	
		0930	27-3	f	1170	1520	062	064	+014

Examination of the NO_x data indicates that the four comparisons (Cases I, III, IV, and XI) in which O_3 increased had higher NO_x concentrations and b_{scat} than the other cases. Also, these four cases were associated with trajectories that either had traveled along the Corridor or across portions of the Midwest within 48 hours prior to reaching Boston. The largest residual (+ 38 ppb; Case III) occurred in a layer which the trajectories and surface O_3 data indicate contained the remains of the New York City plume from the previous day. The concentration of NO_x (mostly NO_2) was 20 ppb and b_{scat} was 2.18 x 10^3 m^{-1} within this layer. In Case IV, NO_x and b_{scat} were also comparatively high (10 ppb and 2.0-3.00 x 10^3 m^{-1}, respectively). The 48-hour trajectory path from northern Indiana and Ohio, eastward across Massachusetts, suggests a contribution from the upper Midwest to pollutant levels aloft. In Case I, the layer had arrived in the Boston area after passing along the Corridor, but to the west of New York City, NO_x was 7 to 8 ppb and b_{scat} was 1.00 x 10^3 m^{-1}. In the final case with an increase in O_3 (Case XI), O_3 was initially fairly low (48 ppb), and b_{scat} was also low at 1.00 x 10^3 m^{-1}. However, the NO_x concentration was relatively high at 14 ppb. The trajectories indicate that this layer had been part of the daytime bounday layer over central and eastern New York State the day before.

Of the seven cases with no change in O_3, all had NO_x levels of 7 ppb or less, with an average concentration of 4 ppb. Except for Case II, the magnitude of b_{scat} was less than 1.00 x 10^3 m^{-1} and averaged 0.51 x 10^3 m^{-1}, indicating that the aerosol content tended to be much lower than in the cases when O_3 increased.

The results of this analysis indicate that O_3 production aloft was apparent in those layers containing comparatively high air mass concentrations

of NO_x and perhaps other O_3 precursors (as indicated by the aerosol content and history of the layer relative to urban areas). It is likely that these layers were within the daytime boundary layer on preceding days and, thus, include the by-products of photochemical processes from boundary layer emissions. However, O_3 levels were fairly stable from sunrise through mid-morning in cases in which NO_x was comparatively low, and trajectories did not indicate transport across areas of major anthropogenic emissions within 24 to 48 hours.

4.4 Comparison of Ozone Levels at the Surface and Aloft

The purpose of this task is to address two questions:

1. Do mid-morning surface O_3 concentrations during the dissipation of the nocturnal inversion reflect average O_3 concentrations aloft prior to mixing? That is, can mid-morning surface O_3 measurements be used to estimate overnight O_3 transport aloft?

2. How well do afternoon O_3 concentrations aloft compare with surface O_3 concentrations at nearby stations? That is, can aircraft measurements be used to infer surface O_3 concentrations in areas without O_3 monitoring sites?

Analyses conducted in the previous tasks indicate that a reservoir of air with elevated O_3 concentrations exists above the nocturnal inversion during many nights. This layer of O_3 has been separated by the inversion layer from deposition at the surface and chemical scavenging by pollutants emitted near the surface. Also, air in the layer containing elevated O_3 aloft is subject to transport over long distances overnight by winds above the inversion layer. As the mixing height rises in the morning, due to surface heating, the O_3 aloft is entrained into the boundary layer and contributes to concentrations at the surface.

4.4.1 Comparison of Morning O_3 Concentrations at the Surface and Aloft

In order to compare early morning levels of O_3 aloft with surface concentrations after inversion breakup, aircraft and surface O_3 data were tabulated for the New York and Boston areas as shown in Table 12. The table contains three main sections. The first section containing five columns, provides the date, spiral number, time, layer thickness, and average O_3 concentration aloft. The second section of three columns lists the three-hour average surface O_3 concentration, centered around the estimated time of inversion breakup, for ground stations near the spiral site. The final three columns list the time of inversion breakup, the O_3 concentration aloft after inversion breakup, and the time of these measurements. The inversion breakup time was determined from sodar data and/or vertical temperature profiles. On days when such data were unavailable, the median time of inversion breakup of 0930 EST was used.

All of the aircraft and surface data were taken from upwind locations in order to avoid the confounding effects of O_3 formation in the urban plume. The early morning average O_3 concentrations aloft were computed for the layer above the surface layer and below 1500m (1500m was used as an approximation for the upper limit of mixing during late morning). The late morning O_3 levels aloft in the New York area were obtained upwind of the city, shortly after the aircraft departed for the afternoon flight. In Boston, the late morning data are layer averages through the boundary layer obtained from spirals upwind at the completion of the mid-morning flight. Two of the Boston study days, August 5 and 6, were not included in this task. August 5 was excluded because surface monitoring sites in the vicinity of aircraft

Table 12. Comparison Of Mid-morning Surface Ozone With Early Morning Ozone Aloft

		Early Morning O_3 Aloft				Mid-morning Surface O_3					
	Date	Spiral Number	Time, EST	Altitude, Meters, MSL	O_3, ppb	O_3, ppb	Averaging[a] Time, EST	Location	Time of Inversion Dissipation, EST	Late Morning O_3 aloft	Time
						New York Area					
I	7/16/80	1	0700	600-1500	085	082 073 087	0900-1100	Flemington Marlboro Chester	1000	-	-
II	7/18/80	1	0545	400-1500	119	062 069	0900-1100	Flemington Chester	1000	065-070	1130
III	7/21/80	1	0545	500-1500	076	079 114 110	0900-1100	Flemington Marlboro Chester	1000	-	-
IV	7/22/80	1	0530	650-1500	056	051 053 053	0800-1000	Flemington Marlboro Chester	0900	065-070	1130
V	7/24/80	1	0530	400-1500	035	037 042	0800-1000	Flemington Chester	0900	045	1200
VI	7/31/80	1	0545	400-1500	060	059 059	0800-1000	Flemington Chester	0830	075-085	1130
VII	8/6/80	1	0530	400-1500	071	069 076 061	1000-1200	Flemington Marlboro Chester	1030	065-075	1130
VIII	8/8/80	1	0530	400-1500	067	097 107 088	1000-1200	Flemington Marlboro Chester	1030	090-100	1130
						Boston Area					
IX	7/15/80	1	0545	485-1500	095	103 104 100	1000-1200	Easton Attleboro Sudbury	1030	108	1015
X	7/16/80	1	0600	600-1500	093	105 088 084	1000-1200	Easton Medfield Sudbury	1100	105	1100
XI	7/17/80	1	0600	500-1500	079	073 057 054	0900-1100	Easton Medfield Sudbury	0930	071	1045
XII	7/25/80	1	0530	500-1500	049	054 050 045	0800-1000	Medfield Attleboro Sudbury	0900	040	1030
XIII	7/31/80	1	0530	500-1500	048	050 048 051	0900-1100	Medfield Easton Georgetown	1000	038	1030
XIV	8/1/80	1	0500	200-1500	067	100 131 098	0900-1100	Easton Medfield Sudbury	1000	105-115	1000
XV	8/8/80	1	0530	450-1500	071	- 087 082	0900-1100	Easton Medfield Worcester	1000	086	1100

[a]Start time of first hour and of last hour in averaging period.

spirals were downwind of Boston as a result of the low level easterly wind flow. August 6 was excluded because there were no early morning aircraft flights on this day. These days were replaced by July 25 and 31 in this task only.

In order to evaluate the use of surface O_3 as an estimate of O_3 aloft, values of residuals were computed by subtracting the surface O_3 concentrations at each site from the respective concentrations aloft. The results indicate a wide variation in "agreement," ranging from exact correspondence to a 57 ppb underestimation of O_3 aloft. To provide a clearer interpretation of the residuals, the data set was separated into two groups. The first group contains the ten cases in which surface O_3 levels were somewhat homogeneous (within $\pm$ 15 ppb) among the upwind sites at the time of inversion breakup (Cases I, II, IV, V, VI, VII, IX, XII, XIII, XV). The second group contains the remaining five cases in which there were relatively large variations in the upwind surface O_3 levels (Cases III, VIII, X, XI, XIV). Such inhomogeneities in O_3 may be attributable to spatial variations in: (1) O_3 aloft; (2) the time of inversion breakup; (3) the strength of vertical mixing; and (4) O_3 formation in the boundary layer.

Focusing on the first group indicates that, except for Case II, average upwind surface O_3 concentration at the time of inversion breakup provides a reasonable estimate of O_3 aloft some three to five hours earlier. Excluding Case II, the average residual (sign ignored) for this group was only 4 ppb indicating good agreement.

In the second group, the average absolute residual values were fairly large (~30 ppb), excluding Case X. An explanation for the large residuals in two of these cases (VIII and XIV) is evident from examining the

late morning O_3 measurements aloft. In both cases, O_3 levels aloft had actually increased substantially during the morning. As seen from the data in Table 12, surface concentrations at the time of inversion breakup are consistent with the later values aloft. That is, in these cases, the relatively large residuals were apparently not due to the inability of average surface concentrations to reflect O_3 concentrations aloft, but rather to a change in the upwind O_3 concentration aloft between the time of the aircraft measurement and the dissipation of the nocturnal inversion.

The large residual values and the difference in surface concentrations in Case XI may be due to the presence of a low level subsidence inversion (600m) which restricted vertical mixing after the dissipation of the nocturnal inversion over portions of the Boston area. In both Case X and XII, the O_3 concentration at 1300 EST had increased to within a few ppb of the concentration aloft, indicating that the reason for the difference in O_3 observed earlier may have been due to a spatial variation in the time of inversion breakup. For Case III, no late morning aircraft data are available, so it is uncertain whether or not the relatively high surface O_3 concentration at the time of inversion breakup might be the result of an increase in O_3 aloft.

Of the 15 cases examined in this task, 12 exhibited close agreement between early morning O_3 aloft and surface O_3 concentrations during the period of inversion breakup. In two of these 12 cases, upwind O_3 aloft changed substantially during the 3 to 5 hours between the initial aircraft measurements and the time of inversion breakup. Thus, mid-morning surface O_3 measurements appear to provide a useful estimate of early morning O_3 aloft, although care must be taken in using mid-morning O_3 data for this purpose,

particularly for cities such as New York City and Boston where urban areas are less than a hundred kilometers apart and fluctuations in interurban transport of O_3 and precursors can be substantial between early morning and the time of inversion breakup.

4.4.2 Comparison of Afternoon O_3 Concentrations at the Surface and Aloft

The second aspect of this task concerns comparison of afternoon O_3 concentrations at the surface and aloft. Of interest is whether O_3 concentrations measured aloft by instrumented aircraft accurately represent the concentrations at the surface. To examine this hypothesis, O_3 concentrations aloft from afternoon flights in the study region were compared with concentrations measured at nearby surface stations. Note that the aircraft measurements used in these comparisons are 20-second average values, while the surface data are hourly averages. In this analysis, pairs of measurements at the surface and aloft were obtained for situations when the aircraft passed within 15 km of a surface O_3 monitoring site. The data for these comparisons are given in Table 13 for the New York area and Table 14 for Boston.

The data indicate that large differences exist in many of the comparisons. However, several explanations exist for the observed discrepancies. As noted, the surface data are hourly averages, while the aircraft data are instantaneous values. This difference in averaging times can influence the comparison. Another important factor is the large concentration gradient which exists near the edge of an urban plume. In a number of cases, as indicated in Tables 13 and 14, comparisons were made near the edge of the plume, where sharp concentration gradients were observed. In this region, small vertical or horizontal separations between the surface site and the measurement point aloft can lead to large differences in O_3 concentration.

Table 13. Comparison of Afternoon Ozone Concentrations at the Surface and Aloft in the New York Area

Date	O_3 Aloft Time (EST)	O_3 Aloft O_3 (ppb)	Surface O_3 Time (EST)	Surface O_3 O_3 (ppb)	Station	Distance from Surface Station, km
7/18/80	1126	064	1100	074	Plainfield, NJ	10.2
	1143	108	1100	097	Marlboro, NJ	7.8
	1253	105	1200	093	Marlboro, NJ	10.5
	1430	120	1400	070[a]	Stony Brook, NY	13.8
	1551	074	1500	068	Stony Brook, NY	1.6
	1558	059	1500	059	Derby, CT	5.0
	1805	100	1800	078[b]	Marlboro, NJ	7.6
	1812	088	1800	068[b]	Linden, NJ	4.1
	1814	083	1800	043[b]	Plainfield, NJ	10.4
7/22/80	1132	077	1100	058	Dumont, NJ	2.0
	1142	072	1100	090[c]	White Plains, NY	4.9
	1144	078	1100	127[c]	Greenwich, CT	6.7
	1205	114	1200	118	Glen Cove, NY	3.6
	1212	115	1200	072[d]	Babylon, NY	9.2
	1316	099	1300	087	Danbury, Ct	8.2
	1324	150	1300	174	Derby, CT	1.9
	1359	167	1300	213[d]	Stratford, CT	10.9
	1427	176	1400	226[d]	Stratford, CT	12.0
	1431	179	1400	092[d]	Stony Brook, NY	2.2
	1617	148	1600	060[d]	Stony Brook, NY	7.1
	1654	161	1600	076[d]	New Haven, CT	10.2
	1701	213	1700	111	Middletown, CT	0.2
	1743	126	1700	125	Danbury, CT	7.8
	1753	079	1700	123[c]	Greenwich, CT	11.0
	1759	083	1700	087	Dumont, NJ	10.4
7/24/80	1202	049	1200	048	Plainfield, NJ	2.4
	1211	041	1200	048	Staten Island, NY	10.8
	1509	060	1500	065	McGuire, NJ	1.0
	1522	046	1500	049	New Brunswick, NJ	1.8
	1525	047	1500	040	Plainfield, NJ	0.7
7/31/80	1142	065	1100	084	Dumont, NJ	7.2
	1148	070	1100	090	Greenwich, CT	11.1
	1203	108	1200	100	Glen Cove, NY	1.6
	1208	112	1200	070[a]	Babylon, NY	0.7
	1229	114	1200	070[a]	Babylon, NY	9.8
	1309	070	1300	059	Danbury, CT	2.4
	1318	069	1300	070	Derby, CT	4.9
	1407	164	1400	115[a]	Stony Brook, NY	9.3
	1721	082	1700	070	Middletown, CT	2.9
	1743	077	1700	070	Middletown, CT	6.5
	1755	072	1700	101[d]	Derby, CT	14.4
	1800	070	1800	049[b]	Danbury, CT	6.5
	1809	079	1800	034[b]	Greenwich, CT	11.8
	1815	097	1800	054[b]	Dumont, NJ	8.8
8//6/80	1155	071	1100	085	Dumont, NJ	0.5
	1223	201	1200	171	Glen Cove, NY	1.8
	1248	100	1200	090	Danbury, CT	7.0
	1255	162	1200	180	Derby, CT	0.7
	1302	208	1300	249[d]	Stratford, CT	2.2
	1309	170	1300	117[d]	Stony Brook, NY	3.7
	1451	152	1400	100[a]	Middletown, CT	4.0
	1526	208	1500	190	Stratford, CT	1.4
	1549	072	1500	070	Dumont, NJ	7.8
8/8/80	1152	104	1100	101	Dumont, NJ	0.5
	1213	146	1200	152	Greenwich, CT	7.0
	1218	123	1200	120	Glen Cove, NY	0.2
	1222	164	1200	122[b]	Babylon, NY	9.5
	1245	115	1200	112	Danbury, CT	4.0
	1251	122	1200	125	Derby, CT	0.7
	1303	170	1300	141	Stony Brook, NY	5.0

[a] Large O_3 gradient on edge of plume; aircraft was in urban plume but surface site was not.

[b] O_3 depletion in surface layer due to scavenging.

[c] Large O_3 gradient on edge of plume; surface site was in urban plume but aircraft was not.

[d] Sea breeze or complex surface flow resulted in large vertical/horizontal gradients in O_3.

Table 14. Comparison of Afternoon Ozone Concentrations at the Surface and Aloft in the Boston Area

	O_3 Aloft		Surface O_3			
Date	Time (EST)	O_3 (ppb)	O_3 (ppb)	Time (EST)	Station	Distance from Surface Station, km
7/15/80	1525	153	128	1500	Medfield, MA	6.3
7/16/80	1653	159	093	1600	Medfield, MA	9.2
7/17/80	1639	134	110	1600	Medfield, MA	5.9
	1707	125	116	1700	Medfield, MA (124 at 1800)	2.6
8/1/80	1357	126	117	1300[a]	Hamilton, MA (134 at 1200)	11.5
	1420	125	112	1400[a]	Hamilton, MA	3.9
	1423	128	114	1400[a]	Danvers, MA (130 at 1300)	4.8
	1424	130	117	1400[a]	Georgetown, MA (134 at 1300)	8.5
	1432	108	113	1400	Manchester, NH	15.3
	1600	151	098	1500[a]	Portsmouth, NH	13.6
8/5/80	1355	133	096	1400[a]	Georgetown, MA	1.4
	1621	104	100	1600	Worcester, MA	1.9
	1657	125	105	1600	Easton, MA (090 at 1700)	12.3
	1700	107	116	1700	Medfield, MA (109 at 1600)	7.1
	1704	105	100	1700	Sudbury, MA	13.5
	1704	105	042	1700[a]	Watertown, MA	3.3
	1707	107	060	1700[a]	Somerville, MA	8.4
8/6/80	1315	089	111	1300	Sudbury, MA	---
	1326	101	106	1300	Medfield, MA	---
	1332	098	089	1300	Quincy, MA	---
	1538	074[b]	075	1500	Easton, MA	---
	1611	077[b]	068	1600	Tewksbury, MA	---
8/8/80	1516	090	067	1500	Danvers, MA	---
	1551	076	075	1500	Sudbury, MA	8.0
	1555	082	064	1500	Tewksbury, MA	4.8

[a] Sea breeze or complex surface flow resulted in large vertical/horizontal gradients in O_3.

[b] Aircraft in region of large spatial gradient aloft; average concentration as aircraft passed the site.

Comparisons made near coastal areas during a sea breeze flow were likely influenced by the presence of a shallow internal bounday layer, which isolated surface sites from the impact of a plume aloft, or prevented high surface concentrations from mixing upward. In some of the the Boston cases, vertical wind speed shear may have resulted in a faster travel time for upwind transport aloft, such that the surface impact was an hour or so later than that measured by the aircraft. Also, in comparisons of measurements made late in the day (generally after 1700 or 1800 EST), surface concentrations may have been depleted by local scavenging as the nocturnal stable layer began to form and isolate O_3 in the surface layer from O_3 aloft. The cases where these phonomena affect the surface/aloft comparisons are noted in Tables 13 and 14.

Considering the above factors, the 85 cases in the tables were divided into two groups for the evaluation. Group I contains those cases where the atmosphere is likely to be well mixed, and both measurements (surface and aloft) were not on the fringe of the urban plume. Group II contains those cases in which complicating features, as described above, were observed. For Group I - New York (35 cases), the average residual (sign ignored) between surface and aloft was 10 ppb. In 63 percent of the Group I cases, O_3 aloft exceeded O_3 at the surface. In contrast, the average residual for Group II - New York (25 cases) was 49 ppb. In most of the Group II cases O_3 was much higher aloft, due to depletion near the surface or as a result of low surface concentrations in the sea breeze onshore flow.

For Group I - Boston (17 cases), the average residual of 15 ppb was somewhat higher than in New York and, again, O_3 aloft exceeded surface

concentrations in most (71 percent) of the cases. In Group II - Boston (8 cases), the average residual was double the value of Group I.

One conclusion which can be drawn from these comparisons is that aircraft data are most useful for estimating surface concentrations during mid-day when the boundary layer tends to be well mixed, and in areas away from the gradients associated with urban plumes and sea breeze flows. However, in some monitoring circumstances, the existence of such gradients will not be known a priori, and their influence will be difficult to avoid. As a consequence, the use of aircraft data to estimate fixed point surface O_3 concentrations must be viewed with caution in the following situations: (1) in areas with complex wind flow patterns; (2) in the vicinity of an urban plume; and (3) when the column of air from the surface to the height of the aircraft measurement is not well mixed. On the other hand, aircraft measurements appear to be valuable for estimating surface O_3 concentrations in the absence of these complicating situations.

SECTION 5

CONCLUSIONS

It was the purpose of this study to investigate various aspects of ozone formation and transport in the New York City and Boston portions of the Northeast Corridor. At the outset of the study eight questions were posed relative to this topic which were addressed through numerous analyses.

The conclusions of the study pertinent to these questions are presented below.

1. Do concentrations of O_3 and precursors transported into New York City and Boston differ during along-Corridor and non-Corridor transport regimes?

For New York City, morning precursor concentrations transported into the urban area at the surface were twice as high with along-Corridor transport than when transport was from outside the Corridor. Aloft, precursor concentratins, particularly NMOC, were also much higher when transport was along the Corridor. The analysis indicates that high morning precursor concentrations transported into the New York area with along-Corridor flow were attributable to overnight emissions in the Philadelphia area. During mid-afternoon the impact of the Philadelphia O_3 plume was typically observed at one or more monitoring sites on the upwind (southwest) fringe of New York City.

In Boston, there was little difference in surface precursor concentrations during along-Corridor versus non-Corridor transport regimes. However, the concentration of NMOC aloft during along-Corridor transport was triple the magnitude of aloft concentrations when transport was from outside the Corridor. Average O_3 aloft transported into Boston during the morning was also higher with along-corridor flow (100 ppb versus 76 ppb). The impact of the New York

city O_3 plume on portions of the Boston area was observed during the evening across the upwind (southwest) fringe of Boston on days when transport was along the Corridor.

The analyses indicate that the concentration of O_3 and precursors transported into New York City and Boston can vary substantially depending upon transport direction. Vertical variations in transort direction overnight were often associated with large gradients in morning pollutant concentrations aloft. Also, on occasion, transport of high O_3 concentrations from major upwind cities resulted in O_3 exceeding the NAAQS in portions of the Boston and New York areas.

2. What is the diurnal variation of O_3 and precursors in the air parcels leading to the maximum O_3 concentration in the urban plume?

In New York City, the concentration of O_3 decreased as the air parcel traveled from upwind rural and suburban locations into the urban area in the morning, then increased rapidly later in the morning as the air parcel departed the city and the rate of photochemical reactions increased. In almost every case, the maximum O_3 concentration in the plume occurred between 1300 and 1500 EST. The concentrations of NO, NO_2, and NMOC generally peaked as the air parcel crossed the city in the morning. The diurnal varition of O_3 and precursor concentrations are provided for 10 days in Section 4.1.2.

3. What is the average transport time and distance to maximum O_3 in the urban plume? What is the typical downwind distance to maximum NO_2 in the urban plume?

For New York City, the analyses indicate that the highest O_3 concentrations were associated with air parcels crossing the city at approximately 0800 EST. On the average, air parcels crossing the city at 0800 EST generated an O_3 maximum of 219 ppb at 1400 EST. The average downwind distance to maximum O_3 was ~100 km. The average transport time to peak O_3 was 5 to 7 hours.

In the Boston area, aircraft data provided the most useful information relative to these questions since the urban plume was transported over the ocean on all but one case study day. The aircraft data indicate that the average distance to the O_3 maximum aloft was 81 km, with a range of 61 to 107 km. The average transport time to peak O_3 was 4 hours.

At the surface, maximum NO_2 concentrations occurred in and immediately downwind of the city. Aloft, away from the effect of local sources, maximum midday NO_2 concentrations were measured 23 to 48 km downwind of New York City, and 34 to 110 km downwind of Boston. For both cities, the transport time to maximum NO_2 ranged from 1 to 3 hours.

4. What is the typical downwind distance to where NO_x in the urban plume becomes indistinguishable from background concentrations?

For three days in Boston and two days in New York City, the distance from the urban area to the point where the urban plume NO_x concentrations aloft became indistinguishable from the air mass background NO_x concentrations were estimated. This distance ranged from 85 to 165 km. The estimated travel time to background NO_x ranged from 5.5 to 12 hours.

5. Can mid-morning surface O_3 measurements be used to estimate early morning upwind O_3 aloft?

The analyses indicate that average upwind surface O_3 concentrations (3 hour average centered around the time of inversion dissipation) do provide a meaningful estimate of early morning O_3 concentrations aloft in many cases. However, there were also a number of cases when such an assumption would lead to signficant underestimation (or overstimation) of the early morning levels aloft. In these situations, it appears that O_3 aloft transported into the city had actually increased (or decreased) between the time of the early

morning aircraft measurements and the time of inversion dissipation. This may have been due to reactions among O_3 and transported precursors or to spatial variations in O_3 aloft transported across the urban area. Thus, using surface data for estimating early morning concentrations aloft should be done with caution, particularly in situations where urban areas are in fairly close proximity or high concentrations of transported precursors are expected.

6. Can mid-day aircraft measurements of O_3 be used to estimate surface concentrations between measurement sites?

In locations where the atmosphere appears to be well mixed, surface and aircraft data agree within 10 to 15 ppb. However, it was observed that strong vertical and horizontal gradients confound the use of aircraft data for estimating surface concentrations in the vicinity of urban plumes and sea breeze circulations.

7. Does O_3 aloft, initially isolated from the effects of surface emissions and scavenging, change substantially prior to the dissipation of the nocturanl inversion when pollutants aloft are mixed to the surface?

The data examined indicate that, in most cases, O_3 concentrations aloft were fairly stable (within ±5 ppb) between early morning and mid-morning measurements made within an air parcel. However, O_3 production was evident in those air parcels containing comparatively high air mass NO_x concentrations and probably other O_3 precursors, as indicated by the aerosol content ansd estimated track of the air parcel relative to upwind urban areas.

8. Is there evidence in the data of O_3 plumes from medium size cities such as Bridgeport, New Haven, and Hartford, CT or Providence, RI?

In general, it was difficult to define O_3 plumes from such cities due to the relatively high air mass O_3 levels, the complexity of airflow patterns

and the frequent incursions of urban plumes from the major Corridor cities. Also, since the monitoring program was not directed toward investigating these cities, comparatively little data were available for this type of analysis. However, on two occasions, there was evidence of the Providence O_3 plume from the Boston area aircraft data. In the clearest example, O_3 in the Providence plume was 20 to 30 ppb higher than the mass O_3 concentration upwind, outside the Boston plume.

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16. ABSTRACT

This report describes the results of a study to analyze portions of the Northeast Corridor Regional Modeling Project (NECRMP) ambient data base collected in the New York City and Boston urban areas. The study includes (1) an examination of the ozone, oxides of nitrogen, and hydrocarbon concentrations transported into each city and downwind in the urban plumes on 20 high ozone days; (2) the temporal changes in ozone above the boundary layer; and (3) the relationship between surface ozone concentrations and mid-boundary layer values.

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