Long-Range Transport of Ground-Level Ozone and Its Precursors:

Assessment of Methods to Quantify Transboundary Transport Within the Northeastern United States and Eastern Canada

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The Commission for Environmental Cooperation

In North America, we share vital natural resources including air, oceans and rivers, mountains and forests. Together, these natural resources are the basis of a rich network of ecosystems that sustain our livelihoods and well-being. If they are to continue being a source of future life and prosperity, these resources must be protected. Protecting the North American environment is a responsibility shared by Canada, Mexico and the United States.

The Commission for Environmental Cooperation (CEC) is an international organization whose members are Canada, Mexico and the United States. The CEC was created under the North American Agreement on Environmental Cooperation (NAAEC) to address regional environmental concerns, help prevent potential trade and environmental conflicts and to promote the effective enforcement of environmental law. The Agreement complements the environmental provisions established in the North American Free Trade Agreement (NAFTA).

The CEC accomplishes its work through the combined efforts of its three principal components: the Council, the Secretariat and the Joint Public Advisory Committee (JPAC). The Council is the governing body of the CEC and is composed of the highest- level environmental authorities from each of the three countries. The Secretariat implements the annual work program and provides administrative, technical and operational support to the Council. The Joint Public Advisory Committee is composed of fifteen citizens, five from each of the three countries, and advises the Council on any matter within the scope of the agreement.

Mission

The CEC facilitates cooperation and public participation to foster conservation, protection and enhancement of the North American environment for the benefit of present and future generations, in the context of increasing economic, trade and social links among Canada, Mexico and the United States.

Acknowledgments

The CEC would like to thank Dr. Peter Summers for his hard work and dedication in serving as the primary author of this report. The CEC also thanks the member jurisdictions of the Eastern Canada Transboundary Smog Issue Group and the Northeast States for Coordinated Air Use Management for their time, resources and input in making this report possible.

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EXECUTIVE SUMMARY

Ground-level ozone, a major component of smog, is recognized as an important public health concern in many parts of the world. Long believed to be a primarily local, urban problem, it has become increasingly evident in recent years that ozone smog is a regional phenomenon, subject to long-range windborne transport across state and national borders. To investigate the regional nature of ozone pollution, a number of data collection programs, data analyses, and modeling efforts have been initiated and carried out both cooperatively and independently in the United States and Canada. These initiatives have helped to demonstrate that the transport of ground-level ozone and its precursors occurs over distances of many hundreds of kilometers in the eastern United States and Canada. Moreover, depending on prevailing weather conditions, ozone can travel across the border in either direction so that both nations are at times the recipient of, and at other times a contributor to, their neighbor's air pollution problem.

This effort was initiated by the Commission for Environmental Cooperation (CEC) to assess the current state of science on the transboundary impacts of ozone air pollution. As part of the initiative, the CEC also seeks to lay the groundwork for a coordinated plan of action to address data and analysis gaps, promote awareness and cooperation among air quality planners in the eastern United States and Canada, and to encourage both countries to establish crossborder regional airshed management efforts. This report is a collaborative effort between the CEC, the Eastern Canadian Transboundary Smog Issue Group (Environment Canada and the provinces of Ontario, Quebec, New Brunswick, and Nova Scotia) and the Northeast States for Coordinated Air Use Management (Connecticut, Maine, Massachusetts, New Hampshire, New Jersey, New York, Rhode Island, and Vermont).

Using a “weight of evidence” approach, this report provides a comprehensive overview of scientific efforts to date and suggests recommendations for future cooperative activities. The weight of evidence approach is very useful for examining a variety of factors that build a more complete and robust picture of the transboundary transport of ground-level ozone.

Two of this report's findings are of special note and reinforce the conclusions drawn by other recent investigations:

1. All of the observationally-based studies lead to the same general conclusion: long- range transport of ground-level ozone and its precursors (volatile organic compounds VOCs, and oxides of nitrogen NO_x) exists in North America, particularly where the typical weather patterns flow from upwind regions with high levels of precursor emissions into downwind regions experiencing high levels of ozone. These conditions exist for at least two trans boundary transport pathways within eastern North America:

    - pollutants flow from the upper Midwest United States and the Ohio River Valley across Southern Ontario and the northeastern United States.
    - pollutants travel up the “northeast corridor” of the United States and flow into the Atlantic provinces of Canada.

2. Factoring in locally generated precursors and long-range transport, ground-level ozone is a regional problem over spatial scales of more than 600 kilometers and temporal scales of several days.

Results from the Ozone Transport Assessment Group (OTAG) investigation add to the available weight of evidence that transboundary transport exists and point to the need for significant broad-based reductions in NO_x emissions. For example, OT AG modeling results predicted that emissions in the upper Great Plains of the United States contributed up to 30 percent of the number of hours that ozone exceeded 100 ppb in the Toronto/southern Ontario region during a July 1995 ozone episode. OTAG recommended reductions from elevated point sources of as much as 85 percent from 1990 NO_x emission rates in order to reduce transport within the eastern United States. Such reductions will also reduce transboundary transport given the evidence provided in this report.

Of importance to air quality planners is the knowledge that transboundary transport of ground-level ozone is not limited to a single pathway nor does it flow in one direction. Furthermore, air quality management efforts focusing on the long-term, regional scale component of the ozone problem will effectively complement traditional efforts that focus on short-term, local peak ozone concentrations.

Equally important but often overlooked is that ground-level ozone is only one example of a pollutant subject to transboundary transport. Other transport pathways may be more important for other types of pollutants and for different segments of the Canada-United States border. Control strategies must account for the multiple dimensions of pollution transport.

Based on this available information, the report makes several recommendations for future work regarding steps needed to reduce the impacts of transboundary transport. Among these are efforts to:

- Apply existing models and modeling studies, some of which have been developed independently within each country, to assess the impact of reducing precursor emissions in one defined region on the ozone concentrations in another defined region. The boundaries should include the Canada-United States border and other regions on each side of the border.

- Meet the monitoring needs for tracking transboundary transport and for regional airshed air quality management in the northeastern United States and southeastern Canada. To accomplish this, the plans for monitoring near the border and within the whole region should be reviewed by the agencies involved to ensure a continuity in essential observations. More importantly, there should be a commitment to the continued maintenance and expansion, where possible, of existing monitoring programs that are currently being undermined by fiscal constraints.

- Integrate and enhance the compatibility of the data being collected by Canada and the United States, and develop common databases for ambient monitoring and ozone precursor emissions data for the study area. These could be used as models for other North American investigations.

- Renew the development of regional pollution reduction strategies for "areas of influence" rather than for isolated areas. Areas of influence are defined as common source regions which affect large, downwind geographical areas rather than isolated locations.

As long as many areas of the eastern United States and Canada continue to violate ozone standards and objectives, a comprehensive joint response to the problem of transboundary air pollution will be needed. The existence of this problem, and the need for cost-effective pollution control strategies to address it, are well established. Coordination of such strategies on a regional basis will enable both countries to reduce ozone pollution levels more efficiently and at lower cost than will fragmented local efforts. To achieve this end, a collaborative, bi-national approach is needed to create a uniform environmental framework on both sides of the border. The health and economic prosperity of millions of citizens in both countries will benefit from a joint approach that protects the shared air resources of Canada and the United States.

1. Introduction

1.1 Background

The Northeast States for Coordinated Air Use Management (NESCAUM) and the Eastern Canada Transboundary Smog Issue Group (ECTSIG) recognize that the resolution of transboundary pollutant flows is paramount to both Canada and the United States addressing their respective ground-level ozone issues. As a result, a joint project has been initiated to assess the transboundary impacts of air pollution and to develop a work plan that will address data and analysis gaps, promote awareness and cooperation between Canada and the United States, and encourage the establishment of regional airshed management schemes between the two countries.

The first phase of this project involves the preparation of this report, which synthesizes the current state of knowledge with respect to ozone transport in the eastern United States and Canada. This synthesis document will form the basis for the work plan, which will be developed jointly by both NESCAUM and ECTSIG.

This phase is supported by the NAFTA - Commission for Environmental Cooperation (CEC).

The specific tasks are to:

- Collect and synthesize available data on ozone transport across state, provincial and international boundaries, including monitoring data and modeling tools for the quantitative measurement of ozone transport;

- Identify key data needs and information gaps, including monitoring needs for public information programs and tracking requirements for regional airshed management schemes;

- Develop scientific recommendations based on the synthesized data and recommendations for future work.

1.2 Overall Approach

The region to be considered, henceforth called the “study area” is shown in Figure 1.1. It consists of the region in eastern Canada and the eastern United States on either side of the international border from Lake Superior to the Atlantic coast. The sub-regions to be considered are also shown.

Many data analysis studies and modeling results, carried out independently in both the United States and Canada, have shown conclusively that regional transport of ozone and its precursors into the study area occurs over distances of many hundreds of kilometers. This report will review the various analytical techniques that have been used to document the occurrence of regional transport into and within the study area, and identify those which have the best potential for further assessing transboundary transport. Emphasis will be placed on the interpretation of real-world monitoring data, rather than results from numerical simulation models.

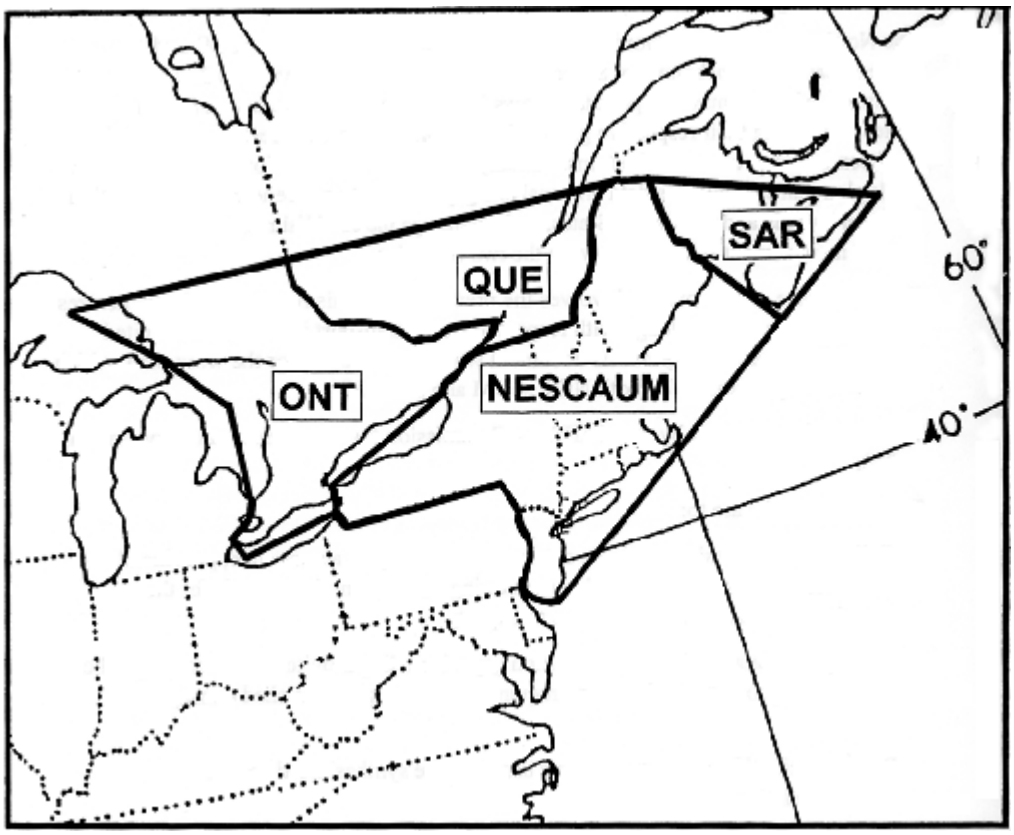


Figure 1.1 Map of eastern North America showing the "study area" for this report.

ONT = southern portion of Province of Ontario

QUE = southern portion of the Province of Quebec.

SAR = southern Atlantic Provinces (New Brunswick and Nova Scotia).

WQC (not identified on map) = Windsor-Quebec City Corridor – strip from SW Ontario along St. Lawrence River Valley to Quebec City.

NESCAUM = Northeast States for Coordinated Air Use Management.

The report will not attempt to be all inclusive there are many other reports that cover some of the topics in great detail-NESCAUM (1992), NESCAUM (1994), CEC (1995), Morris (1996), Miller et al. (1997), and Canadian Assessment (1997a, 1997b, 1997c). Rather than reproduce these earlier overviews, this study will describe the various data analysis and model application techniques from

available reports and the scientific literature, and a few selected results will be given as examples. The main criterion for selection is that they have some relevance to the regional transport and transboundary transport issue. Omission of any particular study does not necessarily mean that it is not important.

1.3 Report Outline

Chapter 2 provides a brief historical perspective on air pollution followed by an outline of ozone chemistry and the meteorological conditions conducive to ozone formation and atmospheric transport.

Chapter 3 discusses the ambient monitoring and meteorological data that are available in the study area. Some comments are made on the availability of precursor emissions data which are essential inputs for both model simulations and interpretation of data analysis results.

Chapter 4 outlines various approaches that have been used to link observed ozone concentration fields with precursor emission sources and to make qualitative estimates of long-range transport of both ozone and the precursors. These include analyses of the spatial and temporal behavior of ozone using a variety of statistical and presentation techniques. Such analyses can be further refined by including meteorological stratification, especially with airflow trajectories. Finally, the use of elemental and artificial tracers is briefly discussed.

Chapter 5 provides a brief overview of numerical models for the simulation of concentration fields and transport of ozone. Several models have been developed and applied in both Canada and the United States. Examples of results that have relevance to transport are discussed.

Chapter 6 discusses the strengths and weaknesses of the various analytical techniques presented in chapters 4 and 5 and their applicability to the region. The most appropriate approach or combination of approaches is suggested. In particular, the advantage of using quasi-independent but complementary techniques to provide a "weight of evidence" approach is emphasized.

Chapter 7 presents the main scientific conclusions, with recommendations on the priorities for scientific work to develop and evaluate effective strategies to reduce the transboundary transport of ozone and its precursors. In particular, studies are identified where using a joint approach will be beneficial through pooling the scientific resources in Canada and the United States.

Chapter 8 raises some of the more salient points from an air planning perspective in addressing transboundary transport of ozone and its precursors.

Finally, an appendix presents an overview of the detrimental public health impacts created by ozone pollution. This provides a contextual background for why ozone is a continuing public health concern in Canada and the United States.

2. Ozone Formation and Long-Range Transport

2.1 Historical Perspective

Humans began to pollute the atmosphere as a result of the discovery of fire, but it was not until after the industrial revolution began that anthropogenic emissions (mainly particulates together with carbon dioxide, sulfur and nitrogen compounds) increased to significant amounts. The problem, however, was considered to be local in nature and generally confined within the regions of the rapidly growing urban/industrial complexes. The first evidence that human activities could affect the atmosphere on a global scale came from the observations of radioactive debris created by nuclear weapons testing in the late 1940s and the 1950s.

Even with the recognition that radioactive debris was transported over long distances, the realization that the air emissions from ordinary, everyday activities could also be transported afar came more slowly. Evidence began to mount during the 1960s and 1970s from several unrelated observations. These observations include: a) the detection of pesticides thousands of kilometers from their known locations of application; b) the expansion of the region of acid deposition in Europe especially into Scandinavia; and c) the detection of persistent haze layers in the Arctic atmosphere. After several years of ground-level and aircraft measurements coupled with detailed interpretation of meteorological patterns, it was eventually concluded that the "Arctic Haze" phenomenon was due to transport of residual air pollutants from mid-latitude sources, mainly in Eurasia.

Evidence of the long-range transport of pollutants continued to accumulate in the 1980s. Freons (chlorofluorocarbons or CFCs) were detected in the stratosphere and acid deposition continued to be a major scientific and political issue over much of Europe and North America. The most acidic rainfall in Bermuda was related to air flow from the North American continent, and from an analysis of routine and special field measurements over the North Atlantic, it was estimated that about 10 percent of the atmospheric sulfur leaving the east coast of North America reached the west coast of Europe. The ability of the atmosphere to transport pollutants in general, and sulfur compounds in particular, was thus well established.

The nature of urban air pollution began to change after the Second World War as populations increasingly shifted from rural to urban areas. In addition, the use of the private automobile rapidly expanded as a means of personal transportation. Particulate and sulfur concentrations at first peaked then decreased due to various clean-air measures enacted in the industrialized world, but the emissions of volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) increased dramatically. As a result, the chemistry within urban atmospheres, particularly in North America, became dominated by nitrogen rather than sulfur species. Under favorable meteorological conditions (warm temperatures and strong sunshine), the changed atmospheric chemistry led to the production of high concentrations of ozone, and the total mix of air emissions became known as photochemical air pollution (also commonly referred to as "smog"). This new urban pollution problem was first detected in the Los Angeles Basin in the 1940s, then over and immediately downwind from other large cities in the eastern United States. By the 1980s, photochemical urban

pollution was an issue in many of the world's largest cities where the appropriate meteorological and topographical conditions prevailed. Again, it was originally thought to be a local issue, but during the late 1970s and early 1980s, large regional scale episodes of ozone began to appear over vast areas of the eastern United States that often extended into the southernmost portions of eastern Canada and into New England. These high concentrations of ozone in rural regions well removed from the precursor sources could be accounted for only by the transport of pollution over distances of hundreds of kilometers.

2.2 The Overall Emission- Transport-Deposition Cycle

A full description of the chemistry of ozone formation is given in a National Research Council report (NRC, 1991). Figure 2.1 illustrates schematically the process pathways in the overall emission to deposition cycle for the photochemical pollutants NO_x and VOCs that are precursors for ozone formation. The chemical species, together with the main chemical reactions, are shown in the appropriate portions of the pathway. Because some of the required data are less easy to obtain, the ozone cycle is not as well quantified as the sulfur cycle, but many large monitoring and research efforts are currently underway to rectify this situation.

The cycle starts with emissions of oxides of nitrogen, “NO_x” (= NO + NO_2), into the atmosphere from a variety of biogenic and anthropogenic (mostly fossil fuel combustion) sources. The nitric oxide (NO) is rapidly converted in the atmosphere by the existing ozone (O_3) into nitrogen dioxide (NO_2) and oxygen (O_2). In the presence of sunlight (hν), the NO_2 is photo-dissociated back into NO and atomic oxygen (O). Finally, the O recombines with O_2 to form O_3 with a third molecule “M” acting as a stabilizer to take away excess energy. These reactions are represented by the following three equations:

$$NO + O_3 \rightarrow NO_2 + O_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Rl}$$

$$NO_2 + h\nu \rightarrow NO + O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{R2}$$

$$O_2 + O + M \rightarrow O_3 + M^* \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{R3}$$

Reactions Rl and R3 are controlled slightly by temperature, but the R2 reaction-the important one here-has a strong dependence on the intensity of the sunlight. In the absence of any other reactive chemical species in the atmosphere, the ozone concentration would reach an equilibrium (known as the photo-stationary state) controlled by these continuous formation and destruction processes. Observed ozone concentrations, however, are usually significantly higher than those predicted from the photo-stationary state. This implies that there are other species in the atmosphere that convert NO to NO_2 without destroying ozone.

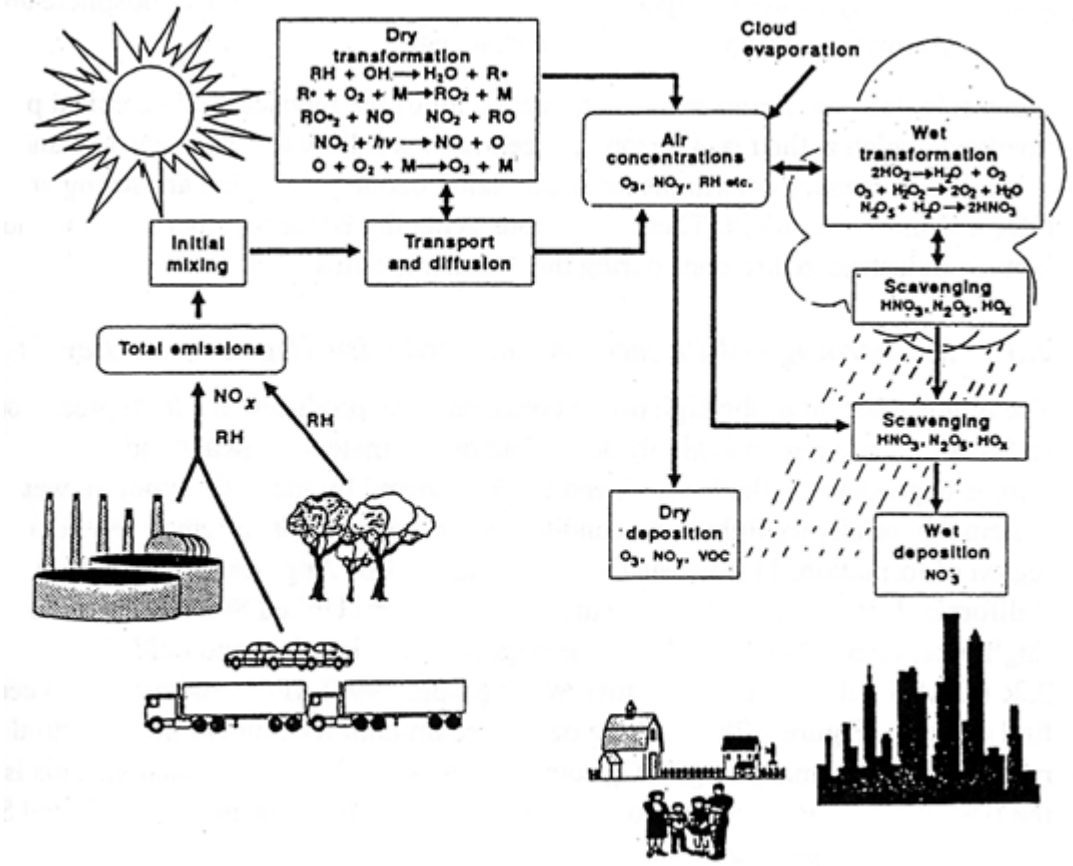


Figure 2.1 The emission-transport-deposition pathway for photochemical pollution. (Source: NRC, 1990)

These are primarily volatile organic compounds (VOCs), which are also called "reactive hydrocarbons" (RH) as shown in Figure 2.1. Reactive hydrocarbons are emitted from a wide variety of biogenic and anthropogenic sources. The main atmospheric reactions of this class of compounds are given by the first three equations in the dry transformation box in Figure 2.1. This chemistry is complex and involves hydroxyl radicals (OH) and organic radicals (R). The chemical processes are well known but many of the RH species are difficult to measure in the atmosphere and obtaining emissions information can be a challenge.

Meteorological conditions have an impact on all of the physical and chemical processes involved, which is the reason ozone concentrations follow a strong seasonal and daily cycle. The necessary conditions for maximizing ozone production are strong emissions of NO_x and intense sunlight. These conditions generally occur together in the world's mid-latitude industrialized regions during the summer months.

2.3 Meteorological Patterns Associated with High Ozone Levels

The regional extent of the high ozone concentrations produced in a high precursor emissions source region is highly dependent on the meteorological wind field. This, in turn, is dependent on the location and track followed by the main synoptic weather systems. In relatively light wind conditions, the ozone tends to remain within or near its region of formation. This is usually the case in the Los Angeles Basin of southern California. It is also often the case in the southeastern United States when an anticyclone (high pressure area) is located over the region, producing the wind field shown in Figure 2.2c (OTAG Ad Hoc Air Trajectory Work group, 1996). If the anticyclone is centered further north (Figure 2.2b), then the ozone accumulation occurs in the industrial Midwest region, an area of many large NO_x sources (e.g., coal-fired power plants). This is usually the first phase of an ozone episode that eventually affects the northeast United States as well. As the high pressure area moves off to the east, the wind flow increases from the southwest and transports elevated levels of ozone into the northeast United States as shown in Figure 2.2a.

A study in Canada (Yap, 1988) of the synoptic weather patterns associated with ozone episodes in southwestern Ontario shows that 19 percent occur with the high centered over the Midwest (Figure 2.3a) but the majority of cases (62 percent) occur with a high off the Carolina coast (Figure 2.3b) which leads to a moderate southwesterly flow from the Midwest into Ontario. A study of ozone episodes in Montreal and the Southern Atlantic Provinces (Figure 2.3c) also shows that most episodes occur during the same geographic association with a high pressure area located to the southeast.

2.4 Long-Range Transport

The previous discussion shows that most of the ozone episodes in the study area occur with a wind flow from the southwesterly direction coming from a region with strong emissions of NO_x. This transport occurs over distances of several hundred kilometers and is defined as long-range transport (sometimes referred to as regional transport).

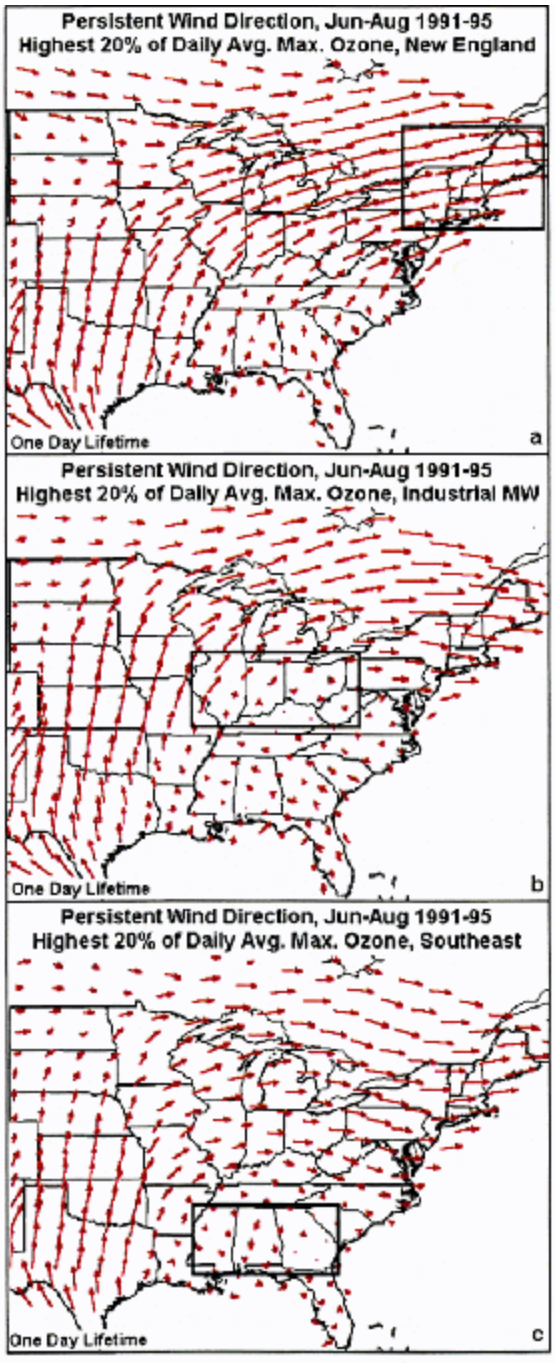


Figure 2.2 The persistent wind directions associated with highest 20% of the daily average ozone occurring in three regions of the United States during the months June to August 1991-1995. (Source: OTAG Ad Hoc Air Trajectory Workgroup, 1996)

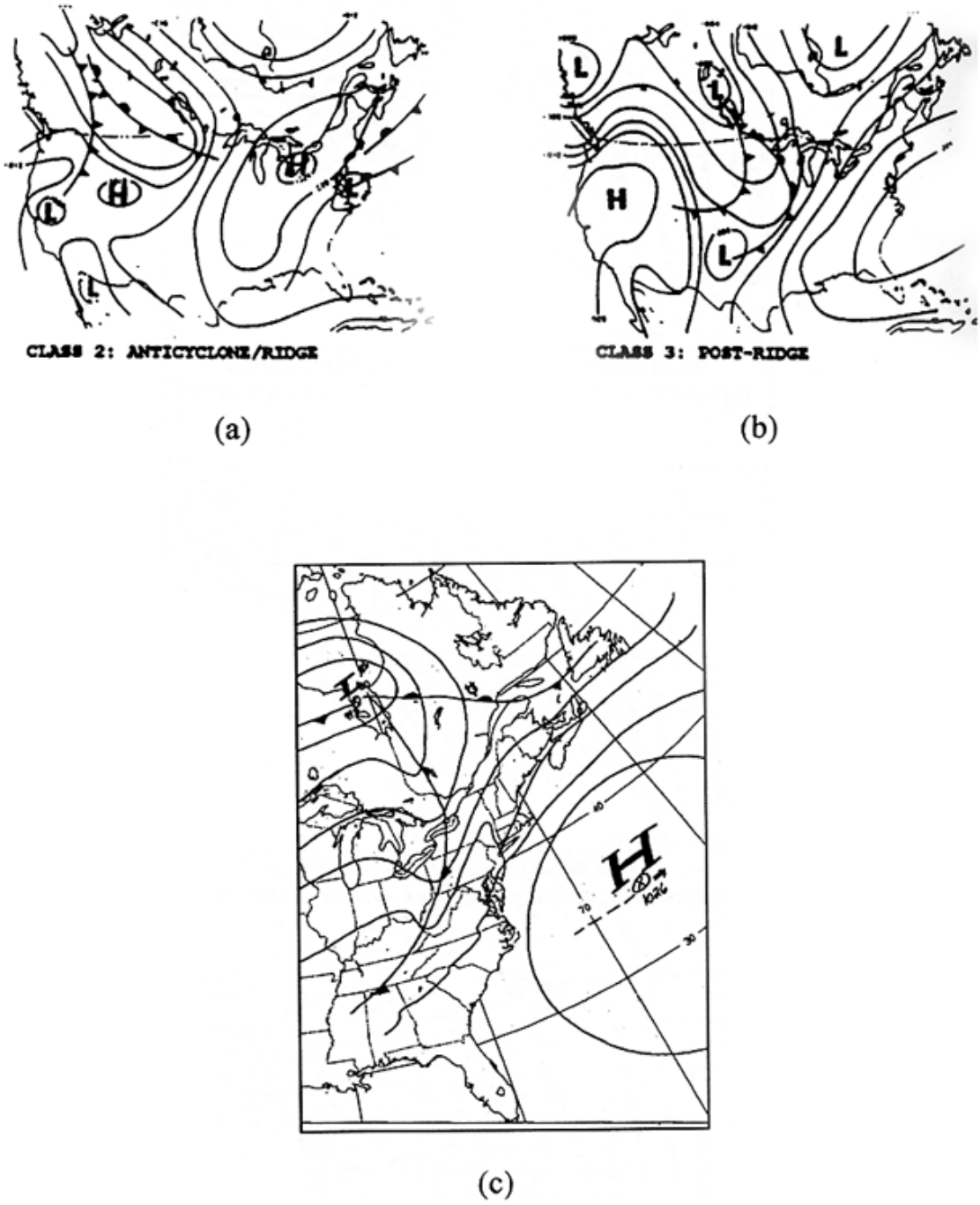


Figure 2.3 Synoptic weather patterns associated with ozone episodes in Canada
a) in southern Ontario 19% of cases,
b) in southern Ontario 62% of cases,
c) most common case in the Southern Atlantic Provinces.

(Source: Canadian Assessment, 1997a)

The frequency, duration and intensity of ozone episodes in any given summer is thus controlled by the general weather pattern over eastern North America. The pattern of particular interest is the track followed by the eastward migration of high pressure areas from the central United States towards the east. The behavior of this track is, in turn, controlled by the large-scale zonal upper-air wind flow (the jet stream) which varies considerably in mean location and intensity from year to year. If the track is further south than normal, the study area has a smaller than usual number of ozone episodes and a cool summer. If the track is further north than normal, then episodes occur more frequently along with a warm summer. The speed of motion of the synoptic weather systems also varies from year to year. With slower motion, the episodes tend to last longer and are more intense, as happened in 1983 and 1988.

3. Available Monitoring and Emissions Data

3.1 General Discussion

Many ambient air quality monitoring networks have been established in North America over the last several decades. Initially, these were in response to increasing air pollution levels in urban and industrial areas. The main pollutants monitored by relatively simple techniques were sulfur dioxide, particulates and smoke. Around large point sources such as power plants and smelters that were often in rural or remote areas, local monitoring was carried out to assess the impact of emissions and to ensure compliance with control measures as they were implemented. During the late 1970s, with the gradual realization that pollutants could be transported long distances from their sources (especially as higher stacks were being built), monitoring was introduced into more remote areas, particularly those that were ecologically sensitive. This monitoring expanded rapidly in the 1980s in response to the "acid rain" issue, and many regional and national networks were set up to monitor both ambient air and precipitation chemistry. Most of these efforts strongly emphasized sulfur chemistry.

Meanwhile, with the rapid growth of the petrochemical industry and the transportation sector, emissions of another set of chemical species, namely hydrocarbons, increased dramatically. With the increasing demands for electricity, the emissions of NO_x from large power plants also continued to rise, along with NO_x from traffic. These species are much more reactive than sulfur species, especially in the presence of sunlight, and lead to the formation of ozone. As the population in major urban areas in North America grew along with the use of road transportation, urban ozone levels increased. By the 1980s, these levels had become a large scale regional problem in the eastern United States, sometimes extending into regions of Canada close to the border. In response to the smog or ozone issue, many monitoring networks were set up, at first concentrating on urban and suburban areas and then on a more regional basis. In some cases, the monitoring of ozone and its precursors was merely added to the existing sites. In other cases, new networks were set up because of the need for greater spatial and temporal resolution in the observations.

In recent years, due to budgetary constraints, many attempts have been made, with some success, to combine or better coordinate these networks. Nonetheless, there is still a large array of networks operating in North America. Each has its own set of objectives, spatial and temporal resolution requirements, and suite of chemical species to be monitored. The Commission for Environmental Cooperation held a workshop in 1995 for which several background documents were prepared summarizing the then current status of atmospheric monitoring and modeling (CEC, 1995). The reader is referred to these reports and the Canadian Assessment (1997b) for a more complete description of the networks and maps showing all the station locations.

3.2 Ambient Ozone

Of all the species involved in the smog issue, ozone is the easiest to measure. The instrumentation is relatively inexpensive, easy to operate, and with routine calibration can give very reliable results. Instruments for measuring the range of concentrations generally observed in the atmosphere have been readily available for many decades. As a result, there are now some extensive records from which time trends of ozone can be evaluated.

From the point of view of assessing long-range transport, ozone data are required from monitoring locations that are defined by Environment Canada and the US EPA as being "rural." In general, most of the locations are regionally representative and located away from the strong modulations (either ozone formation or destruction) caused by local emissions. Monitoring stations meeting these requirements are shown in Figure 3.1. One exception is Torrington, Connecticut, a suburban site which is indicated on the map because it is referred to in another context in this report.

Although the same protocols are used in most of the many networks measuring ozone, the observations are not all stored in the same format in the respective data archives. It is not a trivial task, therefore, to combine the data sets in order to carry out analyses that span jurisdictions, for instance between Canada and the United States.

3.3 Ambient Precursors

The precursors from which ozone is formed in the atmosphere are described in section 2.2. These are more difficult to measure than ozone, especially in rural and remote regions that are far removed from the major emission source regions and where concentrations are often near the detection limits of standard instrumentation. As a result, routine monitoring of these species started later than for ozone and even now is much less spatially extensive. While NO and NO_2 can be measured with the same time resolution as ozone, many of the VOC species require measurements over longer time periods, from several hours up to a day, in order to obtain sufficient sample sizes for reliable results. Longer sampling times, however, are more problematic for reactive organic species such as isoprene, which have relatively short diurnal lifetimes. Just as with the different formats of ozone databases, precursor data are also not always maintained in the same format in Canada and the United States.

3.4 Meteorological Parameters

Meteorological parameters characterizing the physical state of the atmosphere have been measured at a few observatories around the world for as long as 200 years. As with atmospheric chemistry measurements, meteorological parameters and the locations at which they were measured responded to the requirements of the time. Initially, general climatological information was needed for agricultural and hydrological purposes. Once telegraphic communication became available, real-time data from coastal areas were of primary importance for the needs of an expanding

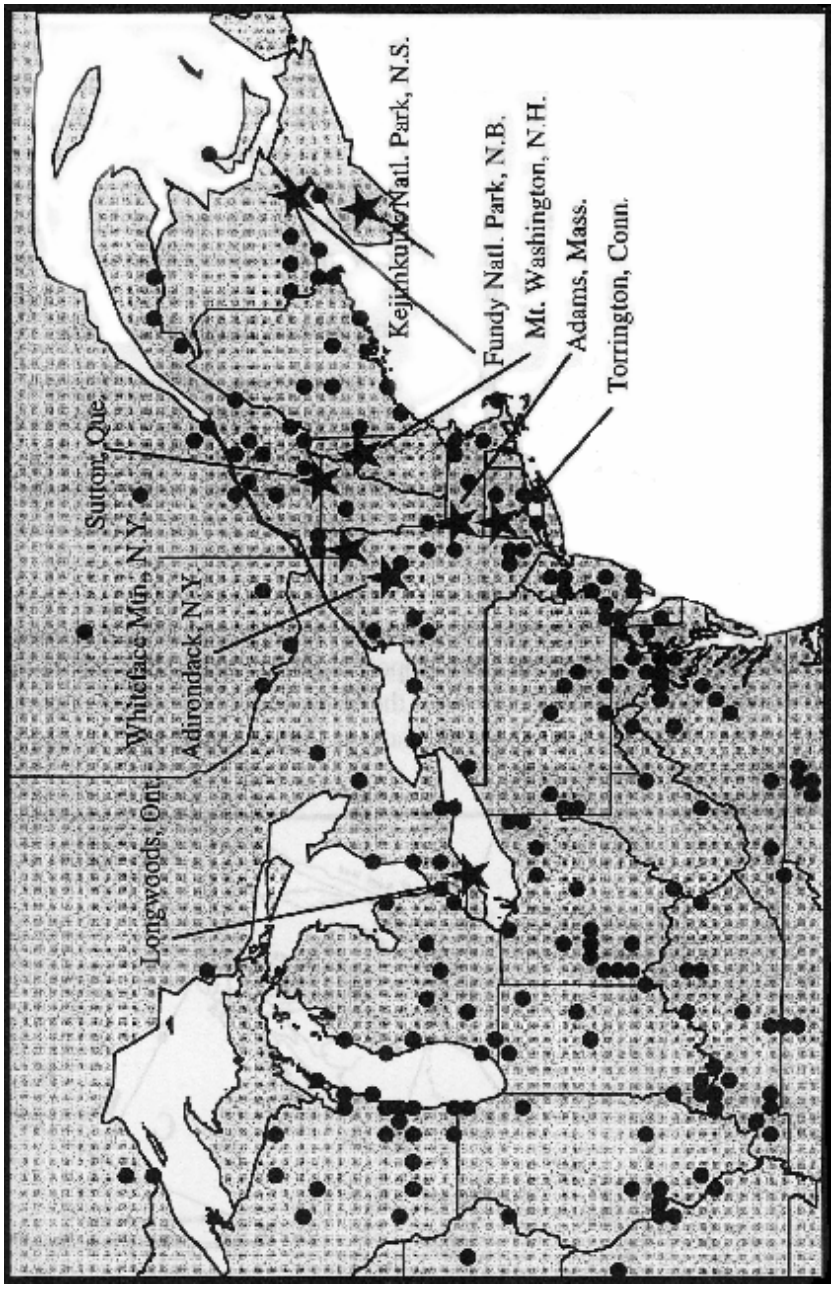


Figure 3.1 Map showing the location of the non-urban ozone monitoring sites in the northeastern US and eastern Canada. Also shown are some of the lesser known locations referred to in the text.

shipping industry. Ultimately, widespread, routine measurements became necessary with the rise of military and civil aviation.

The International Meteorological Organization (later to become the World Meteorological Organization-a technical agency of the United Nations) was established early this century specifically to foster cooperation among the meteorological services around the globe. Standard procedures were developed for the measurement and exchange of meteorological observations. Today, both real-time and climatological data are generally available in standard formats that are readily exchanged between countries. Data collection networks are designed to provide information on the synoptic weather scale. Surface observations are available every hour from a network of stations located primarily at major city airports. Typical spacing of these stations is in the order of one station per 100 kilometers over the eastern United States and extreme southern Canada.

Upper air observations of vertical wind profiles, temperature and humidity are obtained on a routine basis twice daily (at about 0700EST and 1900EST) at the sites in the study area shown in Figure 3.2. In this case, the horizontal spatial resolution is of the order of 500 km. Although these networks were designed specifically to meet the needs of aviation, they do provide sufficient information to calculate airmass trajectories. The trajectories can be used to assess the long-range transport of pollutants on the scale of hundreds of kilometers with reasonable accuracy for periods of up to approximately two to three days. The resolution, however, is not sufficient for monitoring the meso-scale meteorological flow patterns that are often important for understanding ozone behavior on the local scale. This is especially true near the Great Lakes and Atlantic shorelines, as well as other types of special topographical features. Field studies may be needed in these situations to obtain the relevant data.

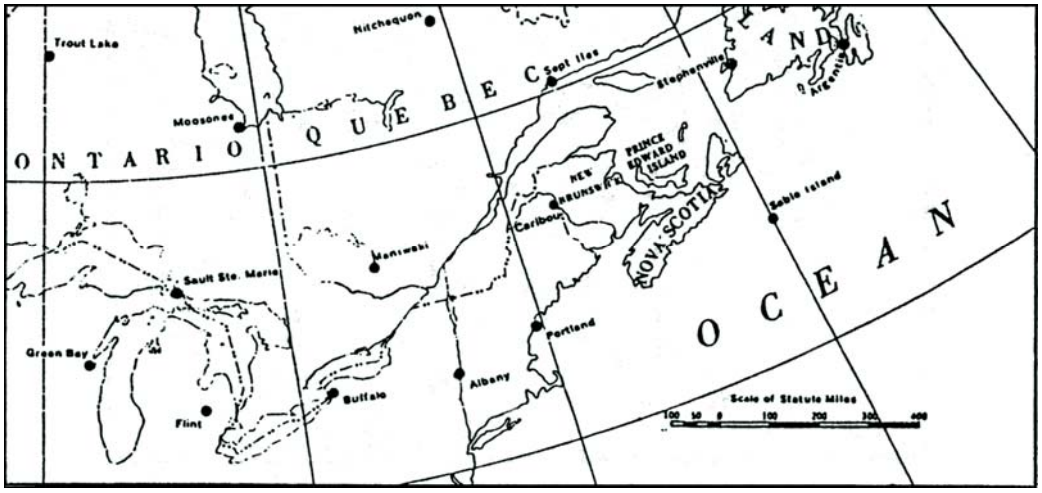


Figure 3.2 Map showing the location of the upper-air sounding stations within and near to the study region.

Another important parameter is the ultraviolet light intensity from the sun. This is measured directly at very few locations on a routine basis. Cloud cover, however, which is measured at all hourly reporting stations, can be used as a surrogate for some purposes.

3.5 Precursor Emissions Data

In the context of this report, emissions data are essential for two purposes:

- as input for air quality models, and
- understanding and interpreting the results obtained from analyses of air quality observations.

Actual emission rates are obtained by in-stack monitoring of most of the large point sources. The bulk of the information for smaller point sources and mobile sources is obtained by engineering estimates, albeit based on extrapolation from occasional field measurements and limited automobile exhaust testing. Most of the information required is collected by state or provincial pollution control agencies and collated into national data banks by federal agencies. The main purpose of these inventories is to support the development and tracking of pollution control strategies, and in many cases they are not in the most appropriate form to support scientific research activities. Indeed, the scientific community has devoted a large effort over the last two decades to restructuring these data into a format suitable for input into air quality models. For many species of interest, however, there is still a large mismatch between the time and space resolutions of the emission fluxes into the atmosphere and the time and space resolutions required in the models to accurately calculate the chemical and transport processes.

For a full description of emission inventory information, the reader is referred to the annual reports published by the environmental agencies in the United States and Canada. Tables, graphs and maps of the emissions of many of the relevant species are presented for each country separately. At present, it is not possible to obtain maps showing emissions data in common units, over and upwind of the study area, and in a uniform and simple to understand presentation format.

4. Data Analysis Techniques for Estimating Long- Range Transport of Air Pollutants

4.1 Analysis and Interpretation of Ambient Concentrations

4.1.1 Temporal Analysis

One of the easiest, and therefore most common, ways of analyzing and presenting ozone data is to generate time-averaged statistics of the observations at a single point. Such statistics are usually presented in varying detail in most annual reports from monitoring agencies. Although these basic statistics provide a useful characterization of ozone behavior on a variety of time scales at each station, they do not in and of themselves provide any information on long-range transport. Further analysis, however, involving comparisons of the time behavior at nearby sites, or comparisons of the time behavior at a given site for days when local or upwind emissions have changed, can begin to provide some insight. These studies can be divided into three categories: long-term changes or trends, changes within a given day, and changes between days.

Long-term trends

Multi-year time trends in ozone, NO_x and, to a lesser extent, VOC concentrations have been established at many locations in North America. In principle, by comparing these with trends in the emissions of NO_x and VOCs over the same time period, it should be possible to get an indication as to whether the ozone is responding to changes in local or regional emissions. In fact, this has been difficult to do and results have not been consistent.

Over eastern North America, the frequency of regional scale episodes varies considerably from year to year. Furthermore, the number of one-hour exceedances of 82 ppb or 120 ppb at any given location varies even more. During the last 18 years, two years (1983 and 1988) stand out for the severity of the ozone problem. Since emissions do not change very much on an annual basis, it seems that changes in meteorology drive the fluctuations, with maximum temperatures being a key parameter (1983 and 1988 were both very warm summers). Thus, in order to make sense of long-term changes in ozone concentrations and relate them to trends in precursor emissions, the meteorological signal must first be removed. Several statistical techniques have been used to do this (Canadian Assessment 1997). The broad conclusions that have emerged are that meteorologically adjusted maximum ozone concentrations have increased at most Canadian urban sites, but have slightly decreased at a few rural sites.

An analysis of ozone data in the eastern United States (Rao et al., 1995) showed that at nearly all sites daily maximum ozone concentrations, corrected for meteorology using temperature as the surrogate, declined slightly between 1983 and 1992. When the time series was split at 1988 (Zurbenko et al., 1995), the geographic plots showed that from 1982 to 1988, the ozone had either not changed or had increased slightly over much of the region. From 1988 to 1992, there was a general decrease over most of the area.

Ozone trends as summarized by Morris (1997) suggest moderate decreases in ozone concentrations in many (but not all) urban areas, but little change in rural areas. This would be consistent with a lack of significant NO_x reductions on a regional scale.

It must be noted that statistical studies only quantify and test the significance of associations between parameters-they do not prove cause and effect. In this case, because the signal is small and not always in the same direction, and the exact quantification of emission reductions is difficult, it is not clear how such studies can provide much in the way of useful information on cross-border transport. They may, however, corroborate the results from other studies.

Within day temporal changes

Temporal changes of ozone concentration, especially the geographic location of the ozone maximum, can provide useful information on local- and regional-scale transport. It has been noted that the afternoon peak in ozone concentrations is delayed by a few hours downwind from many large urban areas, and that high ozone values in the downwind areas tend to persist longer into the late afternoon and early evening. Because local photochemical production of ozone is decreasing by mid-afternoon, the continued local increase in ozone concentrations in downwind areas can only be accounted for by transport of ozone produced earlier in the upwind urban areas.

Perhaps the best example of this effect occurred along the coast of Maine on 21 July 1994 (NESCAUM, 1995). Figure 4.1 shows that with persistent southwest winds, the hour of occurrence of the ozone maximum progressed steadily later along the coast starting at 1200 EST at Lynn, MA and ending nine hours later at Jonesport, Maine. Data from New Brunswick (personal communication) for this date show that the progression does not move neatly into New Brunswick. Maxima, however, were recorded late in the day (1700 and 2000 EST) at two sites in the province.

Downwind from Vancouver, where topography constricts the pollution plume, the progress of peak ozone concentrations during episodes up the Fraser Valley is well documented. Also, this effect shows up in the long-term average time of the peak ozone.

In southwestern Ontario, the same effect is noted downwind from Toronto for episode days (O_3 > 82 ppb). At Stouffville (about 40 km northeast of the downtown core), the maximum is reached one to two hours later than the Toronto peak. During intensive field studies, a monitoring station at Hastings (150 km downwind from Toronto) detected the “Toronto plume” several hours later, with the peak value occurring on average at 1800 EST during August 1992.

At a rural site (Simcoe, just 12 km from the north shore of Lake Erie), both the long-term average and episode day (> 82 ppb) time for maximum ozone occurs in the late afternoon (about 1800 EST). This indicates transport from sources 150-250 km upwind in the Detroit/Windsor area or across the Lake Erie border.

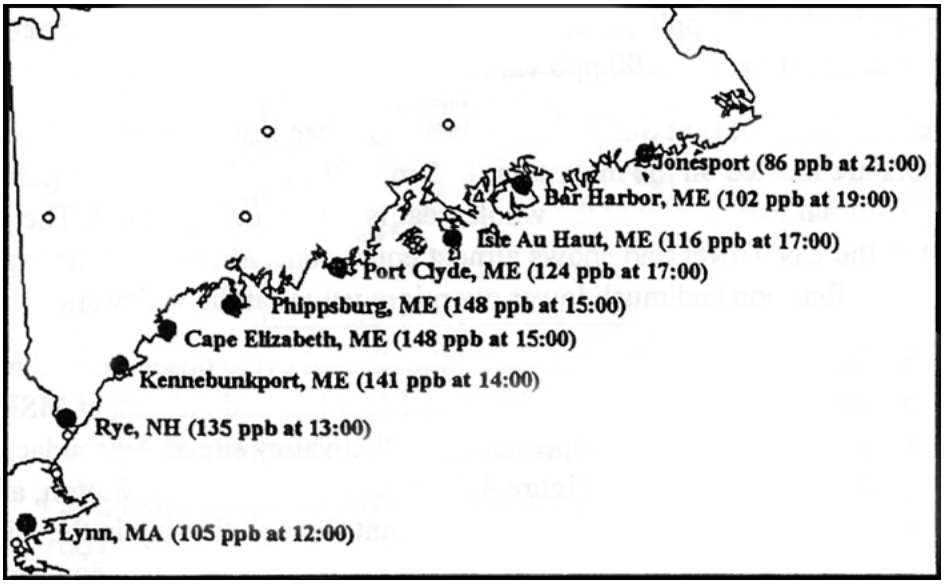


Figure 4.1 The steady progression of the time of maximum ozone occurrence up the Maine coastline on 21 July 1994. (Source: NESCAUM, 1995)

The diurnal variation of ozone concentration at Kejimkujik National Park in southern Nova Scotia is shown in Figure 4.2. Averaged over 24 episode days (max. O_3 > 82 ppb), ozone increases at the usual rate from its minimum concentration at 0600 EST in the morning until 1400 EST in the afternoon. It then increases at a slower rate during the late afternoon, reaching a maximum at 1800 EST, before slowly falling during the evening, and remaining relatively high overnight. On a few occasions, the daily maximum occurs in the early morning hours. On days when ozone exceeds 82 ppb at rural sites in southern New Brunswick, the peak value is reached during the early evening (1800 to 2000EST) and elevated values persist overnight. All of these are consistent with the findings along the Gulf of Maine coast and thus show that the transport does in fact continue northwards into the Bay of Fundy region.

Diurnal Variation at Nearby High and Low Elevations

Another important aspect of diurnal variation, is the difference in behavior between ground-level and elevated sites. There are two locations in Canada where simultaneous measurements of ozone concentration are made at two elevations. The first location is urban in the city of Toronto. One monitor is on the CN Tower immediately south of the city core on the north shore of Lake Ontario where measurements are made at an elevation of 524 meters above mean sea level (MSL). The winds are from a southerly direction, which makes the location directly exposed to transboundary flow from the United States.

The nearest ground-level site is to the west-northwest at Junction Triangle, about 4 km away in the city. This site is at an elevation of 116 m MSL. The average diurnal variation during episodes (O_3 > 82 ppb) is shown in Figure 4.3. Note the small amplitude at the tower site, with concentrations remaining above 50 ppb overnight and rising in the afternoon to about 90 ppb.

At the low site, concentrations fall to near zero at about dawn and rise to about the same 90 ppb value in the afternoon.

The second location is at Sutton in southeast Quebec just north of the Vermont border. Monitors are located on the mountain (845 m MSL) and in the valley (250 m MSL). The average diurnal variation over the whole year is shown in Figure 4.4. The pattern is similar to that at the CN Tower and shows almost equal concentrations at the top and bottom during the afternoon and much lower overnight values at the valley site.

The NESCAUM study (1992) compared the diurnal cycle observed at three high elevation sites (Mt. Washington, Whiteface Mountain and Adams, at MSL elevations of 1917 m, 1480 m and 1140 m respectively) with a valley site at Adirondack, New York (523 m). The results shown in Figure 4.5 are similar to those for Sutton, and show that the upper level values remained almost constant through the day in the 35 to 45 ppb range. Only during the mid-afternoon did the valley and upper site concentrations correspond.

An elevated site (but with no corresponding low-level site) is located at Fundy National Park at the northern end of the Bay of Fundy at a height of 350 m. This site, along with Mount Sutton, has the highest yearly mean concentration of ozone recorded in Canada — 36 ppb. There is a very small amplitude in the daily cycle, about 5 ppb on average and 20 ppb during episode conditions.

All of the above results corroborate, on a climatological basis, what aircraft have found for individual vertical profiles of ozone (see field study results in section 4.4). They clearly show that a semi-permanent layer of ozone at concentrations of 35 to 45 ppb exists over the study area at a height of several hundred meters above ground level. This is caused in part by the transport of aged ozone from far upwind emissions and in part by downward mixing of the mid-tropospheric pool of global background ozone. These findings are important because ground-level measurements alone can give false information on the actual amount of ozone in the lowest layers of the atmosphere and, therefore, the full magnitude of regional transport.

Between day temporal changes

Another use for temporal changes that in principle appears attractive is to look for the impact of a sudden change in an emission source. This was attempted when a large source of sulfur emissions changed dramatically at Sudbury, Ontario (during a prolonged strike) and in Tacoma, Washington (when a large smelter permanently closed). The resulting analyses and interpretation turned out to be more difficult than expected, but useful results were obtained concerning the contribution of these sources to regional air concentrations and the deposition of sulfur.

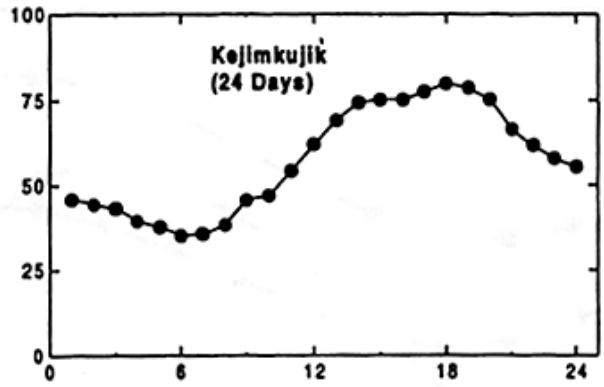


Figure 4.2 Average diurnal variation of ozone concentration at Kejimkujik National Park, Nova Scotia on days when ozone exceeds 82 ppb for the years 1986-1993.

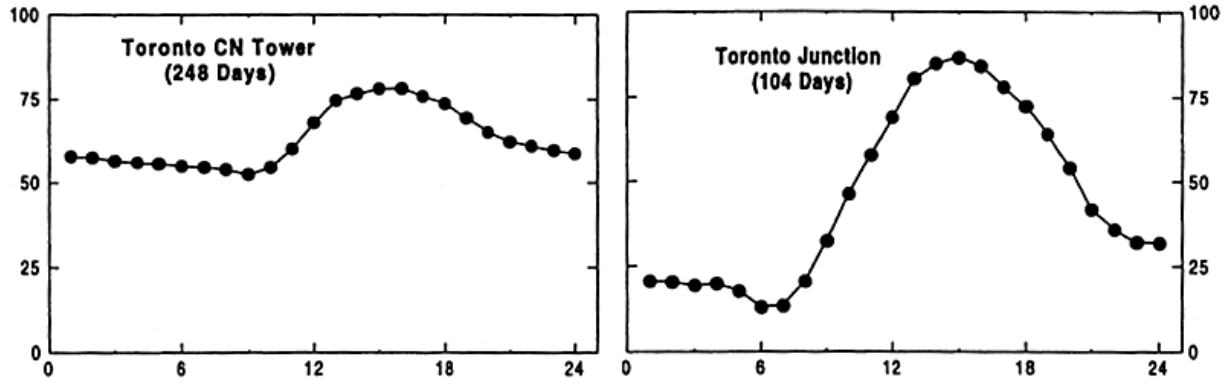


Figure 4.3 Average diurnal variation of ozone concentration at a high elevation (Toronto CN Tower) and a nearby low elevation site (Toronto Junction) on days when ozone exceeded 82 ppb during 1986-1993.

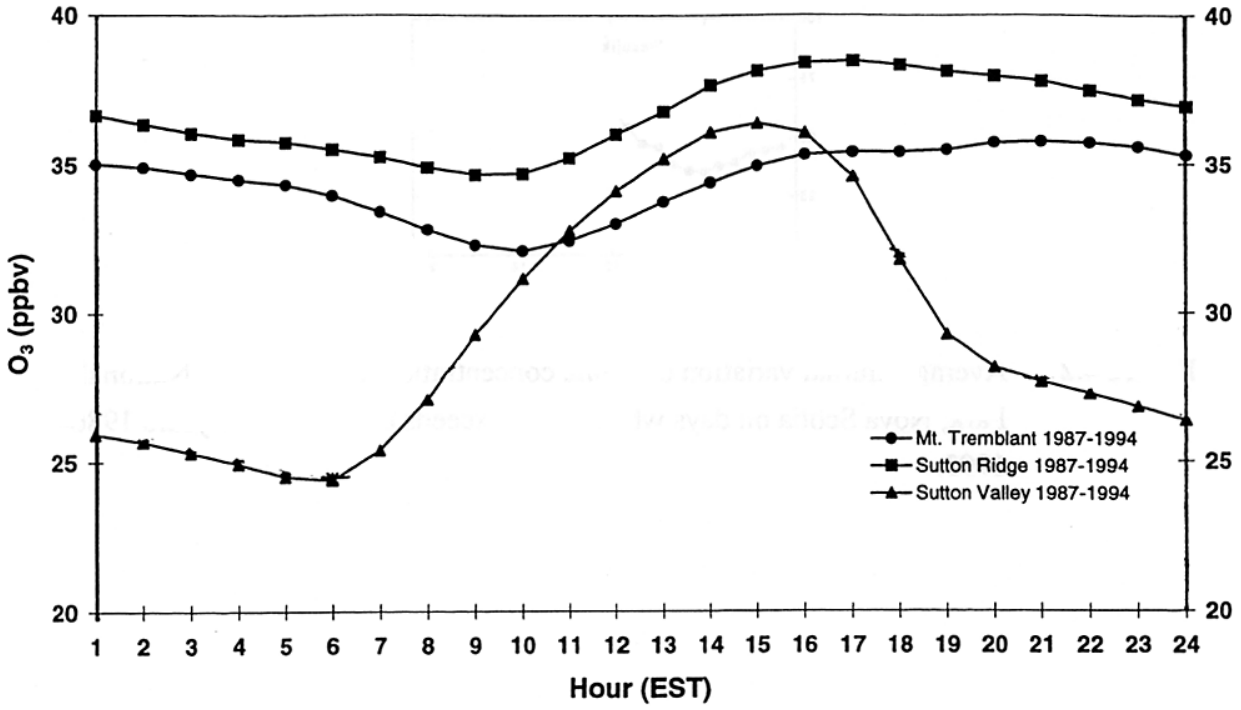


Figure 4.4 Average diurnal variation of ozone concentration (ppb) at adjacent high and low elevation sites (Sutton, Que.) and a second high elevation site (Mt. Tremblant, Que) over the whole period 1987-1994.

(Source: Canadian Assessment, 1997a)

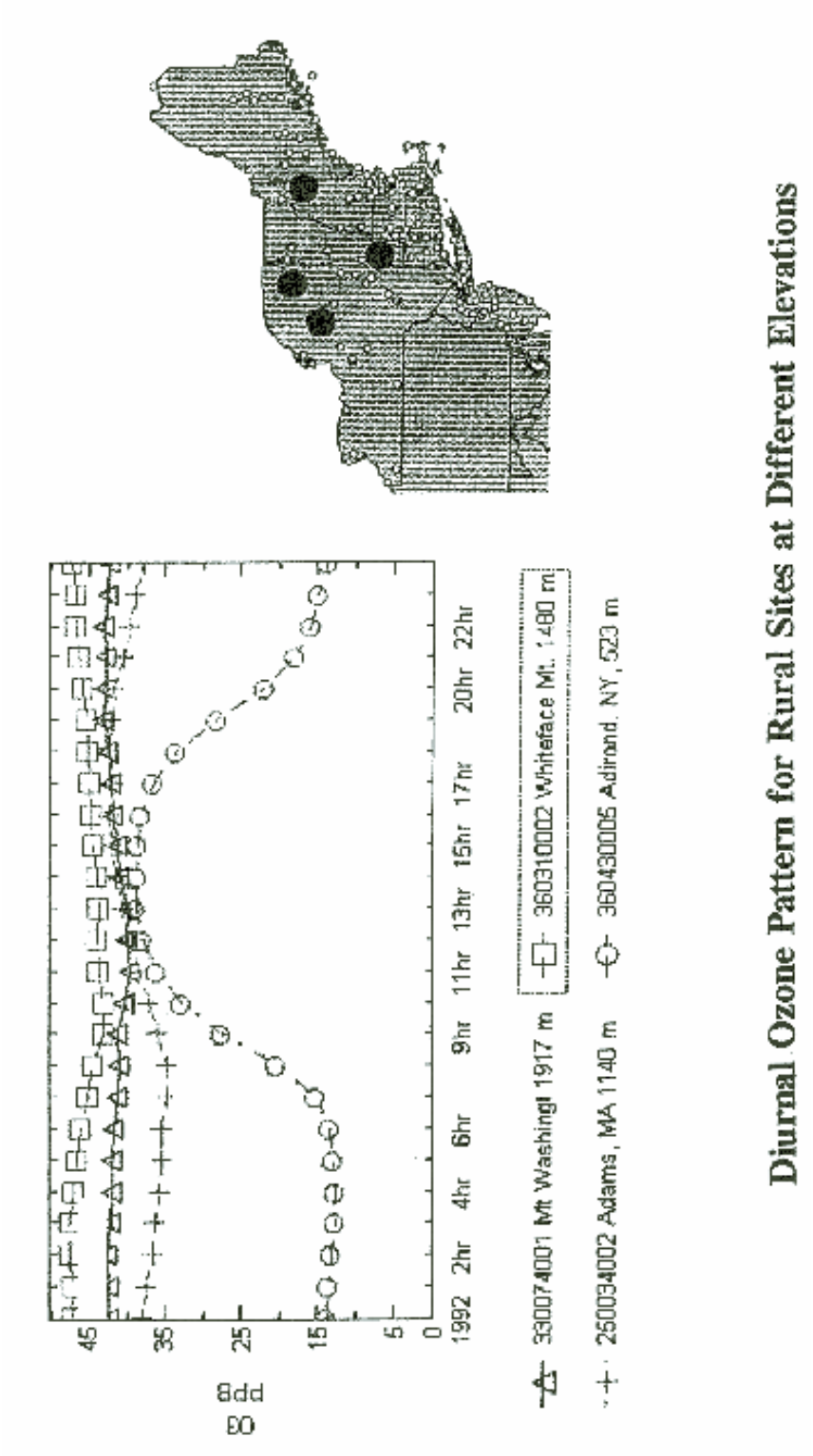


Figure 4.5 Average diurnal variation of ozone at three elevated and one valley location in the NESCAUM region during August 1992. (Source: NESCAUM, 1992)

In the case of ozone, no such large and continuing reductions of precursor emissions have occurred. There is a difference, however, between the weekday and weekend strengths, timing (hours of the day), and spatial distributions of one of the major sources for ozone precursors-vehicular traffic. Also, due to less industrial activity and lower power demand, many of the large point sources of NO_x probably emit less on the weekend. The impact of this has been studied on two scales.

On a large regional scale, Husar (1996a) has produced maps showing the pattern of the average 90th percentile concentration of ozone for each day of the week using AIRS and CASTNet data for June-August, 1991-1995. To study the "weekend effect," the difference between Friday and Sunday was plotted (Figure 4.6). A strong effect shows up in the regions downwind from the major urban complexes in Michigan and the northeastern United States, with the largest differences being > 15 ppb. Differences are small over the remainder of this region.

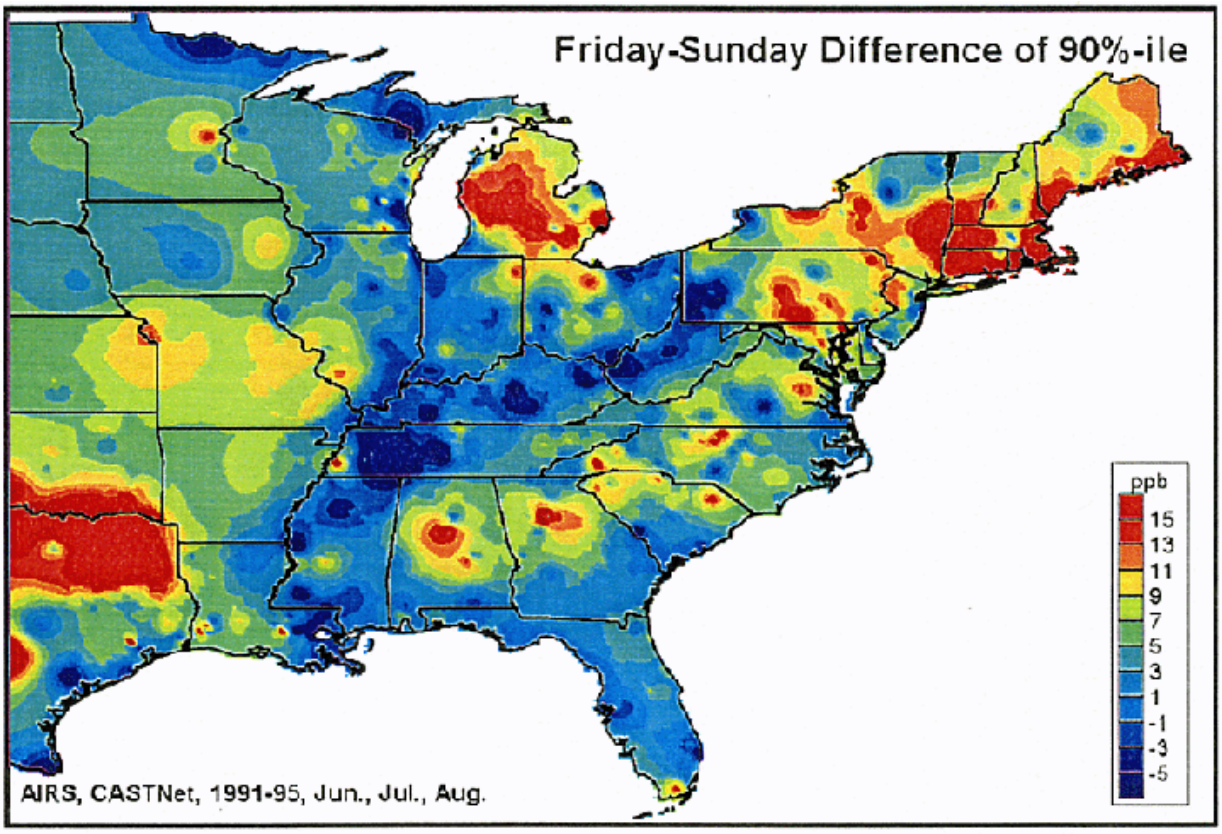


Figure 4.6 Difference between the 90th percentile value of ozone on Sunday and on Friday in the eastern United States based on June-August 1991-1995 data. (Source: Husar, 1996a)

The percentage of hours of exceedances (O_3 > 82 ppb), sorted by day of the week for stations in the Southern Atlantic Region, are shown in Figure 4.7 (Beauchamp, personal communication). Although these graphs were not interpreted in detail or compared to other information, the Nova Scotia data demonstrated a large drop in the number of exceedances from Friday to Sunday, thus corroborating the results along the New England coast (Figure 4.6), where the 90th percentile value drops by over 15 ppb. Furthermore, the drop is still evident on Mondays. Thus, if the precursor emissions are reduced on Saturday and Sunday, then the one-day time lag of the reduced number of exceedances strongly suggests that it is the emission sources located one day upwind that are having a major impact. On the other hand, however, sites in Nova Scotia over the same period showed a significant increase in the number of exceedances from Friday to Saturday before dropping on Sunday. Additional study will be needed to discern what trends are occurring in this region due to changes in emissions from weekdays to the weekend.

A detailed study of the diurnal cycle difference between weekdays and weekends in Canada for the summer months over a 14 year period produced some interesting results (Canadian Assessment, 1997a). In large urban centers, there was a significant increase in the average afternoon peak ozone on weekends. The effect was most pronounced at stations located close to busy traffic routes. The effect was attributed to the lower NO emissions from traffic on weekend mornings and, therefore, a reduction in the early morning scavenging of ozone that is usually evident in urban areas. As a result, the ozone concentrations started off higher in the morning and, with the same rate of photochemical production, the resulting afternoon peak was higher on weekends. No direct comparison can be made with the Husar results because extreme value changes were not examined in the Canadian study. At rural sites there was no significant change on weekends and thus the effect appeared to be confined to urban areas.

An analysis by NESCAUM (1992) compared daily average ozone levels by day of the week during the summer months for several sites in the study area as shown in Figure 4.8. At urban sites, there was an increase in the average ozone on Saturday and Sunday, but a reverse effect at rural sites, including the Whiteface Mountain and Adams sites. Further analysis showed no difference in average temperature by day of the week. It was concluded that changes in human-related emissions were driving this effect.

The daily average concentrations of hydrocarbons emitted by the transportation sector measured at Kejimkujik, Nova Scotia during the summer of 1991 (Bottenheim and Shepherd, 1995) also showed a significant weekly cycle. The lowest values were on Sunday and Monday, again suggesting a one-day time lag with upwind emission reductions.

4.1.2 Spatial Analysis

The most visual method of establishing the link between ozone and its precursors is to compare their respective geographical distributions. Perhaps the first large-scale map of regional ozone concentrations was produced for the eastern United States by Vukovitch

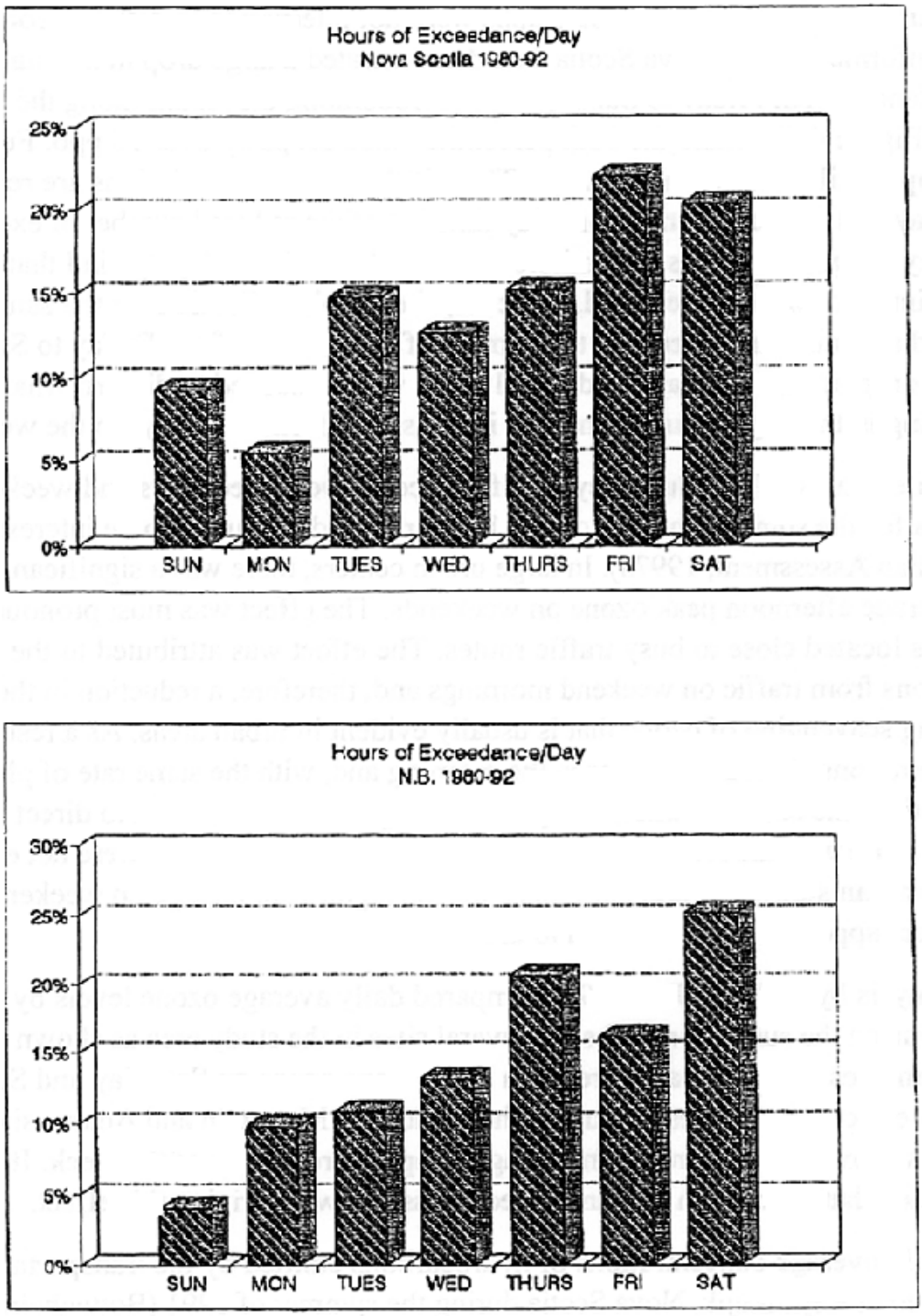


Figure 4.7 The percentage frequency by day of the week of the number of exceedence hours at rural sites in Nova Scotia (N.S.) and New Brunswick (N.B.) over the period 1980-1992. (Source: Beauchamp, personal com.)

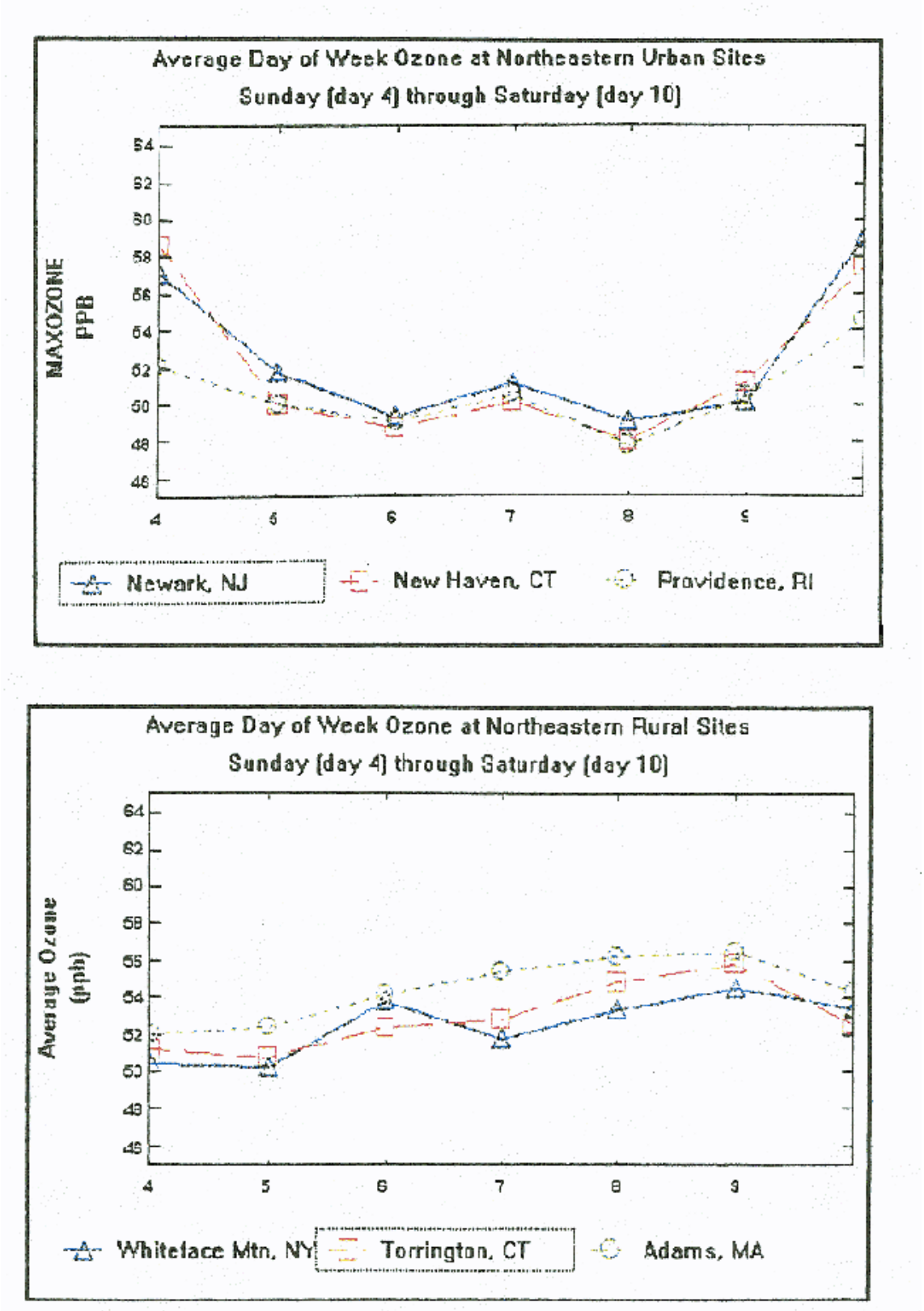


Figure 4.8 Based on May-September 1987-1992 data. (Source: NESCAUM. 1992)

et al. (1977). The map of the average summertime daily maximum ozone concentrations showed what appeared to be a "plume" originating in eastern Texas and expanding in width and intensity eastwards across the Midwest to the Atlantic seaboard. This is consistent with the high density of precursor emissions and predominating westerly winds across the same region, and suggests an eastward transport of ozone. Later analysis by Wolff and Lioy (1980) discussed the formation of an "ozone river" flowing over the eastern United States under the appropriate synoptic weather conditions.

More recent maps (Canadian Assessment, 1997a) prepared from a much more extensive database show that the regional extent of high ozone concentrations over the eastern half of the continent has expanded since 1977. The data show that high ozone levels occur, over a vast region of the rural countryside, in many cases at locations more than 100 kin from the nearest NO_x precursor emissions. The patterns for the number of days, or the number of hours, exceeding the threshold of either one-hour 82 ppb or 120 ppb show a similar geographical distribution. There is an isolated region of high values in the lower Lake Michigan area extending across the state of Michigan, but the main belt extends from the Ohio River Valley towards the Atlantic coast, expanding in width towards the east. There is a strong gradient along the northern edge of this belt with values falling off rapidly into southeastern Canada and northern New England.

A statistical analysis of large regional-scale ozone episodes in eastern North America over the period 1986 to 1993 (Canadian Assessment, 1997a) shows that on average about 24 percent of the episodes in the eastern United States extended northwards into southern Ontario. There is, however, considerable year to year variation in this frequency due to the mean summertime position of a high pressure area (called the "Bermuda high") that is conducive to transport of ozone and its precursors. In 1988, the Bermuda high was more persistent and farther north than usual. As a result, the frequency of episodes extending into southern Ontario increased to 43 percent. By contrast, in 1993, it was as low as 6 percent. There were no cases of significant ozone episodes in southern Ontario without one south of the border.

Figure 2.2a shows the average wind pattern associated with the highest 20 percent of daily average ozone maxima in New England. The pattern indicates flow from the southwest around the Bermuda high located off the Carolina coast. The most common weather situation associated with ozone episodes in southern Ontario and the Southern Atlantic Provinces is also a Bermuda high off the Carolinas (see Figure 2.3). These common weather patterns show that the entire region is linked meteorologically, regardless of geo-political boundaries, when a regional flow of air occurs from the southwest into Ontario, New England, and the Southern Atlantic Provinces.

On a smaller, regional scale, the Lake Michigan Ozone Study (LMOS) generated a very extensive database (including aircraft observations) for an intensive field study in the summer of 1991. Morris (1996) summarized the results of the detailed analyses and interpretation of these data. Again, key findings were that significant amounts of ozone were transported into the Lake Michigan Air Quality Region and that the upwind regions contributed 40-60 percent of the ozone peaks.

Figure 4.9 shows that ozone concentrations averaged over five summer seasons in a large region of the Midwest are about 15-20 ppb higher than in the peripheral regions of the map (Husar, 1996b)

when looking at the whole statistical ozone distribution from the 10th percentile to the 90th percentile. This persistent reservoir of ozone is related to the high density of precursor NO_x emissions in the Midwest region and forms the elevated baseline of ozone concentrations upwind of the study area (recall the typical airflow patterns displayed in Figures 2.2 and 2.3).

4.1.3 Statistical Methods

Statistical methods are useful to suggest relationships between ozone and a whole range of possible predictors. Multiple linear regression and factor analysis are common techniques that have been used, but which have shortcomings. A more powerful and accurate technique developed in the 1980s is the Classification and Regression Tree Analysis (CART) which can be applied in cases where the predictors may be correlated and the actual relationships between the predicted ozone concentrations and predictors are non-linear.

The CART technique has been applied in several regions of Canada using a large number of meteorological predictors (Burrows, 1995). These predictors can be ranked in order of importance in explaining the variance of the computed multiple correlations. In all cases, maximum temperature is at or near the top of the list. In southern Ontario (Canadian Assessment, 1997a), the second ranking predictor was the airmass trajectory path with a southwest flow being associated with the highest class of ozone levels. This indicates the transport of precursors and/or ozone from the southwest.

Another powerful statistical technique is to apply spectral analysis to time-series of ozone data. This was done by Rao et al. (1997) and three components were clearly identified:

- a long-term component,
- a seasonal component driven by the annual cycle of meteorological factors, and
- a short-term component driven by synoptic-scale weather fluctuations.

The sum of the first two components forms the baseline ozone level. It retains global information on a time scale of more than two months and a space scale of more than 300 km.

The last component is the one relevant to the long-range transport issue. The spatial scale over which ozone is highly correlated and retains spatial information is 600 km (Rao et al., 1997). An analysis of the spatial correlation of ozone in southern Ontario using simple linear regression (Burnett et al., 1994) showed a similar relationship between R and distance. Furthermore, Rao et al. (1997) showed that the time scales for the correlation varied from 1 to 2.5 days depending on location. In the southeastern United States, the time scales for both ozone and temperature correlations is associated with slow-moving weather conditions, and in the northeast with fast-moving systems. This is consistent with the flow patterns associated with high ozone concentrations shown in Figure 2.2.

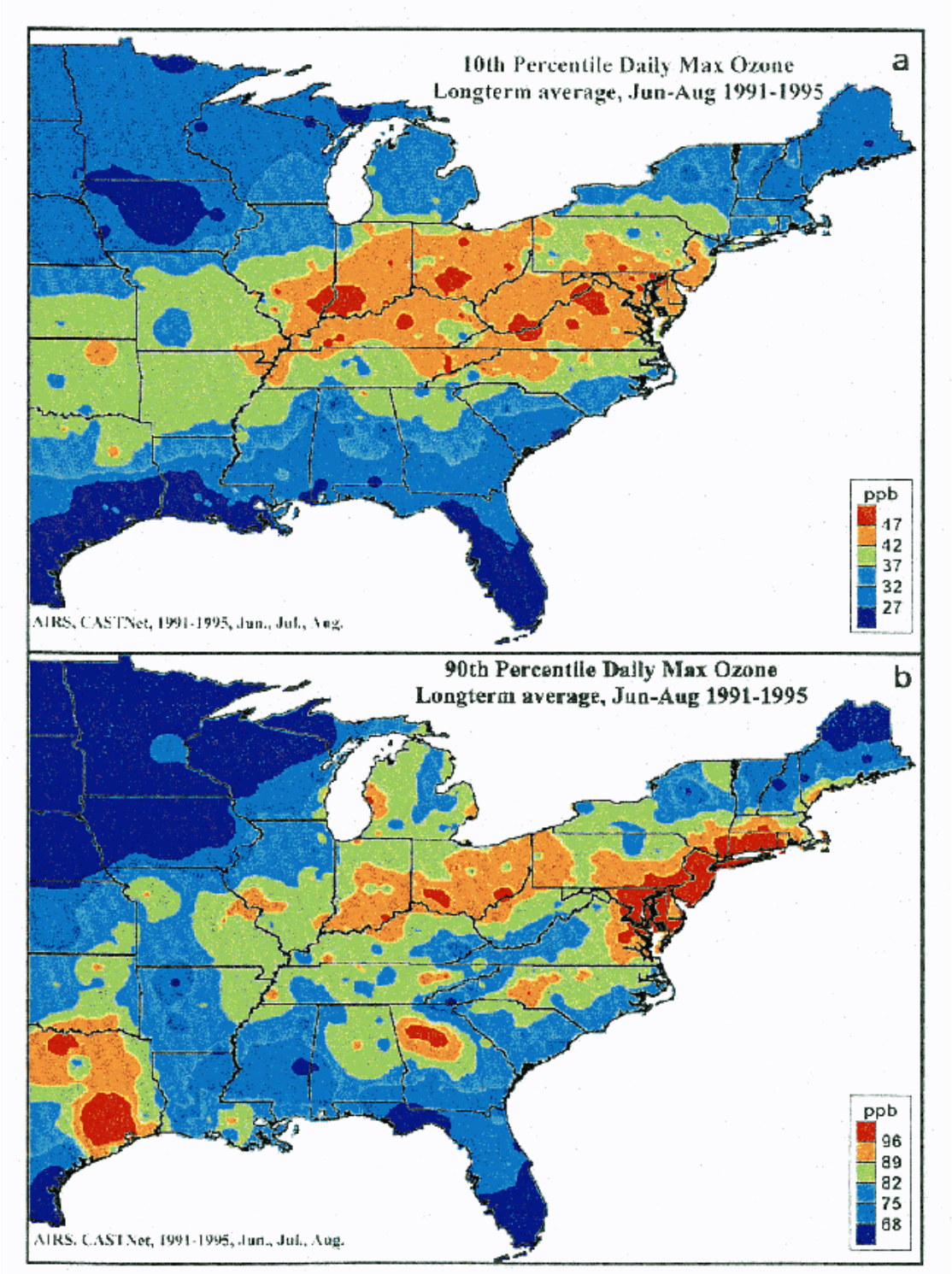


Figure 4.9 The persistent reservoir of summertime ozone over the Midwest indicated by the broad region of elevated values of both the 10th and 90th percentile ozone concentrations averaged over the months of June-August 1991- 1995. (Source: Husar, 1997b)

The correlation pattern for the short-term component of ozone concentrations can be presented in the form of concentric isopleths of decreasing correlation coefficient centered on the base station (Rao et al., 1998). This approach has been applied to five sites in the eastern United States as shown in Figure 4.10. The spatial pattern is similar at all sites with the correlation falling to 0.4 at a distance of about 500 km, showing that ozone concentrations are spatially coherent over large areas and that ozone is a regional-scale phenomena.

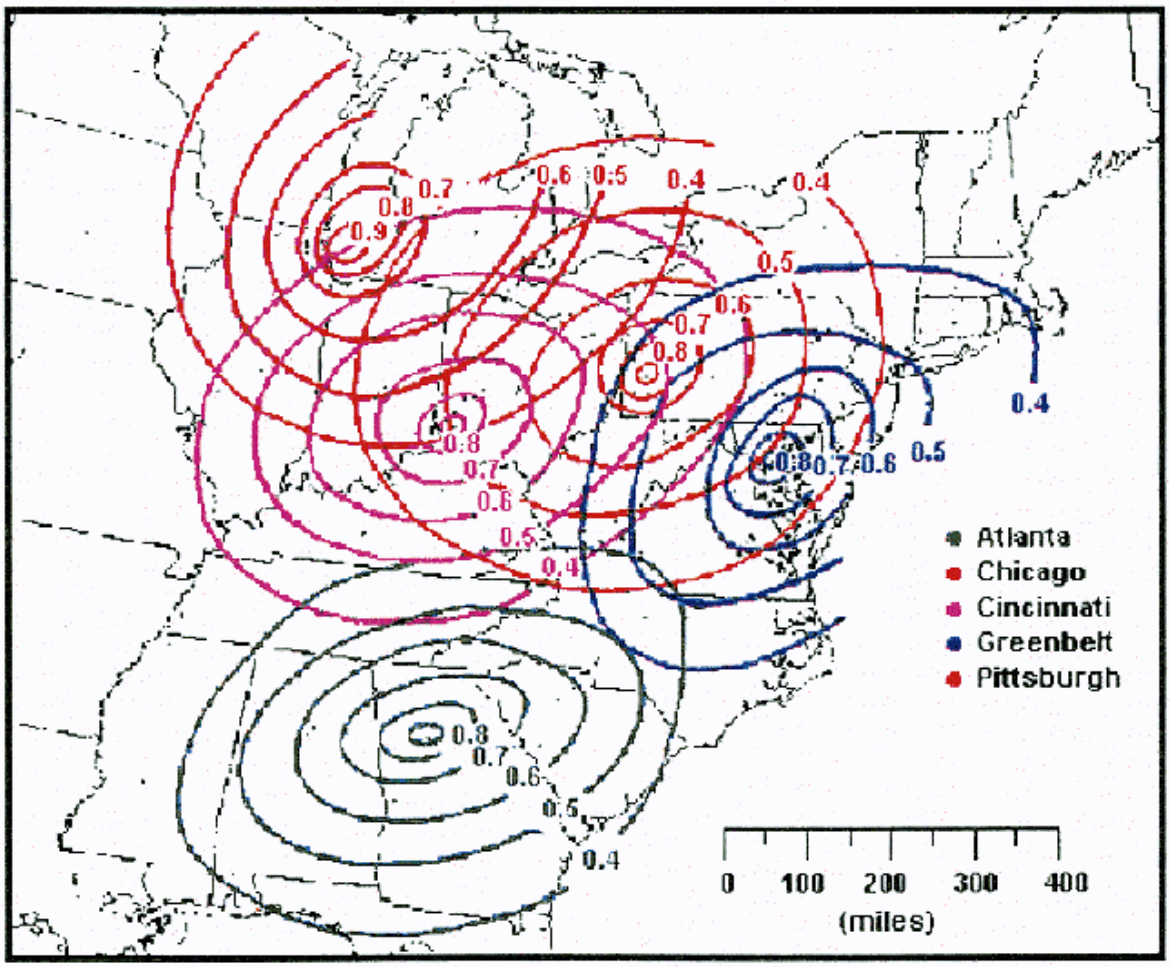


Figure 4.10 The spatial distribution of the correlation coefficient of the daily maximum ozone concentration compared to that at each of five central locations. (Source: Porter et al., 1996)

4.2 Combined Meteorological and Data Stratification Analysis

4.2.1 Local Wind Direction Sector Analysis

Surface wind speed and direction is often measured at air quality monitoring sites or, if not, is available from nearby meteorological stations. The pollutant concentrations can then be associated with a concurrent wind direction. The wind is then broken down into directional sectors (usually eight) around the compass and statistical distributions generated for the pollution data within each sector. Differences in the mean and extreme values between sectors are then evident. This technique was commonly used in early analyses of air quality monitoring data and proved to be useful for identifying potential sources that could influence the measured concentrations.

One of the earliest documentations of regional-scale ozone resulted from studies of tobacco fleck in southwest Ontario, where ozone was identified as the cause (Mukammal, 1965). Subsequently, Mukammal et al. (1982) showed that the highest ozone concentrations were associated with a southwest wind flow across Lake Erie. Analysis of the directional wind patterns associated with high ozone concentrations in the northeastern United States (Wolff et al., 1982) identified source regions to the southwest in the midwestern United States.

A disadvantage of this approach is that several emission sources may exist within a given wind sector, and this type of analysis on its own cannot distinguish between the relative contributions of nearby, versus distant, upwind sources. This limitation can be overcome by carrying out the analysis concurrently at several receptor sites and using triangulation to zero in on possible source regions. Another problem is that the local surface wind (which is often affected by local topography) is not necessarily a good measure of the actual pathway followed by an air parcel over the preceding few hours or days. This problem, which can be reduced by relating the observations to airmass trajectories arriving at the monitoring site, rather than the local wind, is discussed in the next section.

One exception where local winds are more indicative of the general wind flow is at high elevation sites. Eight years (1987-1994) of hourly observations were collected at Mount Sutton in southeastern Quebec (about 15 km north of the Vermont border) at an elevation of 845 m. There is also a site in the valley at an elevation of 250 m that enables the differences in behavior of ozone at the surface and in the free atmosphere to be studied. The upper site has continuous wind measurements, so each hourly ozone value can be associated with a local wind value. All observations were classified into one of eight 45 degree directional sectors and monthly averages produced as shown in Figure 4.11, taken from the Canadian Assessment (1997a). There is only a small difference between the sectors during the cold months (November through April). In the warm season there is a large spread in monthly average ozone concentration between sectors. The southerly sectors have the highest concentrations and the northerly sectors have the lowest. From June until September, the south to southwest sector has average concentrations about 7 ppb higher than the next highest sector between the southwest and west, and about 15 ppb higher than the average of all the data.

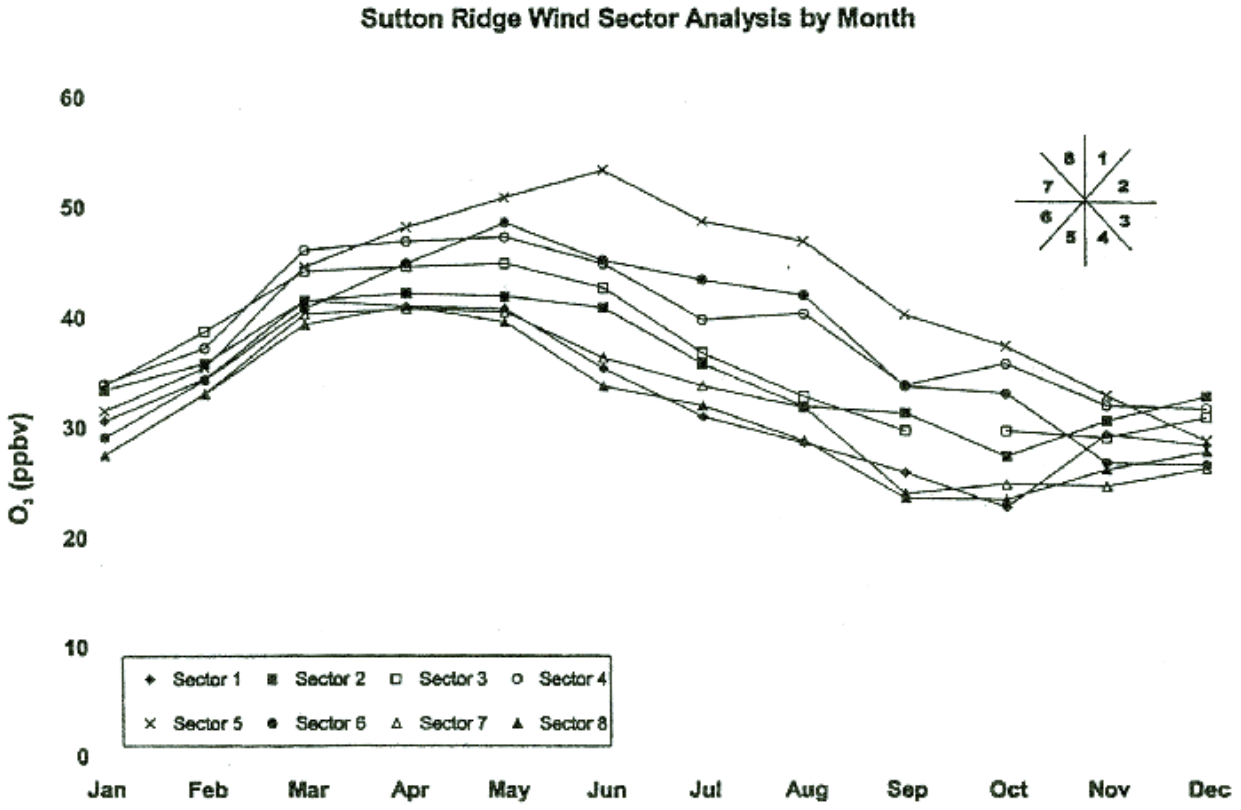


Figure 4.11 The average monthly ozone concentration sorted by eight local wind sectors for the Mount Sutton ridge site for the period 1987-1994.
(Source: Canadian Assessment, 1997a)

The first sector involves transboundary transport only from the United States. The second sector would include both Ontario and US sources. When this result is combined with the lack of any significant diurnal variation aloft (Figure 4.4), it provides strong evidence for long-range transport at this elevated level during all hours of the day.

4.2.2 Airmass Trajectory Analysis

Airmass trajectory analyses have been increasingly used over the last two decades as a relatively simple technique to obtain an easily understood, and sometimes quite dramatic, visual display of source regions for the air arriving at a given receptor site. When the trajectories are stratified by receptor site pollution concentration ranges, and the trajectory maps are overlaid on emission density maps, there is a strong qualitative geographical association between the two. This approach was used successfully in the early days of the acid rain studies (especially in Scandinavia and eastern Canada) to identify potential source regions up to 1000 km from the receptor site. The success was due in part to the fact that sulfur mass is a conservative quantity (i.e., once emitted into the atmosphere it is not destroyed or converted into a non-sulfur containing compound). It is removed from the atmosphere only by deposition processes and has a lifetime in the atmosphere on the order of a few days.

In the case of ozone and its precursors, this technique must be used with some caution because of the shorter and more variable atmospheric boundary-layer lifetime of the chemical species involved. Also, ozone is a non-conservative quantity. Near the ground, it has a strong diurnal cycle in which it is being formed during the day and depleted during the night. At only slightly higher elevations, nighttime depletion is much less significant and winds are usually stronger so that the total boundary-layer column ozone transport is not uniform with height. Nonetheless, trajectory plots are still of value for identifying, the pathway of air parcels and the potential source regions for ozone precursors.

Figure 4.12 shows two-day back trajectory plots for all days when the maximum ozone concentration exceeded 80 ppb at eight or more stations in southwestern Ontario during the summer months of 1988-1991. They indicate a source region for ozone precursors from the sector between west and south. Note that due to differences in the weather patterns between years, the flow in 1988 was more from the west-southwest, implicating different sources than in 1991 when the flow was more often from the Ohio River Valley region.

An extensive analysis of the synoptic weather patterns and the trajectories associated with ozone episodes in southern Ontario was carried out by Yap et al. (1988). It was found that in over 95 percent of the cases the air had arrived from the south or southwest after having traversed the high emission regions south of the Great Lakes. In an attempt to quantify the local versus cross-border contribution to ozone in southwest Ontario, the summer data from four stations near the border were selected for cloud-free days with high solar insulation. These data were then further separated into days with flow from within Ontario and days with flow from the United States' sector.

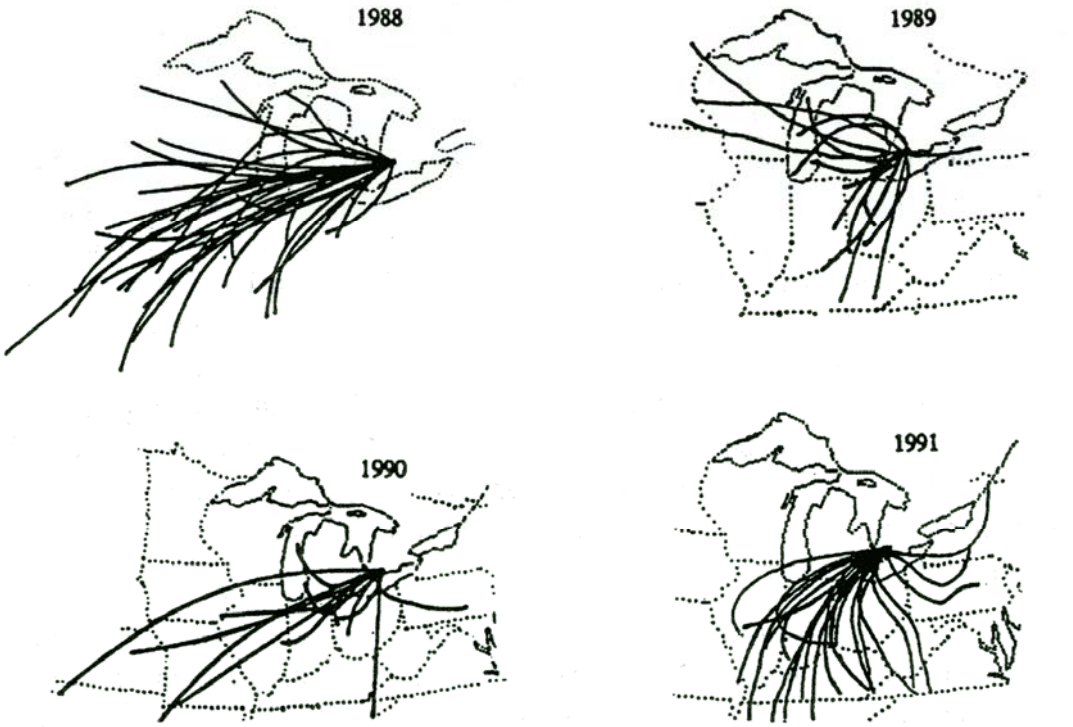


Figure 4.12 Two-day back trajectories at 925 hPa(mb) from Longwoods for each day with maximum ozone greater than 80 ppb at eight or more stations in southwestern Ontario. (Source: Canadian Assessment, 1997a).

The average diurnal cycle was then constructed for each set of data (see Figure 4.13). The difference between the two was then assigned to the cross-border contribution. The results indicated a cross- border contribution of about 20-30 ppb to the daily average and about 30-50 ppb to the daily maximum, which constitutes an overall cross-border contribution of 50-60 percent to the ozone measured in southwest Ontario. Note that this result is consistent with the findings of the Lake Michigan Ozone Study in terms of upwind contributions from the transport of ozone itself (see section 4.1.2).

In the Southern Atlantic Region (SAR) of Canada, 14 years of ozone data at several monitoring sites were used to identify all occasions with ozone exceedances (O_3 > 82 ppb). The back trajectories at three different altitudes were calculated for these events and then sorted into six equal sixty-degree sectors for direction of origin. The results are shown in Table 4.1 (Torden et al., 1994; Canadian Assessment, 1997a). The choice for the most appropriate height for trajectories is difficult for this region because of the local topography and the effects on windflow by the cold waters in the Bay of Fundy. The results indicate that at the surface level there are an overwhelming number of cases with flow from the northeastern United States. Also at this level, there is a small percentage of flows from the south off the Gulf of Maine suggesting a return flow of ozone that had previously moved off the coast. At the 925 mb level (approx. 800 m), the flow is more from the west due to the natural veering of the wind with height. If transport occurs at this level, then sources to the west are implicated. The main conclusions from this study are that there is significant transboundary transport into the SAR region, and that both the northeastern United States and the Windsor-Quebec corridor are sources of precursors, with the former predominating.

As an alternative to first sorting the ozone concentrations into classes and then averaging trajectories, the trajectories can first be sorted and then the statistical behavior of the data in each trajectory class can be examined. This was done by Brankov et al. (1997) and Brankov and Rao (1997) using a combined trajectory-clustering-correlation methodology. The cluster analysis was first applied to a set of 612 trajectories at Whiteface Mountain, which led to the identification of eight clusters. The short-term component of the ozone data (that related to the synoptic weather patterns - see section 4.13) is presented as a statistical distribution in the box-whisker plot of Figure 4.14. The results show a higher median and extreme value that is associated with the southwest, south and southeast trajectory clusters. The average trajectory for each of the eight clusters, together with its percentage of the total number, is shown in Figure 4.15. The shading shows three different levels of ozone concentration, with the highest level in the darkest shade. A further analysis was done using the southwest trajectory cluster ozone data at Whiteface Mountain and correlating it to all other stations within the spatial extent of the cluster using zero-, one-, two-, and three-day lags. The time lag giving the highest correlation for each station is indicated on the map in Figure 4.16. These analyses combined to show a consistent and spatially coherent pattern that indicates a flow of ozone from the southwest over the three days preceding the ozone measurements at Whiteface Mountain.

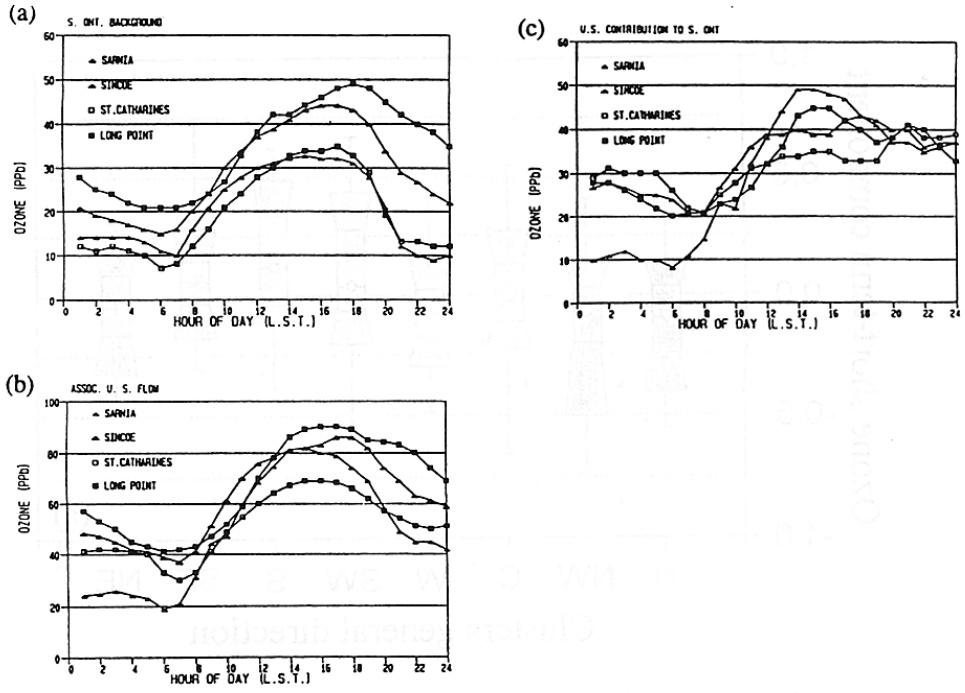


Figure 4.13 Diurnal variation of ozone at four southern Ontario sites near the U.S. border for cloud-free days during the summer months 1981-1985:
(a) background flow from within Canada,
(b) airflow from the U.S.
(c) the difference, estimated to be the U.S. contribution.
(Source: Yap et al., 1988).

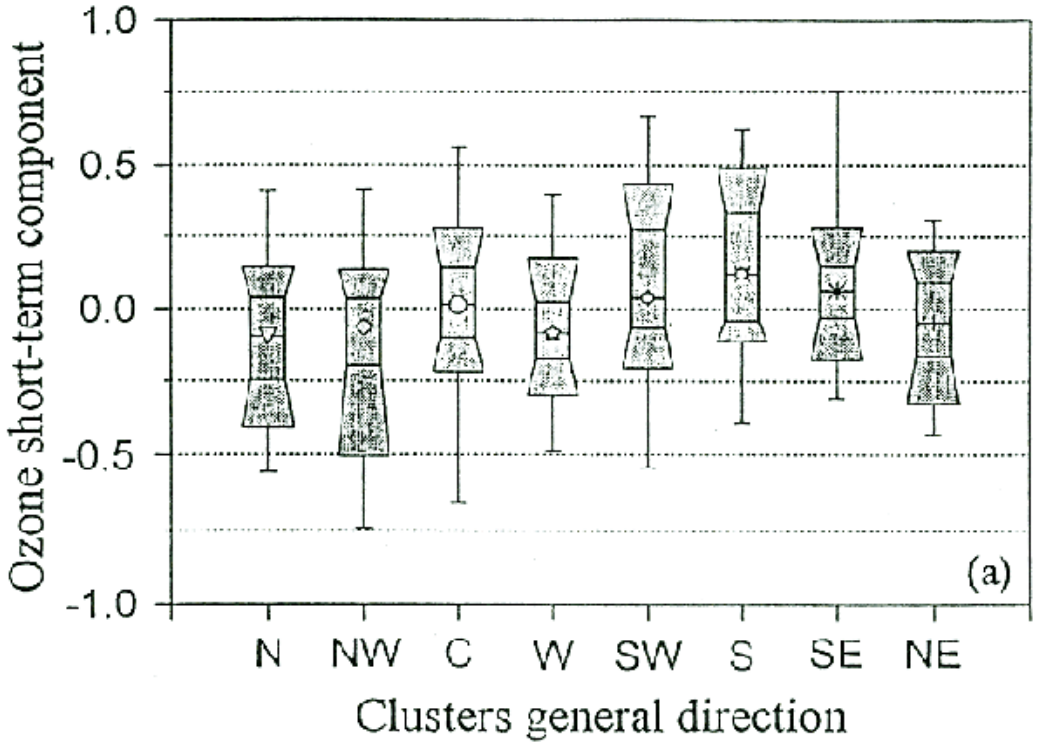


Figure 4.14 "Box and Whisker" plot of the "short-term" ozone component distribution in each of eight trajectory clusters for Whiteface Mountain, NY. The middle line in each box represents the median. The other two lines within the box represent the 25th and 75th percentiles. The ends of the box are the 10th and 90th percentiles, and the whiskers show the extreme values.
(Source: Brankov et al., 1997)

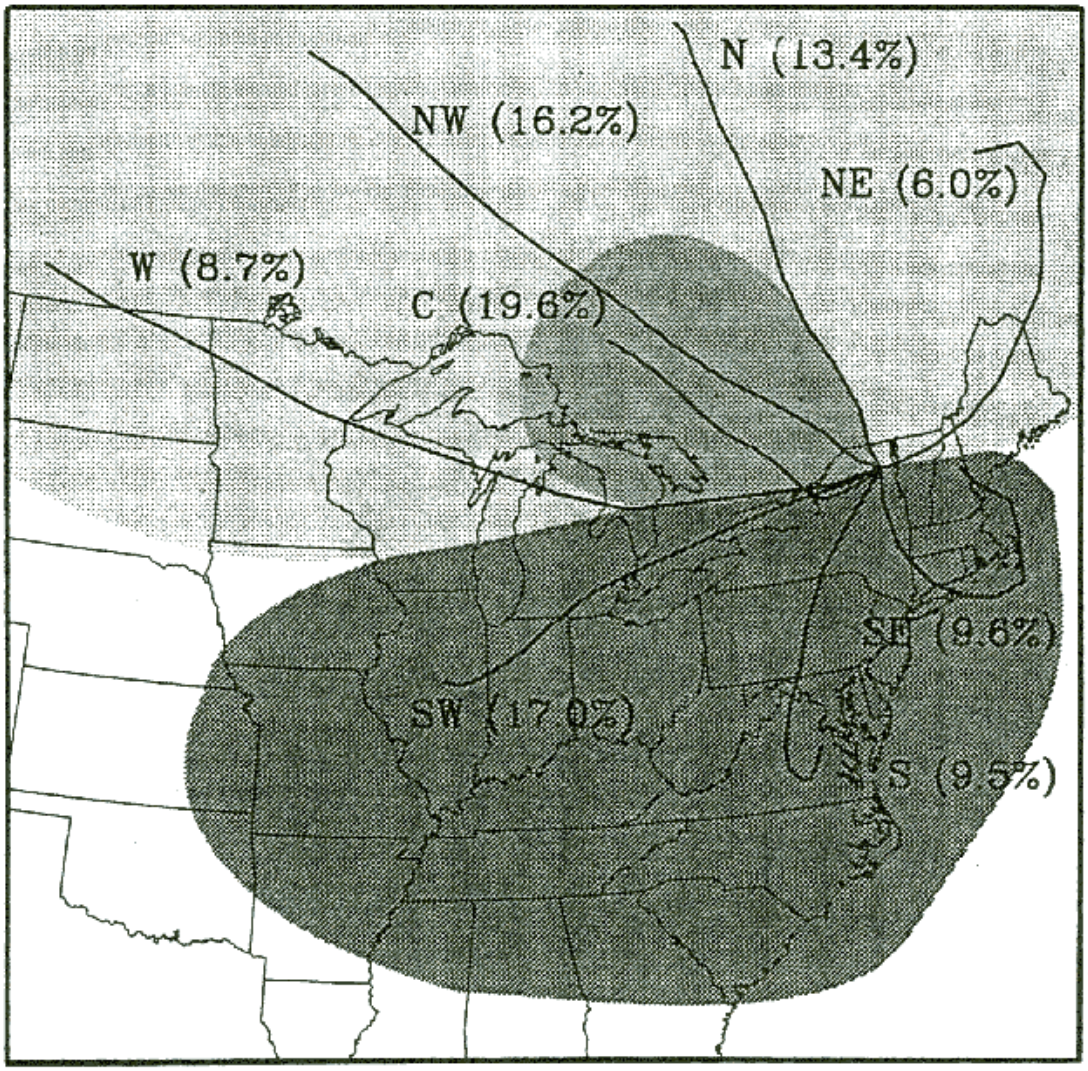


Figure 4.15 The average back trajectories for the eight clusters at Whiteface Mountain. The numbers show the percent of trajectories in each cluster. The shaded areas show the three regions from which the transport results in significantly different ozone concentrations.
(Source: Brankov et al., 1997)

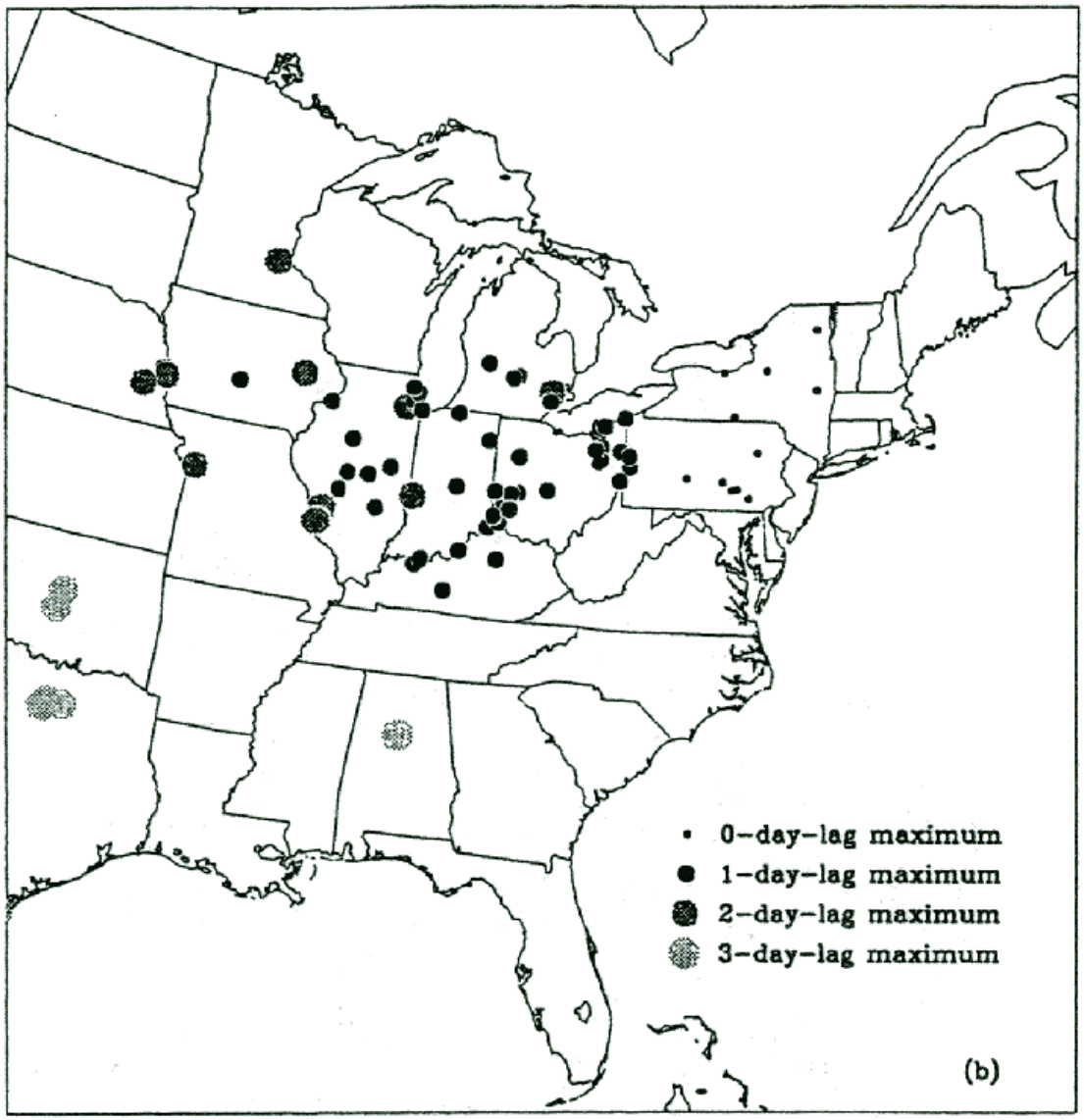


Figure 4.16 The spatial pattern of the short-term ozone concentration inter-site correlation with Whiteface Mountain for the southwest trajectory cluster. The indicated time-lags in days are those which maximize the spatial correlation.
(Source: Brankov et al., 1997)

Table 4.1 Ozone exceedances in southern New Brunswick (NB) and southern Nova Scotia (NS) during the period 1980-1993 stratified by source region for several airmass trajectory heights. Numbers shown are percent of total cases in each sector for each province.

	TRAJECTORY SECTOR						
	NE US	W-Q Corr	North	Nfld	SE	South	No. of Cases
NB 1000 hPa (mb)	79	8	2	1	1	10	209
925 hPa (mb)	30	62	3	1	1	3	209
850 hPa (mb)	22	72	3	1	1	1	209
NS 1000 hPa (mb)	87	4	0	0	2	7	56
925 hPa (mb)	64	36	0	0	0	0	56
850 hPa (mb)	39	61	0	0	0	0	56

W-Q Corr. = The Windsor-Quebec City Corridor Nfld = Newfoundland

Another useful method of utilizing airmass trajectory plots is to construct contours that represent the mean travel distance from a given source location for differing durations (i.e., one or two days). An example is shown in Figure 4.17 for days with the 20 percent highest average ozone maxima over New England (OTAG Ad Hoc Air Trajectory Workgroup, 1996). The inner contour around each site represents the one-day "zone of influence" assuming the ozone lasts for one day. The outer contour represents the "zone of influence" assuming the ozone persists for two days. In the latter case, the ozone would travel from the Ohio River Valley towards the east for a distance of about 800 km.

The contour approach to displaying mean travel distances has been used in reverse by Summers and Young (1987). In this case, the contours were plotted representing the region from within which the air could have arrived at a given receptor point over periods ranging up to five days. Thus, if the lifetime of a pollutant was known, the outer limits of the potential source region for a given receptor could be determined. This region was called the "atmospheric region of influence." An example for Long Point, Ontario on the north shore of Lake Erie is shown in Figure 4.18 (Summers and Young, 1987). This analysis was not done for specific pollutants but rather to prepare a general climatology for the seven-year period 1979-1985. Both of these techniques, one source-oriented and the other receptor-oriented, have potential to assess transboundary transport if applied at border locations, especially when used in conjunction with lagged ozone correlation analysis.

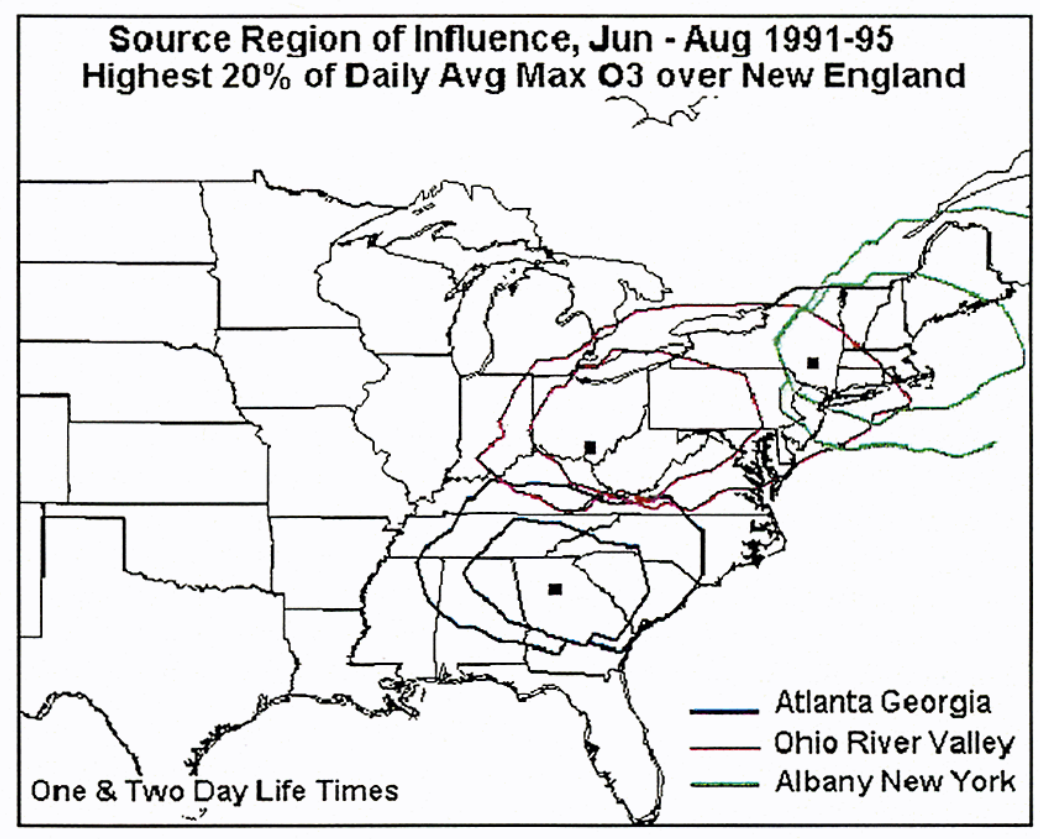


Figure 4.17 Contours showing the average forward trajectory location, for a one and two day period from three fixed points, on the 20% highest maximum ozone days over New England during the summer period 1991-1995. These contours represent the "source region of influence" depending on the atmospheric life time of the pollutant. (Source: OTAG Ad Hoc Air Trajectory Workgroup, 1996)

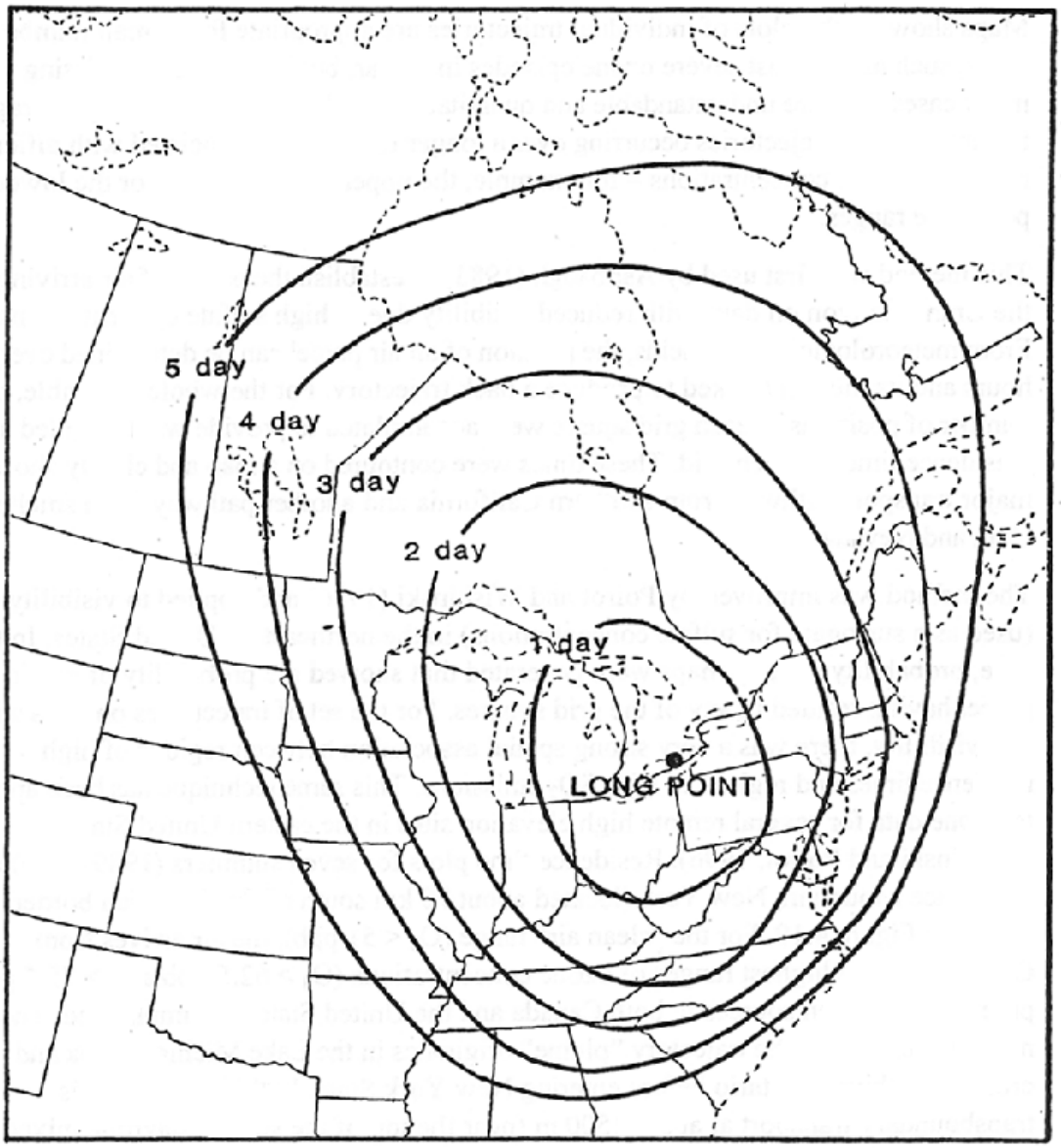


Figure 4.18 Contours of the median location of air parcel starting points one to five days prior to arrival at Long Point, Ontario. These contours represent the median "atmospheric region of influence" within which emission sources could have an impact on the receptor depending on the lifetime of the pollutant.
(Source: Summers and Young, 1987)

4.2.3 Residence Time Analysis

Maps showing the plots of individual trajectories are appropriate for a small number of cases, such as the most severe ozone episodes in a year, but become too confusing with many cases. A more understandable and quantitative result can be obtained by averaging the ensemble of trajectories occurring over a longer time period associated with different ranges of ozone concentrations - for example, the upper 10th percentile or the lower 10th percentile ranges.

This method was first used by Ashbaugh (1983) to establish the origin of air arriving in the Grand Canyon on days with reduced visibility due to high sulfate concentrations. From meteorological wind fields, the position of an air parcel can be determined every six hours and its motion tracked to produce a back trajectory. For the whole ensemble, the number of positions in each grid square were accumulated to provide what is called a "residence time" in each grid. These times were contoured on a map and clearly showed a major transport pathway from southern California and another pathway from smelters in Utah and Nevada.

The method was improved by Poirot and Wishinski (1986) and applied to visibility data (used as a surrogate for sulfate concentrations) in the northeastern United States. In this case, probability density maps were generated that showed the probability of an air parcel having resided in any of the grid squares. For the set of trajectories on days with low visibility, there was a very strong spatial association between regions of high residence times and regions of high SO_2 emissions. This same technique has been applied to ozone data for several remote high elevation sites in the eastern United States (Wishinski and Poirot, 1996). Residence time plots for seven summers (1989-1995) at Whiteface Mountain, New York (located about 70 km south of the Canadian border) are shown in Figure 4.19. For the "clean air" range ($O_3 < 51$ ppb), the air arrives from Canada. For the highest ranges of ozone concentrations ($O_3 > 62.5$ ppb and > 75.5 ppb), precursor emission sources in both Canada and the United States are implicated. The northerly branch of the trajectory "plume" originates in the Lake Michigan area and crosses southwest Ontario before entering New York State. In this case, there is transboundary transport at about 1500 m (near the top of the surface daytime mixed layer) into and out of Canada across two borders.

Another concept introduced by Poirot and Wishinski (1996) is incremental probability. In this approach, the residence time in each grid square is compared with the residence time in the same grid square for all days to produce an incremental probability of the air having resided in each grid square for any given observed ozone concentration range at the monitoring site (e.g., the upper 25 percent). Using this concept, a total of 23 regionally representative sites in the eastern United States were analyzed to generate a trajectory climatology for seven summers (1989-1995) for various ranges of observed ozone concentrations. The days with lowest ozone values at many of the northern US sites were frequently associated with flows from Canada. Intersite correlations between the afternoon ozone concentrations were used to group the sites into six regionally coherent sub-regions (Figure 4.20).

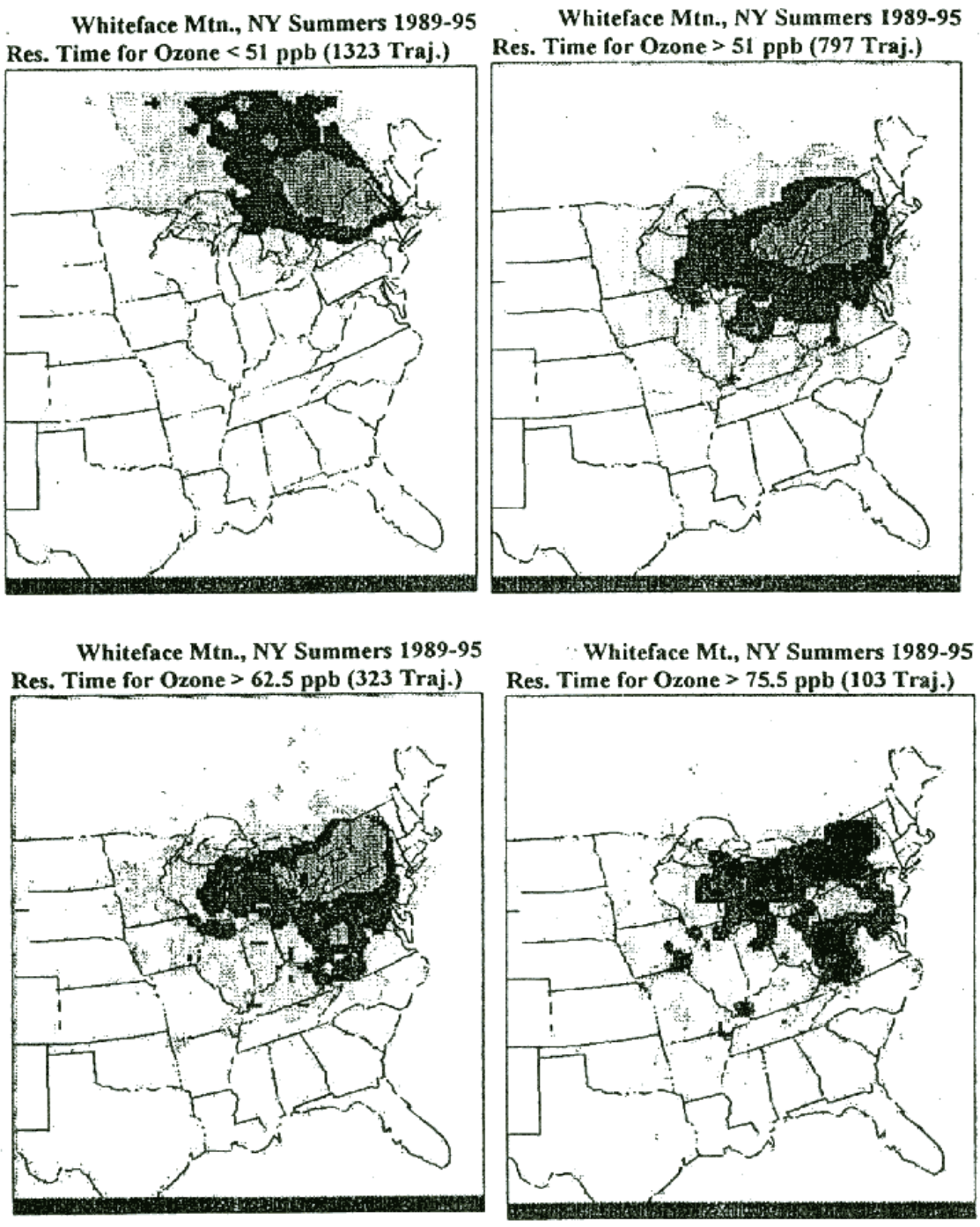


Figure 4.19 The trajectory residence-time plots for the lower 50%, upper 50%, upper 25% and upper 10% of ozone concentrations observed at Whiteface Mt. for the summer months 1989-1995. Each shaded area contains 25% of the residence-time hours. (Source: Wishinski and Poirot, 1996).

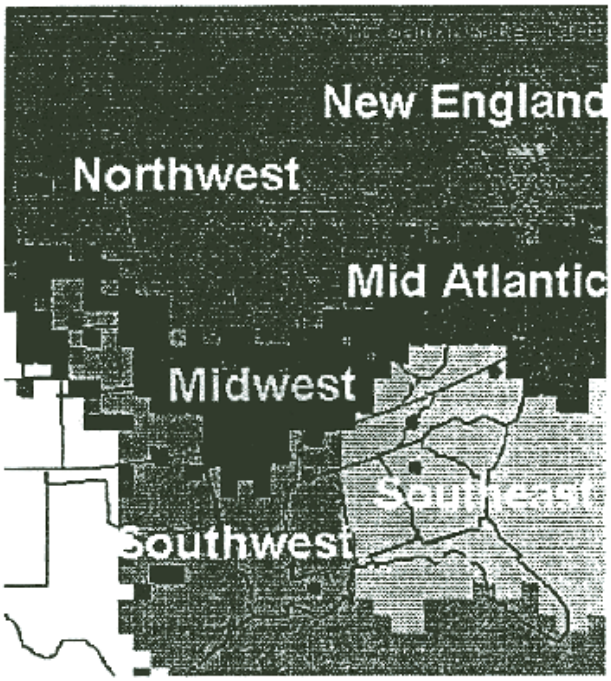
The trajectory analysis was then combined for the sites within each region to produce regional incremental probability maps. An independent analysis was made of the correlations of the ozone concentrations between the sub-regions with zero-, one- and two-day time lags. In nearly all cases, the highest values of the lagged inter-regional correlations coincided with the transport patterns as indicated by the trajectories. This joint analysis shows inter-regional transport from the Midwest, mid-Atlantic and Great Lakes States into New England.

Two examples of residence time plots in Canada show strong cross-border components. Residence time plots for 48 hour back trajectories at London, Ontario (Canadian Assessment, 1997a) show a very well defined flow pattern (Figure 4.21) at both the surface and at 850 hPa (about 1200 m), with essentially all the air crossing the border from the southwest on ozone episode days. Another plot (Figure 4.22) for Kejimkujik National Park in southern Nova Scotia (Sirois and Bottenheim, 1995) shows that for the lowest 10 percent of observed ozone concentrations, the air arrives from the northwest or from the Atlantic. In contrast, for the highest 10 percent of concentrations, the air flows in two major pathways-one up the eastern seaboard of the United States and the other from the west, originating in southern Ontario.

Another study in Quebec (Leduc, personal communication) using 400 km grid squares over eastern North America calculated 36 hour back trajectories associated with high ozone concentrations in Quebec. The study also calculated contributions by geographic area. In southwestern Quebec (at Montreal and Hull), contributions were approximately equally split between Quebec, Ontario and the United States. Further northeast in Quebec, contributions from Quebec dominated.

A further extension of the trajectory method by Summers (1987) used the same approach as Poirot and Wishinski (1986) to generate residence times in each grid square, but then included emissions input to the air parcel based on the known emission fluxes in each square. A decay factor was then applied to this initial emissions input to allow for losses en route to the receptor site. This exponential factor was based on an analysis of monitoring data across eastern Canada during sulfur pollution episodes (Summers and Fricke, 1989). In this way the percentage contribution to the observed ambient concentrations at the receptor site from any of the geographical regions (individual or combinations of grid squares) in the eastern North America domain could be estimated. Unfortunately, application of this technique to ozone is not possible because it is not a directly emitted quantity.

The possibility of using the latter technique for NOx was investigated (Canadian Assessment, 1997a). There are no remote stations measuring NOx lined up along a predominant pollution pathway that would enable estimates of an air parcel's residence time to be made using the method of Summers and Fricke (1989), therefore, the CART approach was used. The NOx emissions in each grid square, depleted by an exponential time decay factor depending on the time of travel from the input grid square to the receptor site, were introduced as a new predictor variable to the CART analysis described in Section 3.1.3 above. The “lie decay time” for NO_x was varied until the highest correlation was found between this new parameter and the observed ozone at the receptor. The best time was found to be 12 hours, which is not unreasonable based on what is known about the reaction rates for NO_x in the atmosphere. A final and more realistic refinement was to use an exponential decay time of six hours in the daylight hours and zero overnight.



To/ From	NE	MA	NW	MW	SE	SW
NE	-	B				
MA	A, B	-				
NW	A, B	A, B	-	B	A	
MW	A, B	A, B	A, B	-	A, B	A
SE		A, B		A, B	-	A, B
SW			B	A, B	B	-

A. Greater than 15% of upper 50% ozone incremental probability in "source region"
B. Significant correlation with ozone measured 1 or 2 days earlier in "source region"

Figure 4.20 **Upper map** - The area of greatest local residence-time influence for the OTAG sub-regions as defined by grouped trajectory sites.
Lower table - Comparative results of inter-regional transport for the above sub-regions as derived by A. Trajectory residence time analysis and B. Lagged inter-regional ozone concentrations.
(Source: Poirot and Wishinski, 1996).

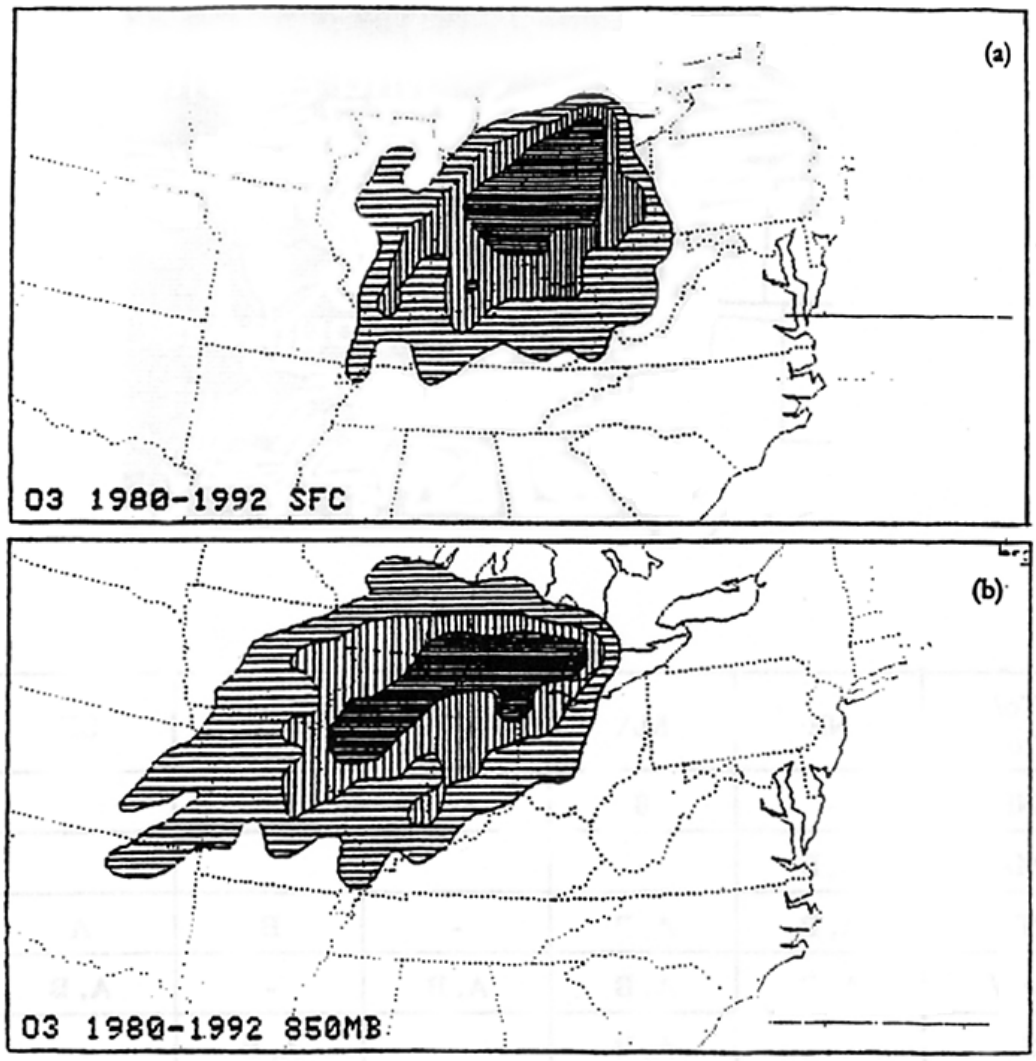


Figure 4.21 Residence time probability plots for the 48 hr back trajectories at: a) 1000 hPa(mb) and b) 850 hPa(mb) arriving at Longwoods, Ontario for all episode days (O_3 > 82 ppb). Each shaded area represents 25% of the total residence-time hours. (Source: Canadian Assessment, 1997).

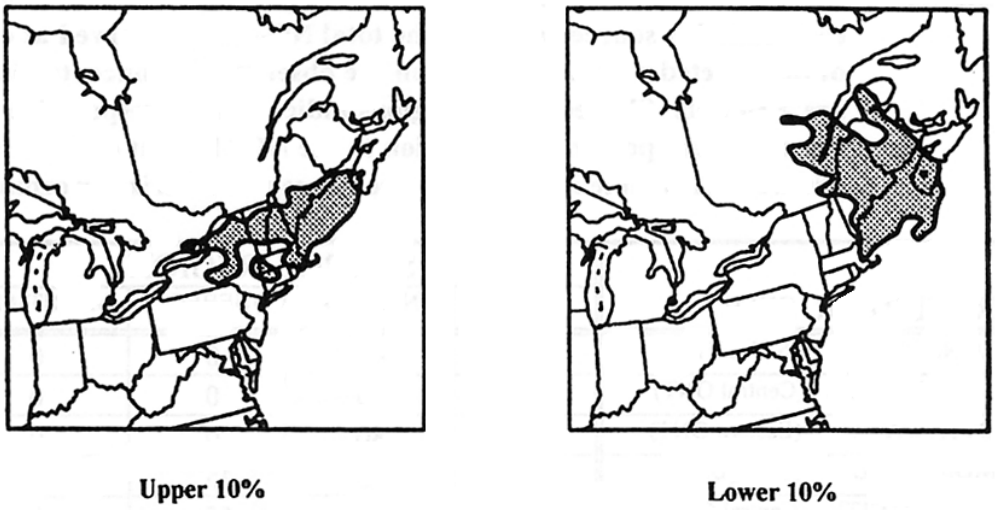


Figure 4.22 The 25% residence-time contour for the 925 hPa(mb) trajectories associated with the upper 10%, and lower 10%, values of maximum daily ozone concentration observed at Kejimkujik National Park, N.S. during the summer months 1984-1989. (Source: Sirois and Bottenheim, 1995).

The results of this analysis are shown in Table 4.2 taken from the Canadian Assessment (1997a). The numbers are rounded off to the nearest 5 percent, but are probably only accurate to within plus or minus 20 percent in light of all the other assumptions involved.

Table 4.2 Estimated source-receptor matrix for the percent contribution of each emission source region to the total NOx load observed at each of the selected receptor sites when the observed 03 concentrations are > 80 ppb. Shaded source regions indicate those responsible for the maximum percent contribution to the NO_x load at each receptor. (NOTE: This table is NOT a source--receptor matrix for ozone.)

RECEPTOR SITE		SOURCE REGION			
		USA	ONTARIO	QUEBEC	MARITIMES
LONDON	(SW ONT)	55	45	0	0
STOUFFVILLE	(Central ONT)	25	75	0	0
OTTAWA	(Eastern ONT)	20	80	0	0
MONTREAL	(SW QUE)	35	25	45	0
QUEBEC CITY	(Central QUE)	20	15	65	0
SAINT JOHN	(New Brunswick)	75	5	5	15

The table shows that during ozone episodes (O_3 > 80 ppb), long-range transport from all upwind source regions contributes to the NO_x loading at all receptors. In the case of two receptors close to the US border (i.e., London and Saint John), the US NO_x emissions account for over 50 percent of the observed NO_x load. At the other receptors, the local source region makes the largest contribution. While this table does not provide a direct estimate of transboundary fluxes, it does indicate the contribution of such fluxes in comparison to the within-border contribution. The next level of sophistication in the use of trajectories and decay factors is to include chemical processes explicitly. This leads into the Lagrangian numerical modeling approach that is discussed in the next chapter.

4.3 Tracer Analysis

Another observationally-based approach that has the potential to estimate source-receptor relationships is the use of atmospheric tracers. The application of tracers has been thoroughly reviewed (Los Alamos National Laboratory, 1984) and falls into two general categories. The first is to use the presence of natural trace substances in the atmosphere that are associated with pollutant emissions. The other is to use artificial tracers deliberately introduced into the atmosphere at the location of the pollutant emissions and measure their transport and dispersion downwind.

Because of the non-conservative properties (as compared to sulfur species) of the species involved in photochemical pollution, tracers cannot be used to obtain quantitative estimates of source-receptor relationships. They are of value, however, in confirming the accuracy of airmass

trajectories and understanding low-level flow patterns in the atmosphere. Some examples of such applications follow.

If the ratio of trace elements to the main species being emitted by emission sources is sufficiently unique to a specific individual source (such as a smelter) or a source region, then measuring the trace elements concurrently with the ambient air pollutants can give valuable information on the origin or pathway of the airmasses. This technique was applied in New England to trace airmass origins back to the Sudbury smelters in Ontario (Poirot and Michaelsen, 1996). Unfortunately, the chemical analyses for trace metals are expensive. Therefore, because there is no advantage over using airmass trajectories (other than confirming their accuracy), this technique does not have the potential for widespread application and will not be discussed further.

Another possibility briefly alluded to by Poirot and Michaelsen (1996) is to use the presence or absence of sulfate in conjunction with ozone when they are monitored at the same sampling sites. The measured sulfate concentration at a monitoring site serves as an indicator of the relative pollution contribution from vehicles in the arriving air mass (small SO_2 emissions) versus large combustion point sources such as power plants (large SO_2 emissions). The relative amount of sulfate present in combination with ozone at a monitoring site can indicate the relative importance of vehicles versus large point sources as the major sources of the NO_x responsible for the presence of ozone in the arriving air mass.

A major five-week experiment, called the Cross Appalachian Tracer Experiment (CAPTEX 83), was conducted in the northeastern United States and eastern Canada in the Fall of 1983 using an artificial tracer. The experiment involved a total of seven 3 hr ground-level releases of 200 kg of perfluoro-monomethyl-cyclohexane (C_7F_{14}) from two predetermined locations - Dayton, Ohio, and Sudbury, Ontario, both locations with high sulfur emissions. The tracer was monitored by a network of 80 samplers across southern Ontario, southwestern Quebec, Ohio, Pennsylvania, New York and New England. A comparison between the measured tracer pathways at ground-level and those determined by the Canadian Atmospheric Environment Service, Long-Range Transport of Air Pollutants (AES-LRTAP) model showed that the path matched best with the trajectories computed at 925 hPa (mb), rather than at 1000 hPa (mb) or 850 hPa (mb). The speed of motion was also accurately predicted for the first 24 hours (RMCC, 1986). In another analysis of the CAPTEX 83, Haagenson et al. (1986) compared the tracer results with several meteorological models and also concluded that the best match was with the 900 hPa (mb) trajectories.

There was one case in which a small portion of a Dayton tracer release moved northeast into southwestern Ontario with the ground-level wind, but the remainder moved aloft in a flow that was de-coupled from the surface. The tracer was detected again 36 hours later when it mixed down to the surface in high concentrations over New England. Again, the 100cation and timing matched best with the airflow calculated from computed 925 hPa (mb) trajectories. Although only a single case, it does show conclusively that pollutants can be de-coupled from the ground while being transported long distances before being mixed down to ground-level again.

All of the CAPTEX 83 tracer releases were made under simple meteorological regimes, with no frontal systems nearby and no precipitation in the region. The conditions for the Dayton releases, with a wind flow from the southwest, are those which also are generally associated with ozone

episodes in the northeast United States and eastern Canada. Thus, the main outcome of the CAPTEX 83 experiment is that one can have confidence in using computed airmass trajectories to a distance of at least 1000 km, for at least 24 hours, to represent the mean flow of pollutants in the surface mixed layer.

4.4 Special Field Studies and Aircraft Measurements

All of the previously described analysis techniques (except tracer studies) use data that are collected on a routine basis. From time to time, however, major field experiments are carried out over a period of a few weeks using a whole array of monitoring techniques to gather data at much finer spatial and temporal resolutions. These studies usually include instrumented aircraft and other sounding equipment to obtain vertical profiles, and thus obtain a complete three-dimensional observational database. One of the objectives of such studies is to evaluate the ability of models to accurately simulate the three-dimensional behavior of the atmosphere and the observed chemical concentration fields, but they also generate huge data sets from which careful data analysis can yield an important physio/chemical description and an understanding of the processes involved. Four major field studies in the last ten years are:

The Eulerian Model Evaluation and Field Study (EMEFS-I) - Summer 1988.

The Eulerian Model Evaluation and Field Study (EMEFS-II) - Spring 1990.

The North Atlantic Regional Experiment (NARE) - August 1993.

The North American Regional Study of Transport of Ozone; (NARSTO-NE) – Summer 1995.

The first two of these field programs were carried out in the lower Great Lakes/central United States region mostly west of the Appalachian Mountain chain and were geared towards model evaluation. NARE was carried out as part of the International Global Atmospheric Program, specifically to study how the continents surrounding the North Atlantic affect atmospheric composition on a hemispheric scale. The initial focus of NARE was to investigate the ozone budget of the temperate North Atlantic region, and a main component was estimating fluxes off the continent into the Gulf of Maine/Nova Scotia region. A special issue of the Journal of Geophysical Research (Vol. 101, No. D22, December 20, 1996) is devoted to papers on the results of NARE. Some of the key relevant findings are described below.

A total of 16 aircraft flights in the Gulf of Maine (Buhr et al., 1996) sampled the pollution plumes moving off the east coast as determined by airmass trajectories. By comparing ozone concentrations with other known anthropogenic ally produced species, it was concluded that anthropogenically influenced ozone production dominated below1500 m. Above 1500 m, transport from a variety of sources contributed to the ozone. The study did not attempt to distinguish between nearby or distant sources. The average vertical profile during the period is given in Figure 4.23 and shows that on high pollution days, ozone maxima are a strong 75 ppb at about a 500 m altitude.

Actual calculations of horizontal fluxes were made from a total of 22 vertical soundings taken by an instrumented aircraft between the altitudes of 30 m and 5 km off the southern tip of Nova Scotia (Banic et al., 1996). The vertical profile of ozone for all soundings is shown as a "box and whisker" plot in Figure 4.24. Note that while the median profile shows a monatomic decrease in ozone concentration with height, the extreme value profile (> 90th percentile) shows a distinct maximum at an altitude of about 1 km associated with trajectories from the polluted regions. The average total column flux of ozone through a vertical plane 1 km across and 5 km high was calculated to be 2.8 g/sec from west to east. By sorting the data on the basis of airmass trajectory origin, it was estimated that anthropogenic ozone accounted for 50 percent of the transport below 1 km; 35-50 percent between 1 and 3 km; 25-50 percent between 3 and 4 km; and 10 percent between 4 and 5 km. This result is consistent with those found further south over the Gulf of Maine discussed above (Buhr et al., 1996). Based on the detection of ozone plumes by aircraft measurements and the day to day variability of ozone concentrations at Cape Race, Newfoundland, Fehsenfeld (1996) coined the term "meandering rivers" to describe the behavior of ozone from the northeastern United States.

In a pre-NARE pilot study, a series of ozonesonde measurements were made at Seal Island and Sable Island, south and east of mainland Nova Scotia and at Cape Race, Newfoundland. A time series spanning 23 July to 6 August 1991 obtained at Cape Race, about 1100 km downwind of the closest significant source of precursors, is shown in Figure 4.25 (Fehsenfeld et al., 1996). In nearly all cases there were significantly higher average ozone concentrations in the 1.5 to 2.0 km layer compared with the surface to 0.5 km layer, often by a factor of two. On one occasion the upper level was 75 ppb compared to the lower level of 30 ppb. Clearly, with concurrent wind information such observations would enable flux measurements to be made.

Recently the flux calculations for NARE have been compared to those for EMEFS over southwestern Ontario (Isaac et al., 1997). Figure 4.26 shows the average north/south and east/west fluxes for all the aircraft vertical profiles. The predominating flux is from west to east, with a slight northerly component below 2 km. The average flux in the layer between 1.5 and 5 km is about four times that in the lowest 100 m in NARE. For EMEFS, the aircraft could not fly below 500 m, but in the layer between 500 m and 1 km the flux was only 60 percent of that above 1.5 km.

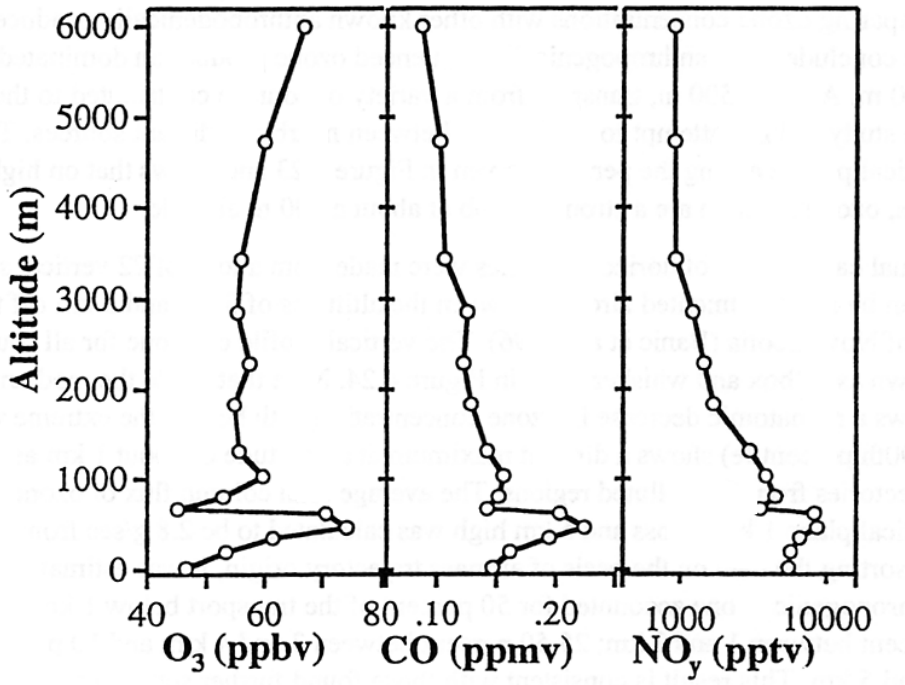


Figure 4.23 The vertical profiles of O_3, CO and NOy measured in the Gulf of Maine during 16 aircraft flights in August 1993. Each symbol except the top one represents the average of 1000 measurements.
(Source: Buhr et al., 1996)

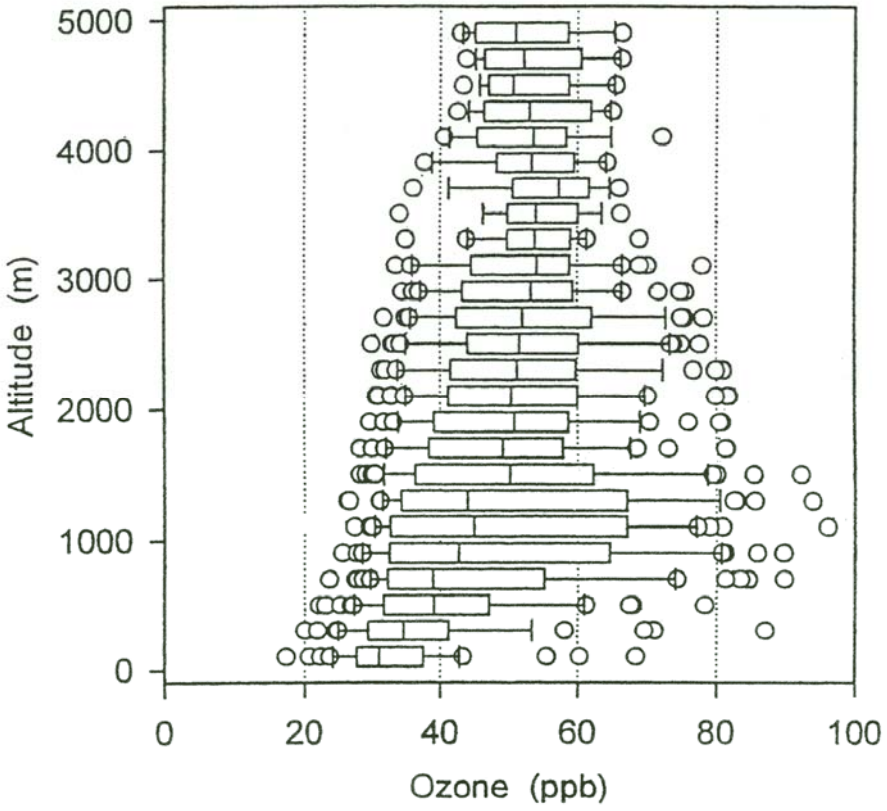


Figure 4.24 Vertical profiles of the frequency distribution of ozone concentration for each 200 m increment in altitude. Measurements were made off the southern tip of Nova Scotia during August 1993. The box covers the range between the 25th and 75th percentiles, with the line in the box representing the median value. Whiskers are the 10th and 90th percentile values and beyond these individual extreme values are shown. (Source: Kleinman et al., 1997)

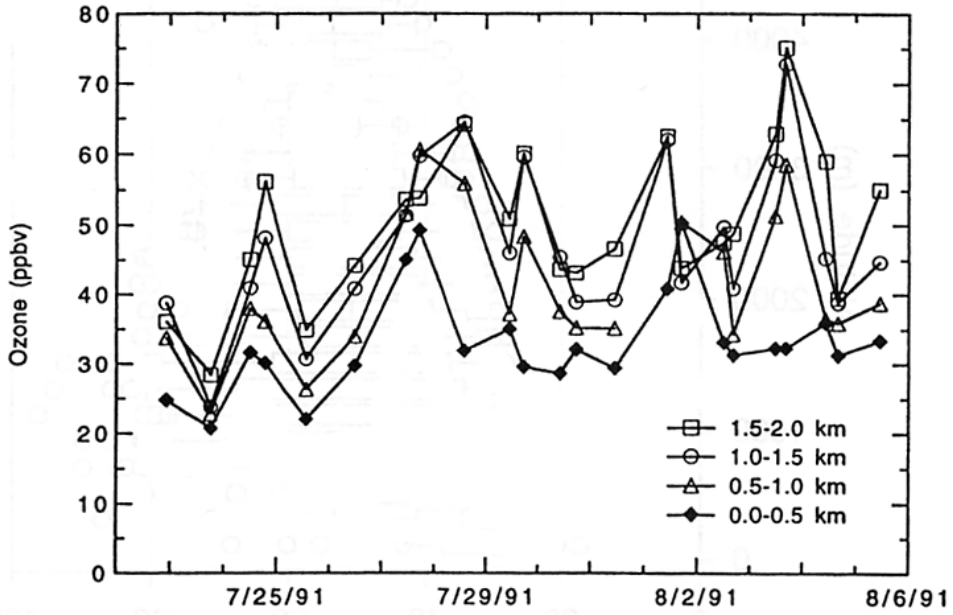


Figure 4.25 Time series of ozone concentrations at four separate heights in the lowest 2 km of the atmosphere measured at Cape Race on the south shore of Newfoundland obtained by ozonesondes during the summer of 1991.
(Source: Fehsenfeld et al., 1996)

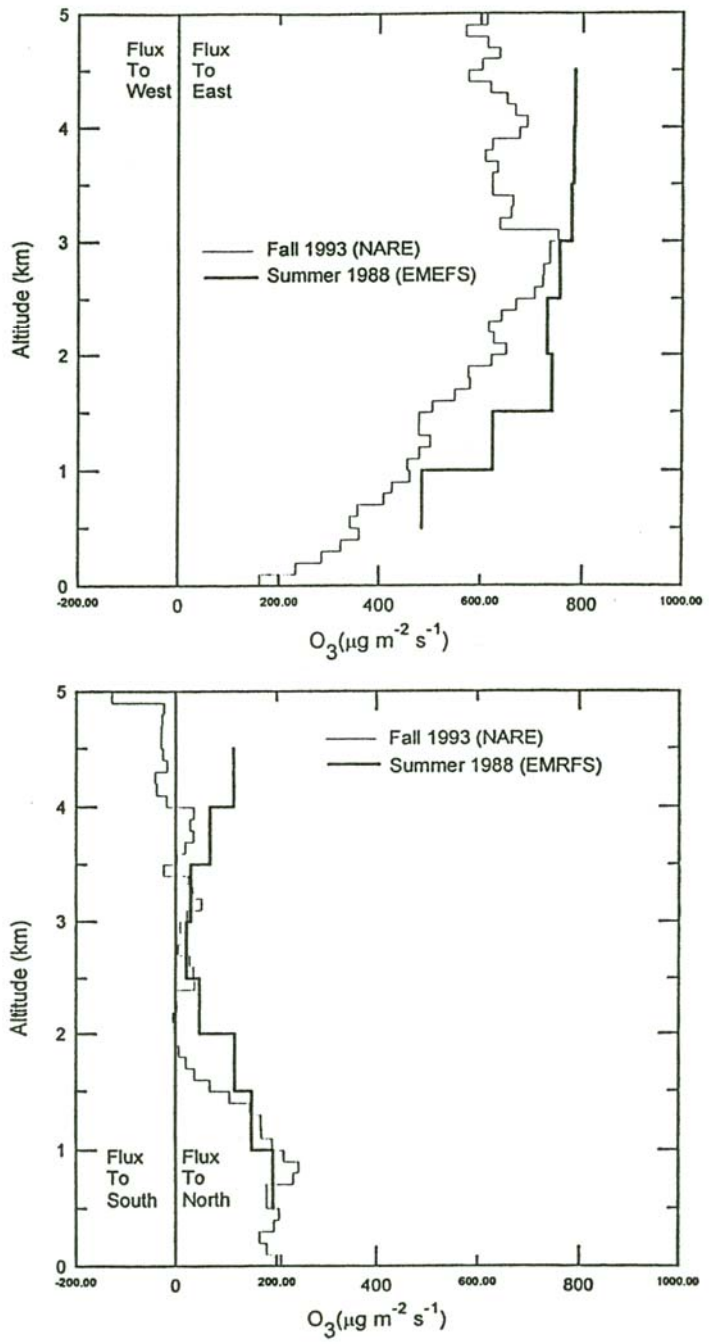


Figure 4.26 Vertical profiles of the ozone horizontal transport flux based on all aircraft profiles obtained off the south coast of Nova Scotia (during NARE 1993) and over southwestern Ontario (during EMEFS 1988). **Upper plot** - net west to east flux. **Lower plot** - net south to north flux.
(Source: Isaac et al., 1997).

An example of vertical profiles from Poughkeepsie, New York, during NARSTO-NE (Figure 4.27) shows clearly the difference between daytime and nighttime structures on the same date. Overnight concentrations increase rapidly from ground level to a maximum of about 130 ppb, at 800 m, probably associated with a low-level channeled air flow ("nocturnal jet"). By the following afternoon, concentrations are uniform at 80 ppb up to an altitude of 800 m in a well-mixed surface layer. The total average column ozone is about the same in both cases, but the ground-level value largely underestimates the true value of ozone transport.

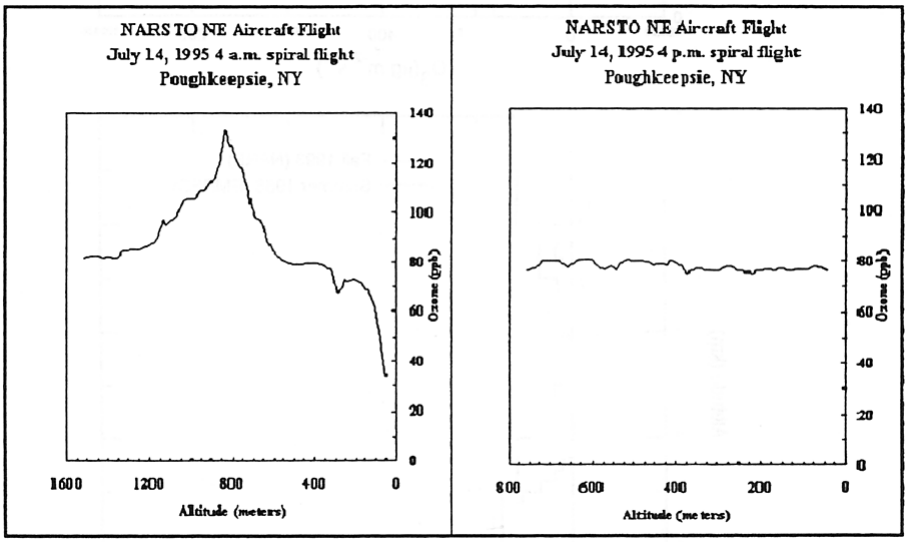


Figure 4.27 Vertical profiles of ozone concentrations near Poughkeepsie, NY at 0400EST and 1600EST on 14 July 1995. (Source: Miller et al., 1997, adapted from NARSTO-NE)

A preliminary analysis of atmospheric transport in the northeastern United States (Blumenthal, personal communication) based on field measurements in NARSTO-NE, describes three regimes: long-range synoptic-scale flow from the west and southwest; medium-range flow "channeled" through gaps in the Allegheny Mountains and in nocturnal jets from the southwest along the eastern seaboard; and intra-region surface transport along the Northeast Corridor, as well as from Boston to Maine in the north.

From all these studies, it is evident that a large fraction of the anthropogenic ozone generated over the continent is transported at heights above ground level. High elevation monitoring sites can give a measure of this transport at their fixed heights, however, only vertical soundings can provide the information necessary to make a quantitative estimate of transport fluxes through the whole of the lower atmosphere layer.

5. Numerical Simulation Models for the Long-range Transport of Ozone and its Precursors

5.1 Types of Models

The simplest form of a model is a qualitative statement such as "maximum sulfur wet deposition occurs from a maximum a few 100 to about 1000 kin downwind from a major source region." Another model could be in the form of a "linear regression equation" that links a certain air quality measure with upwind emissions. Several such linkages are generated by the types of data analyses described in Chapter 3. These are often called "black box" models because the inputs (emissions) and outputs (ambient concentration or deposition) are usually linked without any consideration of the intervening processes (the so-called black box) other than perhaps a transport component.

Numerical simulation models, on the other hand, attempt to incorporate the best available knowledge of the chemical and physical processes involved and express them explicitly in the form of mathematical equations. Table 5.1, taken from NRC (1991), summarizes the main strengths and limitations of the various classes of photochemical models. They are listed in the approximate order of their development, beginning in the 1970s. The first is basically a box model in which volume-averaged conditions are considered as they change with time. With the advent and continual improvement of the computing capacity of high speed computers it was possible to develop grid based models. These started at the urban scale and moved up to the regional scale.

There are two fundamental approaches to solving the sets of meteorological and chemical equations in grid based numerical models. Eulerian models carry out the integration at a large number of grid points in the chosen domain and thus produce the time variation of the output parameters at each point. Lagrangian models follow air parcels through the grid domain and calculate the time variation of the parameters along the trajectories. Other hybrid models attempt to combine the best features of these two methods.

The main components in the atmospheric system for those species that remain mostly in the troposphere and have residence times of the order of a few days are illustrated schematically in Figure 5.1 (from Summers, 1982). This overall emission-transport- deposition cycle for many of the predominant chemical species in the atmosphere is now well documented. Sub-models or modules are developed to simulate the process in each of the boxes in Figure 5.1 and then they are all linked together into the complete model. In this way, as new scientific information becomes available, the modules can be modified individually without the necessity of changing the whole model.

Table 5.1 Strengths and limitations of various classes of photochemical models. (Source: NRC, 1991)

Model Type	Strengths	Limitations
EKMA (Empirical kinetic modeling approach)	Easy to apply, detailed chemistry, computationally rapid.	Lacks physical detail, short model simulations. Does not accurately simulate multiday events or long-range transport.
Urban, grid-based	Physically detailed. Suited for multiday modeling of urban areas (~400km).	Computationally demanding. Sensitive to boundary conditions when long-range transport is important.
Regional	Physically detailed. Suited for studying regional areas (~1000km).	Computationally demanding, limited spatial resolution. (ROM also has limited vertical resolution.) Not well suited to studying pollutant dynamics in cities.
Nested[a]	Advantages of both urban and regional models.	Computationally awkward and demanding. Information travels in one direction.
Multiscale[b]	Advantages of nested, urban, and regional models. Computationally straightforward.	Computationally demanding. In development.

[a]Nested models are models in which finer grid scales are embedded.
[b]Multiscale models are in effect nested models whose character on different scales may be different.

There are two basic ways in which models are used. As diagnostic tools they can be used to generate ambient pollution concentrations or deposition rates in a variety of formats. After these diagnostic outputs have been validated against current monitoring data, the model can then be used in a predictive mode. In this mode the same outputs are produced, but a variety of emission reduction scenarios are used in order to estimate the impact of future proposed control strategies. There are a large number of ways in which the model outputs can be presented and in many cases they can be quite complicated and difficult to understand compared to those shown in Chapter 3. A common presentation format is the spatial distribution of various parameters (e.g., the number of exceedances of an air quality standard per year or the daily maximum ozone concentration). In this way, both the predicted magnitude and regional extent of changes in ozone patterns due to a variety of emission changes are easily visualized.

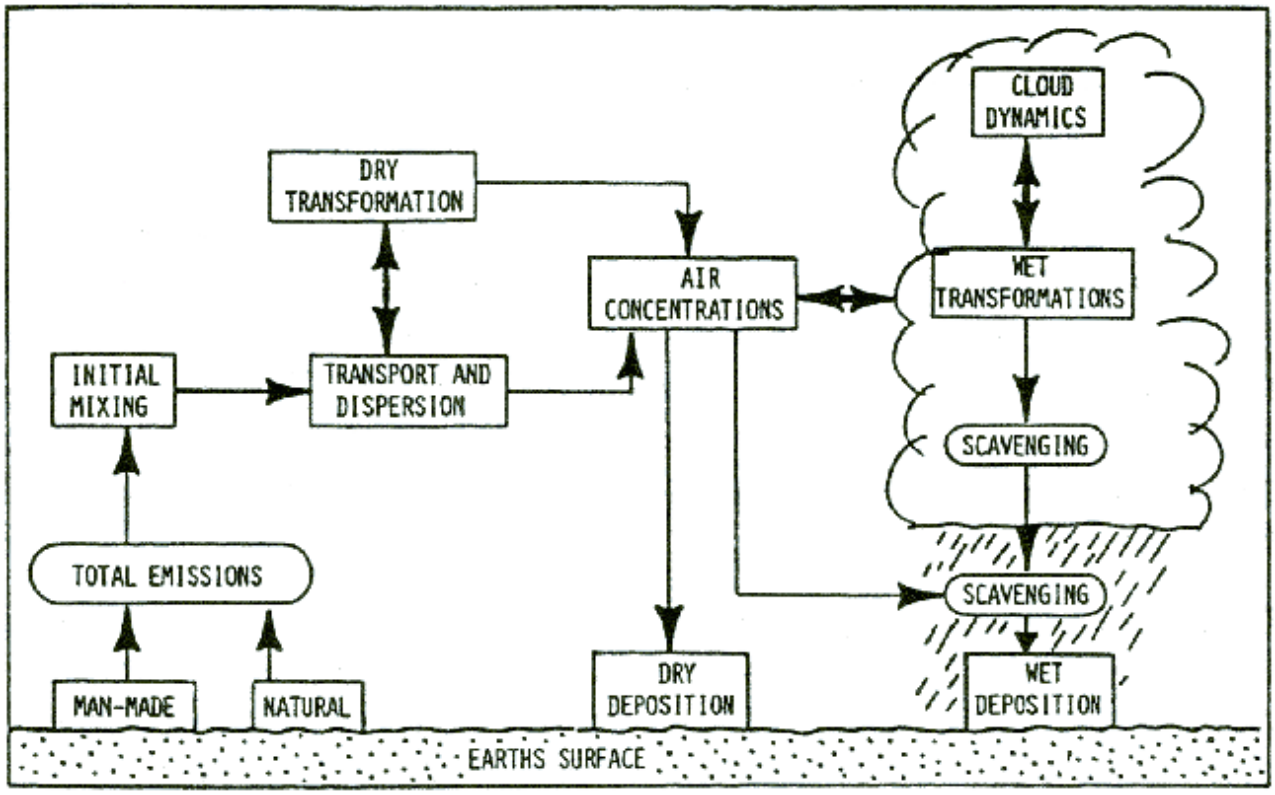


Figure 5.1 Schematic representation of the main processes in the emission to deposition cycle of air pollutants. (Source: Summers, 1982)

Another common use of air quality models is to generate source-receptor relationships between the concentration of a pollutant at a receptor location or within a receptor region and the emissions source of the pollutant or its precursors. The numerical simulation source-receptor models for sulfur, developed first in Europe and then in North America, proved to be very useful in addressing the acid rain issue. They provided information on the optimum locations and amounts of emission control required to bring acid deposition down to acceptable levels in sensitive receptor regions. Some of these models have been adapted for use in the ozone issue. The following is a brief summary of the photochemical ozone models currently in use in eastern Canada and the eastern United States that are relevant in estimating transboundary fluxes in the border region.

5.2 United States Models

5.2.1 Models Considered

This summary of air quality modeling in the Unites States is based on information in two reports. The first of these is the National Research Council report entitled "Rethinking the Ozone Problem in Urban and Regional Air Pollution" (NRC, 1991) which contains an excellent historical review of the modeling underway up to 1990. The second is a report prepared for the Ozone Transport Assessment Group (OTAG)[1]: "Review of Recent Ozone Measurement and Modeling Studies in the Eastern United States" (Morris, 1996) which covers more recent activities.

Because the ozone problem first appeared in Los Angeles and later in urban areas in the east, US modeling efforts have concentrated on the urban scale and have only recently expanded to a larger regional scale. The first approach was based on smog chamber work in the 1950s. Isopleth diagrams of maximum ozone concentrations were generated based on the initial concentrations of NO x and VOCs. An extension of this was developed by the US EPA in the mid-1970s and called the Empirical Kinetic Modeling Approach (EKMA). The EKMA model used observed (or modeled) early morning precursor concentrations in the atmosphere to predict the afternoon maximum ozone concentration in an urban area. In spite of its many shortcomings and the controversy it generated, the EKMA model was simple to apply and was used primarily for attempting to predict whether the formation of local ozone was NOx limited or VOC limited. Since it only has a short-term (early morning to mid-afternoon) meteorological advective component, EKMA is of no real value in addressing long-range transport issues.

Numerical modeling of urban areas based on geographical grids commenced in the early 1970s, and the approach was expanded to the regional scale in the late 1970s. The main models are discussed below in the order of their development.

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[1] OTAG was a multi-state effort convened by the US Environmental Protection Agency from 1995 to1997 to address ozone transport issues within 37 states in the eastern United States. While OTAG did not investigate cross-border transport issues, it yielded valuable insights on the nature and extent of ozone transport and the most effective control strategies for addressing this problem. For example, OTAG recommended that up to an 85% reduction in NOx emissions from 1990 emission rates of utility power plants will be needed to reduce ozone and precursor transport in the eastern United States. Many of these findings are also relevant to ozone transport between the United States and Canada.[1]

Urban Airshed Model (UAM). Developed initially for use in the Los Angeles Basin by Systems Applications International (SAI), it has been the mainstay of urban modeling for about 25 years. This model has been continually updated with an improved chemistry module and has also been adapted by other users. In some cases it has been applied on the small regional scale (up to ~ 400 km^2). This model, or a derivative of it, is in widespread use in the eastern United States in large urban areas. Version V has now been expanded to cover the entire eastern United States.

Regional Oxidant Model (ROM). ROM was developed by the US EPA in the 1980s to address the regional-scale ozone problem in the eastern United States.

Regional Acid Deposition Model (RADM). As the name suggests, RADM was developed initially for use in analyzing acid rain in eastern North America, but the oxidant chemistry has been improved for use in ozone simulations. It uses a mesoscale model (Anthes and Warner, 1988) as the meteorological driver.

5.2.2 Examples of Relevant Applications

Most of these models have been applied to simulate the impact of a wide variety of emission control strategies on maximum ozone concentrations, thereby aiding the United States in developing its State Implementation Plans (SIPs) for pollution control. Often a global reduction in various combinations of both NO_x and VOCs was used to assess the global reduction in maximum ozone concentration in the same region. Most of the emission scenarios involved reductions in given industrial sectors (such as power plants) within a local area, rather than reductions in a fixed geopolitical region that could show an impact on another fixed geopolitical region. Thus, the magnitude of long-range transport was not addressed directly. Some of the studies, however, do give an indication of the long-range transport component, such as in the Ozone Transport Region (OTR) in the Northeast. The following are examples of the use of the UAM model near the Canada-US border.

1. **The Southeast Michigan Ozone Study (SEMOS)**. The UAM model used data from two 1988 episodes (5-7 July and 2-3 August), as well as data from a special field study during 10-11 August 1993. One of the findings was that the transport of ozone and its precursors into the region is important. Because this region is right on the Ontario border, this finding is consistent with the Canadian results that show significant transport into southwest Ontario.

2. **The Lake Michigan Ozone Study (LMOS)**. The UAM-V Model was applied to show that although Chicago/Gary/Milwaukee are significant contributors, ozone and precursors transported in from upwind regions contribute by over 50 percent to the problem in the Lake Michigan Air Quality Region. Note that similar results were obtained from a very detailed data analysis effort (see section 4.1.2). Although not directly related to the transboundary issue, this study once again shows that transport is an important factor in local pollution levels at the northern limits of the high ozone region in eastern North America.

3. **OTAG Modeling**. Using UAM-V, a larger regional version of the earlier urban scale UAM, the OT AG modeling group has run many different scenarios for NOx and VOC emission reductions. Of particular interest is the impact of changing emissions in well-defined sub-regions in eastern North America and then assessing the geographical scale and magnitude of the impact on ozone concentrations during a July episode. The overall "footprint" of ozone reductions extends well downwind from the region where emissions were changed (Figure 5.2).

   Lurmann et al. (1997) have compared the UAM-V output to aircraft measurements from a July 1995 episode during the NARSTO-NE field study. The model underestimates the ozone concentrations aloft by an average of 10-15 ppb and thus underpredicts transport into the Northeast from the Midwest. Conclusions drawn from this modeling effort should be viewed as conservative estimates of the extent of long-range ozone and precursor transport.

4. **Other UAM-V Modeling**. Another application of UAM-V to the eastern United States (Rao et al., 1998) examines the impact on the spatial distribution of ozone during the July 7-18, 1995 episode by selectively shutting off the emissions from North and South Carolina. The predicted decrease in ozone concentration shows an exponential decay with distance from Charlotte, North Carolina with the magnitude decreasing to lie (approximately one-third) of its original value over a distance of about 500 km. It should be noted that this distance is shorter than that found in the northeastern United States because the transport air flows are lighter in the southeast.

Prior to the development of UAM- V, the ROM model was used extensively in the eastern United States and gave much more information on potential long-range transport over larger regions than did the earlier version of UAM. Some examples relevant to the northeast United States or the border region are given below.

1. The **EPA ROM Matrix Study**. This study was designed to test the overall impact of precursor emission reductions over a large 126xl26 grid domain with a resolution of 18.5x18.5 km extending from Texas in the southwest comer to Maine in the northeast. The reduction scenarios were tested with various combinations of 25 percent increments in both NO_x and VOCs for the severe ozone episode of 2-10 July 1988. The various scenarios show that a given percentage NO_x reduction has a larger regional scale impact than a VOC reduction of similar magnitude. In terms of the transboundary impact, emission reductions of 50 percent or more in NO_x and VOC emissions predicted a significant drop (up to 30 ppb) in the simulated daily maximum ozone in southwest Ontario and extreme southern Quebec. Because no reduction in Canadian emissions was in the simulation, the modeling results indicate a significant cross border contribution for US emissions.

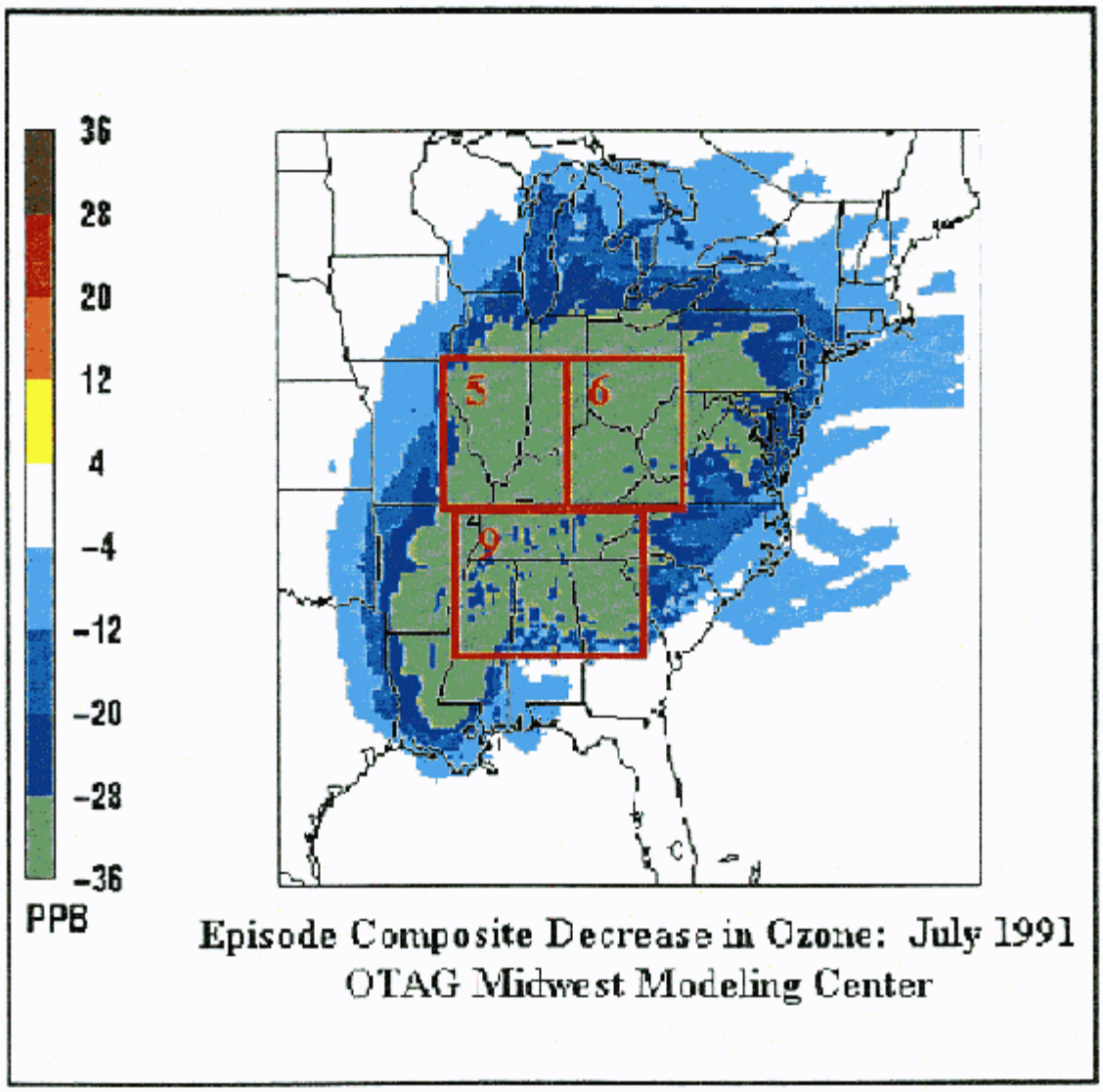

Figure 5.2 Ozone reductions simulated by the OTAG UAM-V model when the anthropogenic emissions in the central three boxes are turned off. (Source: Miller et al., 1997, adapted from OT AG Midwest Modeling Center)

The model simulation also showed significant reductions (as much as 40 ppb) in daily maximum ozone in the New England area. This again demonstrates that long- range transport from emission sources to the southwest plays a large role in the high ozone levels observed in New England.

2. The **OTC/EPA ROM Simulation Study**. This study for the Ozone Transport Commission performed ROM simulations over the grid defined above, but with the specific objective of evaluating alternative control strategies for the OTC. A wide range of potential control scenarios were applied. Simulations with NOx controls outside the OTR provided significant incremental ozone reductions within the OTR, again indicating long-range transport of ozone and precursors into the Northeast, depending on the wind flow conditions.

5.3 Canadian Models

5.3.1 Models Considered

In contrast to the United States, Canadian modeling efforts have emphasized regional scale modeling from the start. Early observations suggested that, except in the Vancouver region, long-range transport was the main issue to be addressed. In eastern Canada, the Urban Airshed Model is not used, and all modeling work addresses the regional and long- range transport scale.

As part of the Canadian Multistakeholder NO_x / NOC Science program, the Windsor-Quebec City Corridor and Southern Atlantic Region Modeling Work Group Report (Canadian Assessment, 1997b) describes five Canadian models used to assess transport. These models are listed below in the order of their development.

1. The **Regional Oxidants Model (ROM 2.2)** is the US EPA model adapted to a more northerly domain, and run by Ontario Hydro in cooperation with the Atmospheric Environment Service (AES). This work has now ceased.

2. The **Acid Deposition and Oxidants Model (ADOM)** was combined with a small scale meteorological driver (GESIMA) developed by the German Meteorological Service and run over a limited area of southwest Ontario by the Ontario Ministry of Energy and Environment.

3. The **AES Lagrangian Oxidants Model (ALOM)** uses the ADOM model and is based on the original AES Long-Range Transport of Air Pollutants (LRTAP) Model. It is run by AES and was originally used effectively in the Acid Rain program.

4. The **ADOM-MC2** uses the ADOM model with the meteorology provided by the newly developed Mesoscale Compressible Community (MC-2) Model. It is run by AES in cooperation with Ontario Hydro. It is also now being run by York University with their own chemistry module.

5. The **Chemical Tracer Model (CTM)** uses the ADOM chemistry formulation with semi-Lagrangian advection and is driven by the MC-2 meteorological driver. It is run by AES and the most recent model versions include several layers in the lower atmosphere. A major effort is underway to make it capable of simulating the strong vertical gradients of ozone near the ground.

5.3.2 Examples of Relevant Applications

Most of the above named Canadian models were evaluated by analyzing the level of agreement between the model simulations and observations for a major ozone pollution episode that occurred 1-6 August 1988. This episode covered a large portion of the Midwest and the northeastern United States as well as extending into southeastern Canada. Full details of the model evaluations are given in the Canadian Assessment (1997c) and will not be discussed here. Suffice it to say that while all models could reproduce reasonably well the overall features of the observed ground-level pattern, the correlation coefficients (R) for the point values at about 70 observing sites were rather low - commonly running in the range of 0.5 to 0.7, thus explaining only 50 percent of the variance at best. The values of R varied substantially from day to day for a given model and from model to model on a given day. This is probably due to the variation in the ability of each model to handle the changes in meteorology from day to day.

Although no explicit estimates of transboundary fluxes were made using the models, one aspect of their results does provide some information on transboundary impacts. Sensitivity tests were carried out on all models including their response to global changes in the emission input, but only for the ROM 2.2 model were emission changes from Canadian and US sources treated separately. The ROM 2.2 domain consists of 16,384 (128 x 128) grid squares of 18.5 x 18.5 km, covering the area in eastern Canada and the northeastern United States. An index was developed that accumulated the number of hours per day in each grid square that ozone concentrations exceeded 82 ppb over the Canadian portion of the modeling domain (about 3000 grid squares). The index thus gives a combined measure of both the areal extent and duration of high ozone values. Table 5.2 from the Canadian Assessment (1997c) shows the value of the model simulated index for the base case using both actual emissions and values simulated with four different emission reduction scenarios. Table 5.2 then presents the results as a percent reduction in the index value for the period 25 July to 6 August 1988. The first part of the period had only a moderate index value, but a widespread episode occurred on the first five days of August that reached a peak during 3-5 August. The table shows that the predicted impact of reducing both NO_x and VOC emissions in Canada by 50 percent would reduce the index by only about 30 percent whether averaged over the whole period, five days or three days. On the other hand, reducing the US emissions by the same percentage predicted a reduction in the index of over 60 percent. The last two columns indicate that reducing only the US NO_x emissions by 50 percent has a larger impact than reducing only the VOC emissions. While not too much emphasis should be placed on the exact percentage reductions in the

index, it is clear that the results are consistent with significant transboundary transport of ozone and its precursors from the United States into Canada. This particular approach could be applied to estimate the impact of reducing precursor emissions in any prescribed region, such as anyone particular province or state, or group of provinces or states, thereby obtaining a quantitative estimate of the role of transboundary pollution transport. Such an approach has been taken in modeling efforts by the Ozone Transport Assessment Group.

As mentioned above, the Ozone Transport Assessment Group investigated the impact of changing emissions on ozone and precursor transport in eastern North America using UAM-V. For one set of modeling runs, specific sub-regions in the United States (as well as a portion of southern Ontario) were defined. Within a particular sub-region, all anthropogenic NO_x and VOC emissions were "turned off" to investigate the influence of emissions within that sub-region on ozone levels in specific downwind receptor regions. A map of the source sub-regions defined by OTAG is given in Figure 5.3. A map of the receptor regions is given in Figure 5.4. Figure 5.2, as mentioned above, is a map displaying the predicted reductions in ozone from turning off anthropogenic emissions in the industrial Midwest for a modeled ozone episode during July 1991.

Two receptor regions from the OTAG UAM-V modeling results are of particular interest in assessing transboundary transport: 1) the Detroit/Windsor border area (box 11 in Figure 5.4), and 2) the Toronto/Southern Ontario receptor region (blue box to the upper right of the Detroit/Windsor box 11 in Figure 5.4). The Toronto/Southern Ontario receptor region was not originally defined by OT AG, but data for this region were extracted from the OT AG modeling results for presentation in this report. A metric for ozone exposure was calculated as an output of the sub-regional modeling effort. Changes in the exposure metric were determined between a primary modeling run in which emissions were not changed, and a "zero-out" run in which all anthropogenic NOx and VOC emissions were turned off in a particular sub-region. The two principal ozone exposure metrics were "areal exposure" (expressed in units of ppb hrs km1 and "grid cell hours" above a given ozone concentration threshold (i.e., the sum of the number of hours grid cells were predicted to be above a particular threshold within a particular receptor region).

The percentage reductions in ozone exposure over three concentration thresholds (80 ppb, 100 ppb, and 120 ppb) in the Detroit/Windsor and Toronto/Southern Ontario receptor regions are given in Table 5.3. As expected, the largest impact on ozone exposure comes from the emission sources within the receptor regions (sub-region 2 and part of sub-region 3 in Figure 5.3). In addition, however, significant impacts are also apparent from emissions occurring far upwind. The results are consistent with the Canadian ROM results discussed above in finding a significant impact in the receptor regions from emissions occurring in areas hundreds of kilometers away.

For the July 1995 episode, significant impacts were seen in the receptor regions from emissions in the US Great Plains (parts of Iowa, Kansas, Minnesota, Missouri, North Dakota, Nebraska, and South Dakota) as well as from emissions in the central Midwest (all or parts of Illinois, Indiana, Kentucky, Michigan and Wisconsin). Due to the predominate windflow pattern from the southwest and west during major ozone episodes, emission sources to the east in Connecticut, Delaware, New Jersey, eastern New York and extreme eastern Pennsylvania (OTAG sub-region 4) had little or no impact on these receptor regions, but still contributed to ozone and precursor transport into downwind areas farther to the east of sub-region 4.

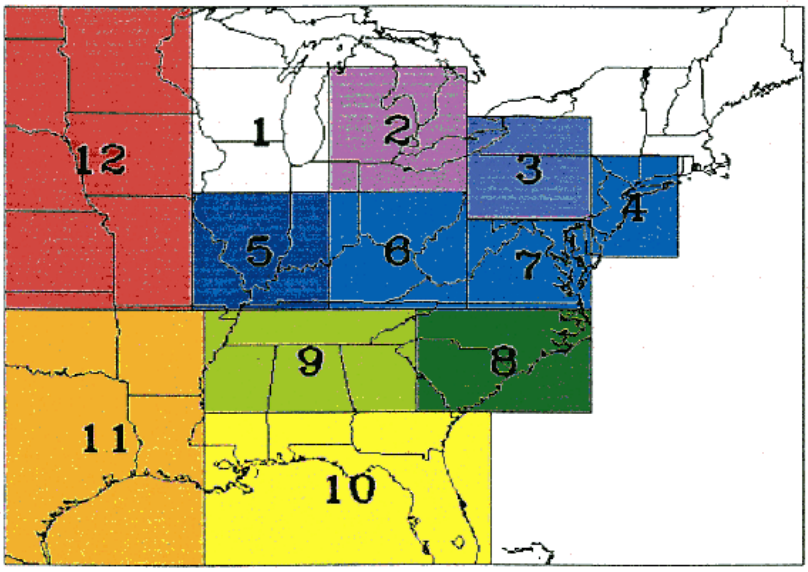

Figure 5.3 Map of sub-regions in which all anthropogenic emissions (NOx and VOCs) were turned off during a series of OTAG UAM-V modeling runs. Downwind impacts were assessed in receptor regions shown in Figure 5.4.

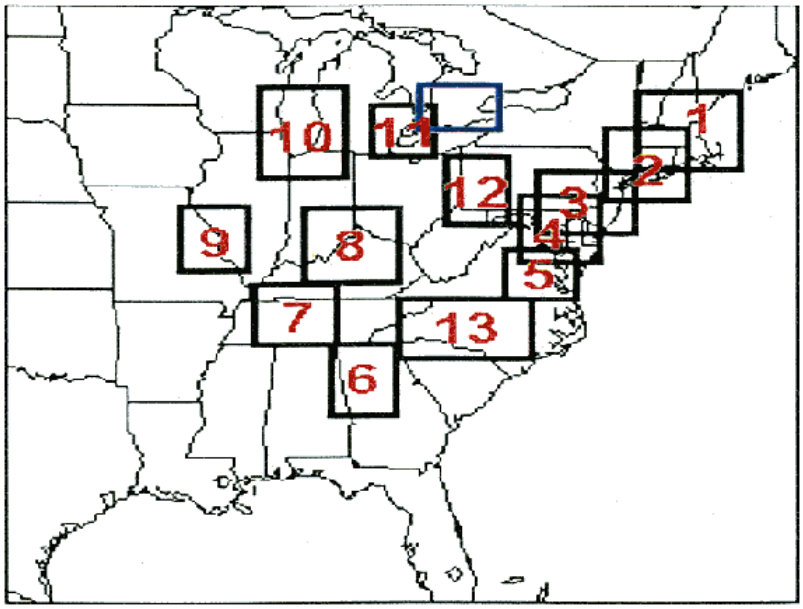

Figure 5.4 Map of receptor regions for assessing ozone transport impacts by OT AG UAM- V modeling. This report focuses on the transborder area of Detroit/Windsor (box 11) and the Toronto/Southern Ontario region (blue box).

For the July 1988 episode, similar significant impacts were also predicted in the receptor regions, but with some differences. Whereas the Ohio River Valley source region ("sub- region 6" - parts of Indiana, Kentucky, Ohio, Virginia, and West Virginia) showed some contribution to the receptor areas for the July 1995 episode, the predicted contribution from the July 1988 episode was significantly larger. In contrast, the influence of emissions in the US Great Plains dropped. These results show that transport pathways can differ between two different episodes, which is consistent with the substantial range of possible pathways for episodes in southern Ontario over a four-year period as shown in Figure 4.12. Thus, the conclusions drawn regarding the lack of transport for one episode may not be valid for others.

Table 5.2 **Table showing the model predicted percent reductions in the Ozone Exceedance Area Index within the Canadian domain for various levels of emission reductions within Canada and the United States during a 13-day period in 1988.**

DATE	O_3 >82ppb AREA INDEX	EMISSION INPUT REDUCTION			
		CANADIAN	US		
		NO_X & VOC by 50%	NO_X & VOC by 50%	NO_X only by 50%	VOC only by 50%
July 25	452	13%	69%	52%	25%
26	410	17	32	25	19
27	347	35	73	65	37
28	552	45	88	80	41
29	902	31	55	40	25
30	333	59	69	58	30
31	66	33	70	38	42
Aug 1	1071	16	78	63	34
2	1993	20	55	45	19
3	3417	26	49	39	12
4	3036	28	63	50	19
5	2723	38	71	61	24
6	400	50	94	84	45
All days	1208	29	62	51	22
Aug 1-5	2448	27	61	49	20
Aug 3-5	3192	31	62	50	19

Figures shown in the main block of the table are percent reductions.

Table 5.3 **Table showing the OTAG UAM-V predicted percent reductions in ozone exposure within the Detroit/Windsor and Toronto/Southern Ontario receptor regions due to "turning off" all anthropogenic NOx and VOC emissions in specific geographical source regions for modeled ozone episodes in July 1995 and July 1988.**

		PERCENT REDUCTION IN OZONE EXPOSURE ABOVE THRESHOLD WITHIN RECEPTOR REGION FROM "TURNING OFF" EMISSIONS IN SOURCE REGION				
		Detroit/Windsor*			Toronto/ Southern Ontario**	
Episode Date	SOURCE REGION OF EMISSIONS	>80 ppb	>100 ppb	>120 ppb	>80 ppb	>100 ppb
10-18 July 1995	Parts of IA, IL, IN, MI and WI (OTAG sub-region 1)	27%	31%	59%	35%	51%
	Parts of IN, MI, OH, and southern Ontario (OTAG sub-region 2)	99	100	100	88	62
	Parts of western PA and NY (OTAG sub-region 3)	0	0	0	12	26
	Parts of CT, DE, NJ, NY and PA (OTAG sub-region 4)	0	0	0	0	0
	Parts of IL, IN, KY, and MO (OTAG sub-region 5)	41	63	56	36	37
	Parts of IN, KY, OH, VA and WV (OTAG sub-region 6)	5	6	0	7	7
	Parts of AL, AR, GA, MS, NC, SC, and TN (OTAG sub-region 9)	6	8	6	3	4
	Parts of IA, KS, MN, MO, ND, NE, and SD (OTAG sub-region 12)	17	27	28	16	30

* The July 1995 predicted reductions in the Detroit/Windsor receptor region are based on changes in ozone areal exposure expressed in units of "ppb hrs km^2." All other predicted reductions are based on changes in grid cell hours above the indicated thresholds.

**There were no grid cells predicted to be above 120 ppb in the Toronto/Southern Ontario receptor region for the July 1995 episode.

Table 5.3 (cont.)

		PERCENT REDUCTION IN OZONE EXPOSURE ABOVE THRESHOLD WITHIN RECEPTOR REGION FROM "TURNING OFF" EMISSIONS IN SOURCE REGION					
		Detroit/Windsor			Toronto/ Southern Ontario		
Episode Date	SOURCE REGION OF EMISSIONS	>80 ppb	>100 ppb	>120 ppb	>80 ppb	>100 ppb	>120 ppb
4-11 July 1988	Parts of IA, IL, IN, MI and WI (OTAG sub-region 1)	22%	31%	36%	26%	19%	29
	Parts of IN, MI, OH, and southern Ontario (OTAG sub-region 2)	98	100	100	73	58	83
	Parts of western PA and NY (OTAG sub-region 3)	4	1	1	26	42	33
	Parts of CT, DE, NJ, NY and PA (OTAG sub-region 4)	0	0	0	0	0	0
	Parts of IL, IN, KY, and MO (OTAG sub-region 5)	15	17	23	13	11	19
	Parts of IN, KY, OH, VA and WV (OTAG sub-region 6)	31	44	29	25	17	31
	Parts of AL, AR, GA, MS, NC, SC, and TN (OTAG sub-region 9)	9	9	18	8	8	11
	Parts of IA, KS, MN, MO, ND, NE, and SD (OTAG sub-region 12)	1	0	0	2	1	0

Data for the July 1995 episode were provided by the OTAG Northeast Modeling and Analysis Center and Jeff Underhill, New Hampshire Department of Environmental Services. Data for the July 1988 episode were provided courtesy of Norm Possiel, OTAG EPA Modeling Center, US EPA, Research Triangle Park, North Carolina.

6. State-of-the-Science for Estimating Transboundary Transport of Ozone

6.1 Definition of Transboundary Transport

Chapters 4 and 5 discussed the various methods of assessing the long-range transport of air pollutants in general, and ozone and its precursors in particular, but not always with reference to any particular boundaries. All of these methods have clearly established that long-range transport does occur, including across the Canada-United States border. This chapter will specifically address the issue of estimating the cross boundary component of such long-range transport within the overall cycle. Clearly those methods which explicitly include a transport component through wind fields or trajectories offer the most promise.

Terms such as long-range transport, inter-regional transport, transboundary flows and others are often used interchangeably without any precise definition. The transboundary flow of a chemical species can be formulated in many ways. The formulation depends on the specific question being asked from both scientific and policy points of view. Following are some of the ways in which the question can be posed ranging from the simplest to the most difficult.

Q1 On what percentage of days in a given time period, such as a year, does the wind transport pollution across a boundary from a known emission source on one side to a receptor on the other side?

Q2 What is the average ambient concentration of a pollutant on days when the wind is blowing into one region from another region versus the ambient concentrations on days when it is not?

Q3 What proportion of the pollutants measured at a given location, or within a given region, can be attributed to the flow across a boundary from another region?

Q4 What is the actual quantitative flux of a pollutant across a given boundary (estimated in units of mass per unit time)? The answer integrates the simpler “how often” and “what concentration” questions. This measure can be physically defined and is used in quantitative regional mass budgets. It is usually referred to as a transboundary flux.

Figure 6.1 shows a schematic representation to illustrate the concept of transboundary transport across a vertical plane along a stretch A-B of a boundary. The magnitude of the transboundary flux (TBF) is the quantitative measure of the flow of a pollutant, in units of mass per unit time across this boundary. It is given by the volume of air crossing the boundary per unit time multiplied by the pollutant concentration in that volume.

$$\mathbf{TBF = C(uhx)}$$

where:

C is the volume average pollutant concentration;

u is the average horizontal wind velocity component perpendicular to the boundary;

h is the height of the surface mixed layer; and

x is the length of the boundary.

For example, if the average concentration of O_3 over the vertical plane is 60 ppb or 120 mg/m^3, the average wind velocity is 10 km/hr and the height of the mixed layer is 1 km, then the flux across a 1000 km long boundary is 1200 tonnes/hr. The time integration could be carried out for one day, over an episode of several days, or for a seasonal or annual average.

The concept of transboundary flux as illustrated above is straightforward, but clearly it cannot be determined by direct measurement, although each of the contributing parameters can be determined individually. In the real world, the actual calculation is difficult. All of the variables **C**, **u**, and **h** vary in space and time in the vertical plane along the boundary, and their values are not determined on a routine basis with a high degree of spatial and temporal resolution. The value of the product of **u** and **C** at each point in space would have to be integrated over the whole cross-sectional area. For example, using the aircraft measurements given in Figure 4.26 (section 4.5) over southwestern Ontario, where the average ozone flux in the surface layer is approximately 400 mg/m2/sec, would yield a flux of 1440 tonnes/hr over the same cross-sectional area.

Actual vertical soundings of u and temperature (from which **h** is calculated) are available only twice daily from the sites near the border as shown in Figure 3.2. There is considerable inter-station variability as a result of the weather patterns themselves and the effects of the topography of the Adirondacks and the Great Lakes. Higher resolution is available from special intensive field studies, and these can be used to help develop parameterization schemes that then enable better use of available routine data. Both **u** and **h** have some spatial coherence and climatological averages are available for both variables in the United States (Holzworth, 1972) and Canada (Portelli, 1977). Pollutant concentration (**C**) presents a major problem because, although only ground-level ozone measurements are available on a routine basis with reasonable spatial and temporal resolution (see Figure 3.1), there is no routine information on the vertical profile within the surface mixed layer. Available evidence indicates that ozone concentrations are generally higher aloft (see section 4.5), especially at night as the flow just above the ground becomes de-coupled from the surface layer where ozone is depleted.

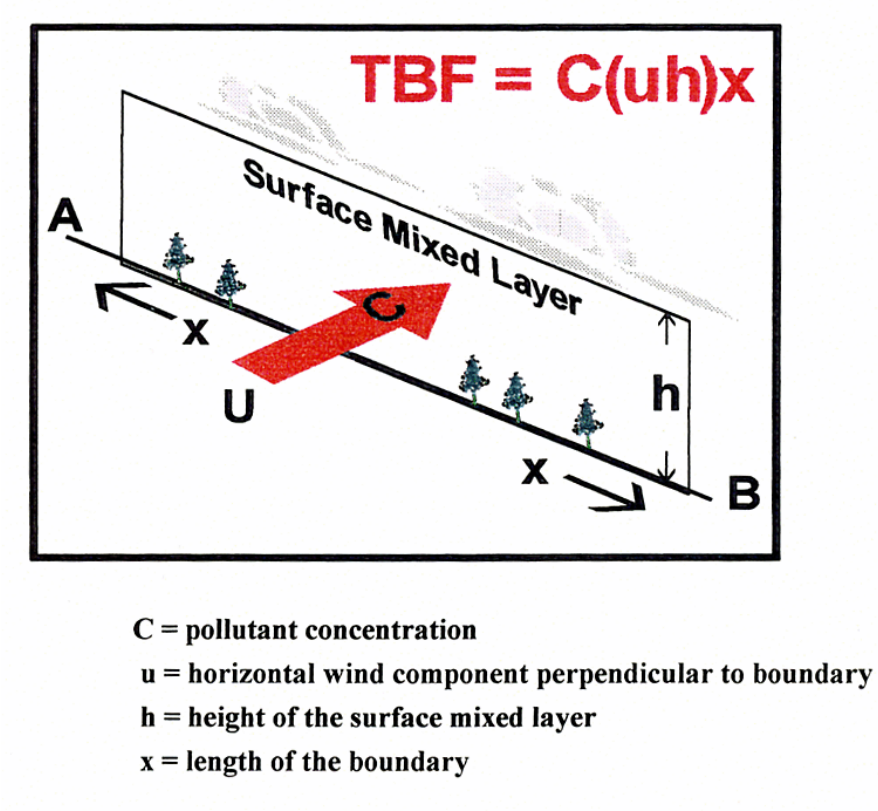

Figure 6.1 Schematic illustration of a vertical plane along a segment of a boundary and the parameters required to calculate the transboundary flux (TBF).

6.2 Synopsis of the Techniques for Assessing Transboundary Transport

In this section, the various techniques described in Chapters 4 and 5 will be assessed in terms of their proven ability or potential to answer the four questions posed in the previous section. Spatial plots of a variety of parameters (e.g., daily maximum ozone) can describe the ground-level geographical distribution of pollution and can identify the regions of concern. When related to the regional distribution of pollution sources, the plots can give an indication of where there is transboundary transport. Temporal analysis, by considering the difference between the time sequence of events at adjacent locations, can, in certain circumstances, provide evidence of transport between the locations.

Analyses of ozone and precursor concentration variation by day of the week are all consistent with a reduction of precursor emissions on the weekend. At the more remote sites, the impact is observed with a time lag of one day. Thus, if the weekly cycle in emissions could be more precisely quantified by source region and source sector, further day of the week analysis of ambient concentrations could provide a powerful tool to estimate the impact of emission reductions on both the local and regional scale, and provide information on long-range and transboundary transport.

Statistical techniques provide a powerful method of analyzing the spatial and temporal variations of ozone concentrations simultaneously. These have shown that high ozone concentrations are correlated over time scales of 1 to 2.5 days, depending on location, and spatially over distances of up to 600 km, indicating that ozone is a regional-scale problem. Serial correlation using time lags of one to three days between regions provides evidence of transport in preferred directions.

All of the above methods provide a useful characterization of the long-range transport issue, but are only inferential in that they do not explicitly include any meteorological or emissions information. The next level of detail is to include some function of transport into the analysis. The most easily obtained parameter is the local surface wind. A very common technique that has been used extensively over the years is to sort the ozone concentrations according to wind directional sectors. In this way “pollution roses” can be generated which indicate the wind sector within which potential sources for the ozone may reside. Provided that the monitoring sites are located close to a boundary, they can provide valuable information on both the frequency of transboundary flux and associated pollutant concentrations. However, because the local wind is not always a good indicator of the previous history of the airmass arriving at the monitoring site, apportionment of concentrations amongst precursor emission source regions is not always possible. The transboundary flux calculated as a product of the surface wind and concentration could be seriously in error (see later discussion).

The main component of transboundary flux is the airmass flow pattern itself, so the next natural level of sophistication in data analysis is to include airmass trajectories. Each observation can be associated with a trajectory arriving at the monitoring site. These trajectories are calculated from the wind fields generated every 12 hours by the meteorological services, and can be single level, multi-level, or boundary layer average. The results from a limited set of tracer experiments show that the 925 hPa (mb) trajectory (representative of the mixed layer wind) does a good job in simulating the motion of a ground-level release. The most realistic model is one which includes

some vertical structure and handles the de-coupling of transport at night from the immediate surface layer.

Once a data set is available at a given monitoring site containing ozone concentration and concurrent airmass trajectory, there are two fundamentally different ways the data can be sorted and analyzed. First, a statistical distribution of concentrations can be prepared, and the trajectories associated with a particular range plotted. Occasions with ozone greater than some specified threshold (i.e., > 82 ppb or > 120 ppb) are common selections. The second approach is to first sort the trajectory data by direction. This can be done by a pre-determined selection of directions, or better still, by means of statistical cluster analysis. The statistical distribution of the ozone observations within each trajectory cluster can then be determined.

The first method has been used extensively. By including a residence time and decay factors, one can get semi-quantitative information on the contributions from upwind emission precursor source regions.

The second approach has been used much less frequently, but from the transboundary flux point of view it is more useful. At monitoring sites close to a border, this method enables the whole range of ground-level concentrations associated with cross-border flows to be accurately determined. Information on the general magnitude of the near-ground transboundary transport can be determined as well as differences in this flux with transport in opposite directions across the border.

Techniques that involve trajectory flows between fixed geographical regions combined with time lag correlations of the ozone data between the same regions offer another powerful tool with which to examine transboundary transport in a semi-quantitative way.

The only observational way to determine an actual quantitative flux to answer Q4 is from vertical profiles that measure ozone (or precursor) concentrations and wind components simultaneously as a function of height. There are a few sets of such profiles obtained during major field studies such as EMEFS, NARE, NARSTO-NE and NARSTO-CE over time frames of a month and in limited geographical areas. Several profiles from the first two studies have been published, but only one paper has calculated the vertical profile of fluxes. The horizontal flux integrated up to a height of 5 km through the region of measurements could also be calculated. A large fraction of this flux, however, would be due to the free tropospheric pool of ozone which has little to do with the regional-scale transport nearer the surface. In order to calculate the flux occurring as a result of the regional-scale emissions, it would first be necessary to separate out the short-term component of the ozone time series. Another issue is the height to which fluxes should be calculated. None of these issues have as yet been resolved, thus the value of this technique, while very promising, needs further investigation.

Tracer techniques provide data on the occurrence of transboundary transport and are useful in verifying trajectory calculations. The intermittent nature of these data means that without a much more concerted (and expensive) effort, tracers do not offer much promise for answering Q3 and Q4.

Although there are differing opinions on the value of numerical models, over the long-term they seem to offer the best potential for obtaining fully quantitative estimates of transboundary transport. They were used extensively to do this for sulfur, but up to now they have not been used to provide such an output for ozone. A major issue is their ability to correctly simulate the vertical structure of the atmosphere and the chemical profiles in the lower boundary layer. This capability is continually being improved but until comparisons between the observed and model-simulated structure of the lower atmosphere are substantially improved, they should be used with caution to answer Q4. In the work of the Ozone Transport Assessment Group, the predicted ozone in upper layers of the model were underestimated relative to ambient aircraft measurements. At the very least, information obtained from such modeling efforts needs to be viewed as a conservative, lower-bound estimate of long-range transport. To the extent such models actually estimate significant ozone and precursor transport (as discussed in Chapter 5), air planners can be confident that regional control strategies will have a similar, if not larger impact, on ozone and precursor transport as predicted by the models. Because Lagrangian models are formulated around the wind flow, they have a higher potential value for estimating long-range transport, including transboundary fluxes.

The models appear to simulate ground-level ozone distribution patterns reasonably well, although it is by no means certain that they are doing so for the right reasons. There is some evidence that they tend to overestimate daytime photochemical production but underestimate overnight transport. Assuming that they are simulating ozone correctly, then the impact of changing the emissions rates and/or geographical distribution can be predicted. Most effort has been put into simulating the regional scale impact on parameters such as the daily maximum ozone, or the frequency of exceeding some threshold value, caused by reducing precursor emissions according to several scenarios. Significant impacts are predicted to occur at large distances downwind from the emission changes. In a few cases, the models have been used to simulate the impact on one defined geographical region caused by changing emissions in another region, most recently in the work of the Ozone Transport Assessment Group in the United States. In principle, this seems to be an approach worth pursuing to answer Q3.

An attempt is made to summarize the results of the above assessment in Table 6.1. The number of Xs in each box is somewhat subjective, and would increase for some combinations of the methods. It must be remembered that empirical data analysis results, by definition, are only valid for the current configuration of emissions. Extrapolation to future emission scenarios is not valid—only models can do this. Only those methods which include data on the wind flow determined either by trajectory analysis or simulated by models can provide answers to Q3 and Q4. Except for cases where actual measurements of the wind and pollution vertical profiles are made at or near the border, the methods used must also include some information on emission source strength and location.

While quantitative fluxes of chemical species are necessary parameters needed in regional and global cycling studies, knowing the precise value of the flux across a boundary is not necessarily the most important parameter from a policy point of view. An outstanding issue that is not addressed by the above assessment is to decide what the most important question is from the policy point of view. Is it the answer to Q4 on how much crosses a border, or the answer to Q3 on the effect on ozone concentrations caused by changing emissions on the other side of a border?

Knowing the former does not necessarily enable the latter to be answered. If the latter is more important, then what are the best parameters to define this impact: reduction in the area exceeding the standards, reduction in population time-averaged exposure, reduction in the number of exceedances of extreme values, reduction in the total summer season transboundary ozone flux, or reduction in some other parameter? In the context of the available monitoring data, trajectory studies, and modeling results summarized in the previous chapters, there is sufficient knowledge that transboundary transport exists and has a significant impact along the border. The policy challenge will be to use the available tools along with the appropriate questions to develop and apply effective strategies to reduce transboundary ozone and precursor transport.

Table 6.1 **Table showing a ranking of the potential of the various broad data analysis techniques based on routinely collected data, and modeling applications, to answer the questions regarding transboundary flow. Rankings shown in parentheses are based on non-routine measurements during intensive observation periods.**

X - some potential XX - moderate potential XXX - highest potential

Analysis Technique		Q 1	Q 2	Q 3	Q 4
DATA ANALYSIS	Spatial analysis	X			
	Temporal analysis	X	X	X	
	Statistical analysis	XX	X		
	Wind Sector analysis	XX	XX		
	Airmass trajectories	XXX	XXX		
	Trajectory residence times	XXX	XXX	XX	
	Trajectories & decay factors	XXX	XXX	XX	X
	(Vertical sounding analysis)		(XX)	(X)	(XXX)
TRACERS	(Tracers of opportunity)	(XXX)	(X)		
	(Artificial tracers)	(X)		(X)	
MODELS	Lagrangian models	XXX	XX	XX	XXX
	Eulerian models	XXX	XX	XXX	XX

Q 1 - How often does cross-boundary transport occur?

Q 2 - What is concentration when flow is across a boundary?

Q 3 - What proportion of pollution in one region can be attributed to emissions in another region?

Q 4 - What is the actual numerical value of pollution flux across a boundary?

7. Conclusions and Recommendations for Future Coordinated Scientific Work

7.1 Conclusions

All of the observationally based studies lead to the same general conclusion—long-range transport of ozone is a reality in eastern North America. This is especially so in the northern half of the ozone exceedance region where the typical weather pattern leads to a flow from high emission zones located to the southwest into New England and southeastern Canada. The direction of this transport has been substantiated through trajectory analysis, statistical lag correlations, modeling of historical ozone episodes, and mapping of the actual motion of the region of ozone maxima. This is in contrast to the frequent stagnation periods that occur further south and where transport is over shorter distances.

The short-term component of ozone concentration (related to synoptic weather patterns) shows a strong correlation between nearby sites over space scales of 600 km and time scales of 1 to 2.5 days depending on location, indicating that ozone is a regional-scale problem. Statistical analyses show that the ozone measured at a particular site at a particular time is made up of three components. The first is the global background component which has a small seasonal cycle. At the latitude of the Canada-United States border it averages between 25 and 40 ppb during the summer months. The second component is the regional component on a 600 km scale referred to above. Finally, there is a local contribution which has a strong diurnal cycle and is also very dependent on local meteorological conditions such as cloud cover, temperature and precipitation.

Several useful studies aimed at assessing transboundary transport from regions within and between the United States and Canada have been carried out and offer the potential for further application. Even so, it must be noted that the domain of many US studies ends at the Canadian border, whereas most Canadian studies have necessarily had to include US input data. In some cases, these studies produced outputs in both Canadian and US domains. Several studies using the same technical approach (or slight variations thereof) were carried out independently in each country and the results have not been merged at the border. There were also some studies unique to each country. Thus, in focusing on the Canada-United States transboundary issue, there is obviously an opportunity for more cross border cooperation between scientists, especially those carrying out data analysis and interpretation.

Ozone modeling studies that decrease emissions in one region have shown large changes in the overall spatial distribution of ozone over a much larger area than the region in which emissions were decreased. Modeling results from the Ozone Transport Assessment Group, for example, show significant transport impacts on ozone in the Detroit-Windsor border area and in southern Ontario due to emission decreases in regions of the United States. The results are consistent with the results from the earlier ROM 2.2 effort in Canada. By implication, there are obvious modeled reductions in the transboundary pollutant flux into these downwind regions, although actual quantitative calculations of transboundary fluxes have not been made.

Several promising techniques are available to infer transboundary fluxes from data analysis involving the use of trajectories with a variety of statistical techniques and from the application of models. While no one approach can be as yet declared the most appropriate, using several methods simultaneously provides strong "weight of evidence" conclusions when they all provide results consistent with each other.

A few field studies have made the measurements necessary to calculate mass fluxes of ozone. These measurements have been made with aircraft, ozonesondes and tethersondes and have been limited to a few months in a few regions. Some horizontal transport fluxes above small regions have been estimated, but in no cases has the flux across a specific boundary been calculated although the capability of doing so exists.

One major issue in calculating transboundary flux is correctly measuring or simulating the vertical profile of ozone concentration and wind speed in the near-surface layer of the atmosphere. This profile has a very pronounced diurnal cycle which has only been accurately documented by aircraft measurements during special field studies. Some indication of this cycle is provided on a continuing basis at a few high elevation sites. The general feature of this cycle is that the surface layer is well mixed during the late morning to late afternoon hours and only at these times does the surface observational data give a reasonable measure for the whole layer. From evening until early morning vertical mixing is severely limited. Ozone is depleted near the surface but remains at high concentrations aloft overnight. At the same time, a meteorological feature known as the "nocturnal jet" or "low-level jet" often forms several hundred meters above the ground and is able to transport the undiminished ozone long distances overnight. As the vertical mixing develops the next day, this pool of ozone aloft, now several hundred kilometers downwind from its source region, is available for entrainment down to the surface where it adds to the newly forming local ozone. There is evidence that most models have insufficient vertical resolution to simulate this phenomenon realistically and, even if they could, there is scant data against which to verify their accuracy in doing so. A systematic program of vertical soundings in the lower atmosphere at several locations near the border would be very useful in two ways. First, to provide quantitative measures of the transboundary flux of ozone, and second, to validate and calibrate results obtained by indirect methods.

7.2 Recommendations

In developing recommendations for future studies, the emphasis is on an air quality planner's perspective, from which the problem of transboundary ozone and precursor transport is already recognized and needs to be addressed. The focus is not on what we would like to know about transboundary transport *per se*, but what we would like to know about effective strategies to reduce the existing problem of pollution transport. With this perspective in mind, the following are suggested complementary high priority studies that should be initiated jointly by the United States and Canada. They are listed in approximate order of priority within each category, but the implementation schedule should obviously build on existing relationships between Canadian and US scientists and organizations.

Appropriate Measures to Address Transboundary Pollution Transport

1. **The first priority is to establish the appropriate question to answer regarding transboundary transport**. Four possible questions are proposed in Chapter 6. The answers give information at several different levels of detail—some qualitative, others quantitative. Other questions could be defined. Referring back to Table 6.1, those available approaches that have the highest potential for answering questions 1 through 3 should be given highest priority. Question 4, while necessary in regional and global cycling studies, is not necessarily the most important question from a policy point of view in developing strategies to solve the transboundary transport problem. A full answer to question 4 will require extensive additional monitoring, or the availability of models that have been shown to simulate the structure of near- ground vertical profiles of the wind and ozone concentrations realistically. Some recommendations on how to work towards that goal are given below.

2. **Determine the most robust measures, or indices, of regional pollution transport**. Measures that are of interest scientifically are not necessarily the most relevant from an air planner's point of view. It is, therefore, necessary to examine from a statistical and physio/chemical point of view what, in the absence of a direct measurement, are the most useful measures. For example, is a regional transport measure based on average ozone concentration better than one based on peak ozone that is more subject to local influences?

Modeling

3. **Apply the existing models specifically to assess how reducing precursor emissions in one defined region impacts the ozone concentrations in another defined region**. The boundaries should include the Canada-United States border and other regions on each side of the border. Sub-regional modeling performed by the Ozone Transport Assessment Group has demonstrated the value of this approach in guiding policy recommendations. Several measures of impact should be considered, for example, the measure proposed by the Canadian modeling workgroup {Canadian Assessment, 1997b), i.e., the number of grid squares showing ozone exceedances above thresholds such as 82 ppb or 120 ppb. There are, however, other impact measures having scientific and policy relevance that can be used.

4. **Select and apply the best model(s) to estimate transboundary fluxes and assess source culpability by geographic region and source category.** The existing stable of models needs to be evaluated. One or two that are acceptable and that have the best capability, or can be improved, to calculate pollution transport fluxes in the northeastern United States and eastern Canada should then be chosen. In particular, the ability of the model(s) to simulate the vertical structure of the wind and ozone concentrations in near-ground layers should be further developed.

Monitoring

5. **Ensure that the monitoring needs for estimating transboundary transport and for regional airshed air quality management in the northeastern United States and southeastern Canada are met.** An alarming trend noted in recent years is the closing of

many monitoring stations, some of which have valuable long- term records. Any further erosion will severely jeopardize the ability to track the impact of emission reductions on ozone levels and assess whether the countries are meeting treaty obligations. It is, therefore, **further recommended that the plans for monitoring near the border and within the whole region be reviewed by the agencies involved to ensure continuity of essential observations**. The statistical analyses show that the correlation of ozone measurements on the regional scale remains high (i.e., > 0.7) between stations out to distances of about 200 km. This suggests that stations along or near the border should be spaced no further apart than this distance. Figure 2.1 shows that this criteria is generally met along the two major ozone transport pathways.

6. **It is essential to maintain existing mountain top monitoring at high elevation sites in the study region**, especially those near the border (i.e., Whiteface Mountain and Mount Sutton and by reinstating Mont Tremblant, if necessary). These high level stations, removed from local influences, are ideally located to monitor any changes in transboundary transport due to future emission changes that occur in the upper boundary-layer/lower free-troposphere.

7. **Vertical soundings can playa vital part in future monitoring and assessment**— mountain top measurements, while necessary, are not sufficient in vertical resolution. The need for, and frequency of, routine soundings in the lowest few kilometers of the atmosphere should be established by further review of the existing sounding database. It may be possible to establish typical vertical profiles that can be related to routinely monitored parameters through statistical analysis of airmass, season and trajectories. All available, practical in situ and remote sensing measurement methods should be considered. A few well chosen sites located on the major cross-border transport pathways will probably be needed to provide a larger data set to carry out such analyses, as well as for validation of models.

8. **Develop a common, user-friendly database for all ambient monitoring data in the study area (and, in fact, the entire United States and Canada)**. A reason many past data analysis studies stopped at the border is the difficulty in obtaining .data from the other side without going through a frustrating and time consuming re- formatting of the data into a common usable format.

Emissions information

9. **Prepare a coherent database for ozone precursor emissions in the border regions that provides information in a common format (including simple visual displays) combined for both countries.** This database would be used as the common input for the model application in recommendation 3. A simple common visual presentation format needs to be developed to show the geographical distribution of the emissions so that the results of the data analyses discussed in Chapter 4 can be readily interpreted.

Data Analysis and Interpretation

10. **Generate an airmass trajectory database for representative border points (e.g., every 200 km from the Bay of Fundy to Lake Superior) using an agreed- upon approach**. This database can be used to establish a climatology of the frequencies of airflow in each direction across the boundary and determine an atmospheric region of influence along the border zone for airmass motion over periods ranging from one to five days. Then, using assumed atmospheric lifetimes for ozone and precursors, the most important emission source regions can be identified.

11. **Address the issue of upper level transport by comparisons of data at Whiteface Mountain, Mount Sutton and Mont Tremblant when trajectories are in the appropriate direction.** Also, carry out a systematic analysis of the data from locations where there are two nearby observing stations at different altitudes in order to better understand the diurnal behavior of the vertical structure of ozone concentrations.

12. **Apply the technique of combining trajectory directions for episodes with ozone maxima time-lags but including two new regions: the Windsor-Quebec City Corridor (WQC) and the southern Atlantic region (SAR) of Canada**. The linkages between the three US Northeast, Northwest, and Midwest regions with the new WQC and SAR regions would then provide further insight into the transport between these regions.

13. **Explore further the potential of day-of-the-week analysis at sites near the border.** A weekend versus weekday signal in ozone concentrations has been detected in a few studies and assumed to be related to changes in upwind emissions. This needs to be more fully investigated, especially in locations where inferences could be made about changes in regional transport.

14. **Choose episodes of one or more days when the wind flow is fairly constant in a direction along the major transport pathways, then construct a cross-section of the observations along the direction of flow every hour.** The daily evolution of a pollutant concentration profile along a transport pathway has the potential to provide valuable insight into the role of regional-scale transport. A cross-section could be along the eastern seaboard of the United States into the Bay of Fundy region. Other axes could extend eastward from the Ohio River Valley into New England, from the US upper Great Plains into southwestern Ontario and along the St. Lawrence Valley, from southwestern Ontario into New England or the southern part of the Canadian Atlantic provinces, as well as other appropriate directions.

8. Considerations for Air Quality Planners

As described in this report, the available information from monitoring, trajectory and modeling studies provides strong “weight of evidence” that windborne air pollutants regularly cross the border between the eastern United States and Canada. While this study focuses on the cross-border transport of ozone and its precursors, similar long-range transport mechanisms involve other pollutants of concern, including sulfur dioxide, fine particles, and toxic metals such as mercury. Depending on prevailing weather conditions, air pollutants can travel across the Canada-United States border in either direction. As a result, both nations are at times the recipient of, and at times a contributor to, their neighbor's air pollution problems.

The transport of ozone and its precursors is a joint concern in Canada and the United States because ozone is a serious public health concern and a large number of areas in eastern North America currently violate ozone health standards. Ozone exposure can lead to a variety of well documented health effects. It can increase the severity and incidences of asthma attacks and respiratory infections. It also can lead to an increased prevalence of chronic respiratory symptoms and the development of chronic respiratory bronchiolitis. Children are at greatest risk from ozone exposure because their lungs are still developing, they breathe more air relative to their lung size than adults, and they spend a greater portion of their time exercising outdoors during the daytime when ozone levels are highest. An estimated five to 20 percent of the general population is thought to be particularly sensitive to ozone (Balmes, 1992).

Health impacts have been documented in areas where transboundary transport plays a significant role in ozone levels. For example, OTAG predicted that emissions in the upper Great Plains of the United States contributed about 30 percent to the number of hours ozone levels exceeded 100 ppb in the Toronto/southern Ontario region during an ozone episode in July 1995 (see Chapter 5). The health standard in Canada is 82 ppb averaged over one hour. A study of southern Ontario hospital admissions between 1983 and 1988 estimated that 5 percent of daily respiratory admissions in the months of May to August were attributable to ozone, with sulfates accounting for an additional 1 percent. The largest impact was found for infants, where 15 percent of admissions were attributable to the ozone-sulfate mix (Burnett et al., 1994).

As discussed in this report, aircraft measurements have recorded large regions of consistently elevated ozone concentrations at altitudes above 200 meters at night and in the early morning. Large scale motions of air during certain warm weather patterns move this pollution hundreds of kilometers away from a pollution source region. Downwind, the transported ozone-rich layer mixes down to the surface during the day as the atmosphere warms, providing a mechanism for ozone aloft to reach the ground at later times far downwind from the source region. As a result, ozone pollution problems in many areas of the eastern United States and Canada are composed of both local and regional (transport-influenced) components. The policy implication of this finding is that by themselves, local emissions control measures will be inadequate to achieve healthful air quality in many areas in the absence of broad-based measures to reduce regional background pollution levels and long-range transport. In short, Canada and the United States will need to work together to develop air quality management strategies that effectively address the problem of cross-border transport.

As a first step to that end, renewed efforts are needed to develop pollution control strategies for "areas of influence" (common source regions which affect large, downwind geographical areas), rather than for isolated urban areas. In the transboundary context, this requires several actions: 1) to integrate and make compatible the data now being collected by Canada and the United States on pollution sources and ambient air quality; 2) to compare and merge the results of modeling studies which have been undertaken independently in both countries;[2] and 3) to commit to the continued maintenance and expansion, where possible, of existing air quality monitoring programs, which are in danger of being undermined by fiscal constraints. The Canada-US Air Quality Committee that implements the Canada-United States Air Quality Agreement has indicated the importance of air quality monitoring for acid rain and smog. The Committee requested a status report in 1997 of the programs in place in both countries.

Relative to studies specifically focused on cross-border ozone transport, there is an extensive body of scientific literature devoted more generally to ozone transport. This literature encompasses both modeling efforts and analyses based on observational data, such as ambient air quality monitoring results (*See, e.g.*, NRC, 1991 and references therein). Some key issues that must be faced as policies are developed to address transboundary ozone and precursor transport are summarized below.

- Depending on meteorological conditions and other factors, ozone and its precursors can be transported up to and beyond 750 kilometers downwind from a source region. As a result, elevated levels of ozone commonly persist over broad areas of eastern North America spanning the border between the United States and Canada for many days at a time. The spatial scale of high ozone episodes over eastern North America can be greater than 600,000 square kilometers (NRC, 1991).

- Transboundary flows of ozone and ozone precursors are not limited to a single pathway or direction. Rather, transport into a given region can occur from multiple directions and at different heights in the atmosphere. As a result, control strategies will have to account for the multiple dimensions of transport. This study focuses on I ozone flows across the eastern border of the United States and Canada, where the major axis of transport is from the southwest to the northeast. Different transport pathways may be more important for other types of pollutants and for different segments of the Canada-United States border.

[2] Most US modeling studies have stopped at the border, whereas most Canadian studies have, of necessity, included US inputs and in some cases generated results for the US domain. However, few attempts have been made to reconcile the results of these modeling studies at the border.

- Recent analyses performed by the Ozone Transport Assessment Group (OTAG) in the United States confirm that reductions in NO_x emissions provide the greatest benefit in terms of reducing long-range ozone transport and lowering regional pollution levels. Such reductions would help address other cross-border public health and ecological concerns, such as acid rain, nitrogen deposition in marine estuaries, and fine particle formation.

- To reduce or eliminate the transboundary transport of ozone and its precursors, air quality management efforts focused on reducing the long-term, regional-scale component of the ozone problem will be more effective than efforts focused on reducing short-term local peak ozone concentrations (Rao et al., 1996). A long-term regional strategy will have both public health and ecological benefits (Heck et al., 1997).

While additional research may more precisely quantify the magnitude of ozone and ozone precursor transport across the eastern Canada-United States border (see chapter 7 for detailed recommendations on a future joint research agenda), the existing "weight of evidence" for cross-border ozone transport is robust and points to the need for significant broad based NO_x emissions reductions. Results from the aforementioned OTAG effort indicate that NO_x reductions of as much as 85 percent from elevated point sources (e.g., fossil fuel power plants) will be necessary to address transport within the eastern United States. Given the significant southwest to northeast transport patterns characteristic of severe ozone episodes in eastern North America, such reductions will help to reduce cross-border transport as well as region to region transport within the United States and Canada.

Fortunately, cost-effective and substantial NO_x reduction opportunities are available. Moreover, future joint efforts to reduce long-range ozone transport can take advantage of a variety of control options and strategies that have been successfully employed by states and provinces within the United States and Canada as part of past air quality management efforts. Examples include emissions allowance trading and pollution prevention programs, which may offer some of the most cost-effective reductions over the medium to long-term by eliminating or reducing the need for pollution controls (e.g., efficiency investments to reduce electricity demand). In the case of power plant emissions in particular, the integration of market-based environmental incentives or requirements with the pending deregulation of the United States and Canada utility industry may help to promote the turnover of older, high-emitting fossil fuel power plants and increased utilization of cleaner low or no emission technologies (e.g., advanced natural gas-fired combustion turbines, renewable resources, and fuel cells)[3]. In addition to reducing NO_x emissions and ozone transport, such programs would have benefits for a number of pollutants of concern on both sides of the border, including sulfur dioxide, fine particulates, toxic metals, and greenhouse gases.

[3] Conversely, the failure to integrate environmental protections at this critical juncture in the restructuring of the utility industry has raised concern among environmental officials in both countries about the potential for increased utilization of low-cost, older, coal-fired power plants (many of them concentrated in the Ohio River Valley region) and commensurate emissions increases as a result of deregulation. Such a trend could have serious air quality implications for upwind regions in both the United States and Canada.

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Appendix. Human Health Effects of Ozone

Introduction

Based on numerous human and animal ozone exposure studies, ozone is well recognized as a public health concern. An array of human health effects have been attributed to acute, short term, prolonged and long term or chronic exposures to ozone (Lippmann, 1989, 1991; Bates, 1995a, 1995b; Federal Register, 1996). Acute effects associated with short- term (1-3 hours) controlled clinical exposures include transient pulmonary function responses, increased respiratory symptoms such as cough and pain when inspiring, and effects on performance during exercise, as well as increased airway responsiveness, acute pulmonary inflammation, and susceptibility to bacterial infections. Clinical exposures to ozone under controlled conditions at concentrations as low as 0.08 ppm for several hours or over a period of several days have produced effects similar to the acute health effects (Bates, 1995a). Exposure to ozone under ambient conditions has also been associated with these effects, and additionally, ozone has been associated with effects on public health, in the form of increased hospital admissions and emergency room visits for respiratory causes (e.g. asthma), at concentrations that can be considerably lower than those observed in the clinical exposures (Thurston et al., 1994; Burnett et al., 1994, 1997; Health Canada, 1997; Schwartz, 1994a, 1994b, 1994c; 1995; Stieb et al., 1995, 1996). These latter effects, together with some suggestions that deaths may also be increased by exposure to ozone, have prompted a re-examination in Canada, the United States, Britain, and elsewhere, of the need to control (i.e., to reduce) ozone concentrations and to revise the current ambient air guidelines, objectives or standards for ozone.

Effects of acute and short-term exposures

Respiratory symptoms:

Respiratory symptoms such as cough, throat irritation, chest pain on deep inspiration, nausea, and shortness of breath have been induced by ozone exposures in both healthy individuals and those with impaired respiratory systems (Whittemore and Korn, 1980; Lebowitz et al., 1985). Severity of symptomatic response varies among subjects (Hazucha, 1987; Bates, 1995b); outdoor workers, highly active people, or people who are highly responsive to ambient ozone may experience reduced productivity and/or manual activity (Ostro and Rothschild, 1989).

Pulmonary function:

Strong and quantifiable exposure-response information on pulmonary function responses has come from controlled human exposure studies (Hazucha, 1987), but these occur in a range of ozone concentrations at and above those observed in nature (Bates, 1995a). Lung function decrements are also induced in exercising adults by exposure to ambient ozone in polluted air at commonly monitored levels (A vol et al., 1984). Pulmonary function decrements generally tend to return to baseline levels shortly after short term exposures (a few hours) and are attenuated by repeated short term exposures over several days (tolerance) (Folinsbee et al., 1994). Studies of children and adolescents at summer camps found lung function changes at ambient ozone levels during daily ozone peaks (Kinney et al., 1988, 1996; Spektor et al., 1991; US EPA, 1996).

The transient nature and the inability of investigators to correlate the lung function effects with other clinical manifestations of disease have been pointed out (US EPA, 1996).

Pulmonary airway responsiveness:
Ozone exposure causes increased responsiveness in pulmonary airways to bronchioconstriction by drugs and external stimuli (pollens, dust, cold air and sulfur dioxide) (Seltzer et al., 1986). An increased level of bronchial responsiveness is characteristic of asthma (Bates, 1995b). The increase in bronchial responsiveness after ozone exposure tends to resolve more slowly than other pulmonary function changes from ozone, disappearing after 24 hours (Golden et al., 1978; Folinsbee and Hazucha, 1989), and is less likely to attenuate in severity with repeat exposures (US EPA, 1996).

Bacterial defense mechanisms:
The lung has closely integrated defense mechanisms that provide clearance of inhaled particles and microbes. Ozone exposures result in increased susceptibility to respiratory infection and dysfunction in animal studies. When moderately exercising, human subjects were exposed to 0.08 ppm ozone for 6.6 hours. They experienced reduced alveolar macrophage function, a mechanism for clearance of inhaled micro-organisms and particles in the lower airways and air sacs (Seltzer et al., 1986). Overall data from several human studies suggest that acute ozone exposures impair host defenses against bacterial infections. This suggests that humans, when exposed to ozone, are predisposed to bacterial infections in the lower respiratory tract.

Pulmonary inflammation:
Pulmonary inflammation may be evidence that respiratory cell damage has occurred (Aris et al., 1993; Koren et al., 1991; Devlin et al., 1991). This damage is evident many hours after the exposure has taken place, and often after pulmonary function has returned to normal (Koren et al., 1991). The extent and cause of inflammation and its constitutive elements have been evaluated by bronchioalveolar lavage in humans exposed to ozone (Aris et al., 1993). Exercising humans exposed (1 to 4 hours) to 0.2-0.6 ppm ozone had ozone-induced inflammation and cell damage. Acute inflammatory response and cellular damage usually resolve within 24 hours if exposure is not repeated. Damage from chronic repeated ozone exposures may not resolve and has been suggested to be a public health concern with respect to chronic exposures (Bates, 1995b). These injury-related effects in humans have been confirmed in laboratory animals, in which exposure to ozone for periods of eight hours produced cell damage, inflammation and increased leakage of proteins from blood into air sacs of the respiratory tract (Eustis et al., 1981; Guth et al., 1986).

A major finding has been the discovery that asthma is always accompanied by pulmonary inflammation in mild cases along with epithelial destruction in severe cases (Kuwano et al., 1993; Laitinen et al., 1993). Asthmatics appear to be a sensitive group with respect to damage by ozone (Lebowitz et al., 1985; Holguin et al., 1985; Linn et al., 1994; Burnett et al., 1994). This has suggested a biologically plausible link between ambient ozone, pulmonary inflammation, increased respiratory symptoms leading to hospitalizations, and increased prevalence of asthma (Bates et al., 1995b).

Hospital admissions and emergency room visits:
The most telling evidence for the association of adverse health effects with ambient ozone, has come from recent epidemiological studies that have made use of large administrative databases (national, provincial or state hospital admissions data, death certificates, etc.) in which increases in respiratory hospitalizations and in emergency department visits have been observed in association with daily peak ozone concentrations that are well below current objectives or standards. These effects have been observed in cities in Canada, the United States, Central and South America, and Europe (Burnett et al., 1994, 1997; Thurston et al., 1992, 1994; Schwartz, 1994a, 1994b, 1994c, 1995; Romieu et al., 1995; Thurston, 1995; Ponce de Leon et al., 1996; Schouten et al., 1996). Persons with pre-existing respiratory disease (asthma, chronic obstructive pulmonary disease) are at increased risk of such effects and may also be more sensitive to ozone.

Mortality:
The consistent associations between variations in ambient ozone exposure and respiratory hospitalizations suggest that there should also be some effect on daily mortality rates. While a few studies (Kinney and Ozkaynak, 1991, 1992; Moolkavgar et al., 1995) have found such an association, the evidence has been weak until the recent combined analysis of a number of European studies showed consistent associations of ozone, independent of other co-occurring air pollutants, with total and cardio-respiratory mortality in up to eight locations (Touloumi et al., 1997).

Chronic exposures and respiratory effects

Potential effects in humans from long-term ozone exposures have provided only a suggestive relationship with chronic respiratory effects. Small, but consistent, decreases in lung function are found in residents of highly polluted communities (Schwartz, 1989; Abbey et al., 1991, 1993; Raizenne et al., 1996), but confounding variables in the populations and/or the presence of other pollutants prohibit conclusive linkage with ozone in these studies. No human studies of suitable design are available to shed light on the possible carcinogenicity of ozone in humans, but long-term studies in animals do not suggest that ozone acts as a carcinogen when it is inhaled (Tyler et al., 1992; US EPA, 1996).

Laboratory animal studies:
Laboratory studies reviewed by Amdur (1986), Lippmann (1989, 1991), and the US EPA (1996) indicate the molecular mode of ozone toxic effects. Dose related effects on the respiratory system are linked in many cases to direct damage to the morphologic and biochemical systems of the respiratory system. Animal studies are also valuable in estimating the potential for chronic effects due to long-term exposure to ozone, since such information cannot, for ethical reasons, be acquired from clinical studies on humans, and may be obtained from prospective cohort studies in human populations only with great difficulty and after many years (Bates, 1995a).

The collective laboratory data on long-term exposure to ozone in animals indicate roughly similar results between humans and a number of animal species, where the responses are dependent on concentration, time, and exposure pattern (Barr et al., 1990; Boorman et al., 1995). There is, therefore, a biologically plausible basis for inferring that repeated inflammation from ozone

exposures over a lifetime can produce sufficient damage to respiratory tissue to reduce lung function in later life (Tepper et al., 1991).

The American Thoracic Society (1985) defined adverse respiratory health effects as "medically significant physiologic or pathologic changes such as:

(1) interference with normal activity,

(2) episodic respiratory illness,

(3) incapacitating illness,

(4) permanent respiratory injury, or

(5) progressive respiratory dysfunction."

A panel of medical experts to the US EPA, while reviewing ozone toxicity findings, expressed a consensus view that these "criteria for determination of adverse physiological response was reasonable." (Wolff, 1996).

Ozone health effects are found in each category listed, but the stronger associations are found for levels 1, 2, and 3. A potential but less conclusive association was found for levels 4 and 5 in human studies. Thus there is substantial evidence that the toxic actions of ozone found in humans and in research animals are a public health concern (Whitfield et al., 1996; Bates, 1995b; US EPA, 1996).

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