The Nature of the Ozone Air Quality Problem in the Ozone Transport Region: A Conceptual Description

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TABLE OF CONTENTS

Executive Summary vi
1. Introduction 1-1
1.1. Background 1-1
1.2. Ozone formation 1-2
1.3. Spatial pattern of ozone episodes in the OTR 1-3
1.4. The regional extent of the ozone problem in the OTR 1-4
1.5. Ozone trends in the OTR 1-6
1.6. History of ozone transport science 1-7
1.6.1. From the 1970s to the National Research Council report, 1991 1-7
1.6.2. Ozone Transport Assessment Group (OTAG) 1995-1997 1-8
1.6.3. Northeast Oxidant and Particle Study (NE-OPS) 1998-2002 1-9
1.6.4. NARSTO 2000 1-10
1.6.5. New England Air Quality Study (NEAQS) 2002-2004 1-12
1.6.6. Regional Atmospheric Measurement, Modeling, and Prediction Program (RAMMPP) 2003 1-13
1.7. Summary 1-14
2. Meteorology and Evolution of Ozone Episodes in the Ozone Transport Region 2-1
2.1. Large-scale weather patterns 2-1
2.2. Meteorological mixing processes 2-2
2.2.1. Nocturnal inversions 2-3
2.2.2. Subsidence inversions 2-3
2.3. Meteorological transport processes 2-3
2.3.1. Introduction 2-3
2.3.2. Ground level winds 2-5
2.3.3. Mid-level winds: Nocturnal low level jets 2-7
2.3.4. Upper level winds: Ozone and precursors aloft 2-9
2.4. Atmospheric modeling of regional ozone transport 2-11
2.5. Summary 2-14
3. Ozone-forming Pollutant Emissions 3-1
3.1. Emissions inventory characteristics in the OTR 3-1
3.1.1. Volatile organic compounds (VOCs) 3-1
3.1.2. Oxides of nitrogen (NO_X) 3-2
3.2. Emissions inventory characteristics outside the OTR 3-5
3.3. Are NO_X or VOC control strategies most effective at reducing ozone? 3-7
3.4. Summary 3-8
4. What Will It Take to Clean the Air? – Linking the Science to Policy 4-1
4.1. The three phases of a bad ozone day and the ozone reservoir 4-1
4.2. Chronology of an ozone episode – August 2002 4-3
4.3. Clean Air Act provisions 4-9
4.4. Past regional efforts 4-10
4.5. Summary: Building upon success 4-11
Appendix A: USEPA Guidance on Ozone Conceptual Description A-1
Appendix B: Ozone pattern classifications in the OTR B-1
Appendix C: Exceedance days by monitor in the OTR C-1
Appendix D: 8-hour ozone design values in the OTR, 1997-2005 ..... D-1

Appendix E: The sea breeze and flow over the ocean in-depth.....E-1
Appendix F: Observed nocturnal low level jet across the OTR, July 2002.....F-1
Appendix G: Contributions to the ozone reservoir.....G-1

FIGURES

Figure 1-1. Conceptual picture of ozone formation in the atmosphere.....1-3
Figure 1-2. Map of 8-hour ozone baseline design values in the OTR.....1-5
Figure 1-3. Trends in 8-hour ozone in the OTR 1997-2005.....1-6
Figure 1-4. Conceptual picture of different transport regimes contributing to ozone episodes in the OTR.....1-12
Figure 2-1. Temperature profile taken over Albany, NY, on September 1, 2006 at 7 a.m. eastern standard time.....2-2
Figure 2-2. Schematic of a typical weather pattern associated with severe ozone episodes in the OTR.....2-4
Figure 2-3. Illustration of a sea breeze and a land breeze.....2-5
Figure 2-4. Average 2000 – 2002 wind direction frequency associated with elevated one-hour ozone levels in coastal Maine.....2-6
Figure 2-5. Ozonesonde measurements on August 5, 2005 of elevated ozone concentrations in a nocturnal low level jet above Beltsville, MD.....2-9
Figure 2-6. Altitude profiles for ozone, carbon monoxide, NO_Y, and SO_2 taken on July 15, 1995.....2-10
Figure 2-7. Observed vertical ozone profile measured above Poughkeepsie, NY at about 4 a.m. EST on July 14, 1995.....2-11
Figure 3-1. 2002 MANE-VU state VOC inventories in the OTR.....3-2
Figure 3-2. State level nitrogen oxides emissions.....3-3
Figure 3-3. Plot of monitored NO_X trends in OTR during 1997-2005.....3-4
Figure 3-4. 2002 MANE-VU state NO_X inventories in the OTR.....3-5
Figure 4-1. Median ozone profiles for morning and afternoon flights from 1996 – 2003.....4-1
Figure 4-2. Hourly ozone profiles in the southern OTR, August 12, 2002.....4-2
Figure 4-3. Hourly ozone profiles in the northern OTR, August 12, 2002.....4-3
Figure 4-4. Surface weather maps for August 9-16, 2002.....4-6
Figure 4-5. HYSPLIT 72-hour back trajectories for August 9-16, 2002.....4-7
Figure 4-6. Spatially interpolated maps of maximum 8-hour surface ozone concentrations August 9 – 16, 2002.....4-8

TABLES

Table 2-1. USEPA CAIR modeling results of percent contribution to 8-hour ozone nonattainment in OTR counties in 2010 due to transport from upwind states.....2-12
Table 2-2. USEPA CAIR modeling results of upwind states that make a significant contribution to 8-hour ozone in downwind OTR nonattainment counties.....2-13
Table 3-1. Eastern U.S. RPOs and their state members.....3-6
Table 3-2. VOC emissions in eastern RPOs.....3-6
Table 3-3. NO_X emissions in eastern RPOs.....3-7

1. INTRODUCTION

1.1. Background

Ground-level ozone is a persistent public health problem in the Ozone Transport Region (OTR), a large geographical area that is home to over 62 million people living in Connecticut, Delaware, the District of Columbia, Maine, Maryland, Massachusetts, New Hampshire, New Jersey, New York, Pennsylvania, Rhode Island, Vermont, and northern Virginia. Breathing ozone in the air harms lung tissue, and creates the risk of permanently damaging the lungs. It reduces lung function, making breathing more difficult and causing shortness of breath. It aggravates existing asthmatic conditions, thus potentially triggering asthma attacks that send children and others suffering from the disease to hospital emergency rooms. Ozone places at particular risk those with preexisting respiratory illnesses, such as emphysema and bronchitis, and it may reduce the body's ability to fight off bacterial infections in the respiratory system. Ground-level ozone also affects otherwise healthy children and adults who are very active, either at work or at play, during times of high ozone levels (USEPA, 1999). In addition, recent evidence suggests that short-term ozone exposure has potential cardiovascular effects that may increase the risk of heart attack, stroke, or even death (USEPA, 2006).

The Clean Air Act requires states that have areas designated "nonattainment" of the ozone National Ambient Air Quality Standard (NAAQS) to submit State Implementation Plans (SIPs) demonstrating how they plan to attain the ozone NAAQS. The SIPs must also include regulations that will yield the necessary emission reductions to attain the national ozone health standard. As part of the SIP process, the U.S. Environmental Protection Agency (USEPA) urges states to include a conceptual description of the pollution problem in their nonattainment areas. The USEPA has provided guidance on developing a conceptual description, which is contained in Chapter 8 of the document "Guidance on the Use of Models and Other Analyses in Attainment Demonstrations for the 8-hour Ozone NAAQS" (EPA-454/R-05-002, October 2005) (Appendix A of this report reproduces Chapter 8 of the USEPA guidance document).[a] This document provides the conceptual description of the ozone problem in the OTR states, consistent with the USEPA's guidance. In the guidance, the USEPA recommends addressing three questions to help define the ozone problem in a nonattainment area: (1) Is regional transport an important factor? (2) What types of meteorological episodes lead to high ozone? (3) Is ozone limited by availability of volatile organic compounds, nitrogen oxides, or combinations of the two, and therefore which source categories may be most important to control? This report addresses these

[a] At the time of this writing, the USEPA was incorporating Section 8 of the 8-hour ozone guidance into a new USEPA guidance document covering ozone, $PM_{2.5}$, and regional haze. The new guidance is in Section 11 of Draft 3.2 "Guidance on the Use of Models and other Analyses for Demonstrating Attainment of Air Quality Goals for Ozone, $PM_{2.5}$, and Regional Haze," U.S. EPA, (Draft 3.2 – September 2006), available at http://www.epa.gov/ttn/scram/guidance_sip.htm#pm2.5 (accessed Oct. 5, 2006). The newer guidance, when finalized, may differ in some respects from the text given in Section 8 of the earlier ozone guidance.

questions, as well as provides some in-depth data and analyses that can assist states in developing conceptual descriptions tailored to their specific areas, where appropriate.

1.2. Ozone formation

Ground-level ozone is formed in the atmosphere through a series of complex chemical reactions involving sunlight, warm temperatures, nitrogen oxides (NO_X) and volatile organic compounds (VOCs). Figure 1-1 is a conceptual picture of the emission sources and conditions contributing to ozone formation in the atmosphere. There are natural (biogenic) sources of NO_X, such as formation by soil microbes, lightening, and forest fires, but the dominant NO_X sources in the eastern United States arise from human activities, particularly the burning of fossil fuels in cars, trucks, power plants, and other combustion sources (MARAMA, 2005).

In contrast to NO_X sources, there are significant biogenic sources of VOCs in the eastern United States that can play an important contributing role in ozone formation. Isoprene, a highly reactive natural VOC emitted typically by deciduous trees such as oak, is an important ozone precursor across large parts of the East. Isoprene emissions typically increase with temperature up to a point before high temperatures tend to shut off emissions as leaf stomata (pores) close to reduce water loss. The tendency for increasing isoprene emissions with increasing temperatures (up to a point) coincides with the temperature and sunlight conditions favorable for increased ozone production (MARAMA, 2005).

Human-caused (anthropogenic) VOC emissions are important and may dominate the VOC emissions by mass (weight) in an urban area, even though natural sources dominate in the overall region. Some anthropogenic VOCs, such as benzene, are toxic, and may increase risks of cancer or lead to other adverse health effects in addition to helping form ozone (MARAMA, 2005).

Figure 1-1. Conceptual picture of ozone formation in the atmosphere

Picture provided by the Maryland Department of the Environment.

The relationship between the relative importance of NO_X and VOC emissions in producing ozone is complex. The relative ratio of NO_X and VOC levels in the local atmosphere can affect the efficiency of local urban ozone production, and this can vary by time (hour or day) at the same urban location, as well as across locations within the same urban area. High NO_X concentrations relative to VOC levels may hinder ozone production through the destruction of ozone by NO_X (sometimes called "NO_X scavenging"). The same NO_X, however, when diluted relative to VOCs through the downwind transport and dispersal of a pollution plume, will promote ozone formation elsewhere.

1.3. Spatial pattern of ozone episodes in the OTR

The day-to-day pattern of ground-level ozone varies according to meteorological variables that include, but are not limited to, sunlight, air temperature, wind speed, and wind direction. Generally within the OTR, one would expect elevated ozone to occur more frequently in southernmost areas, where solar elevation angles are greater and cold frontal passages are fewer. A glance at monthly composite maps (for example, July-August 2002) at the USEPA AIRNOW website seems to confirm this (http://www.epa.gov/airnow/nemapselect.html). On some days, however, one notes that the highest ozone levels shift northward to mainly affect the northern part of the OTR. Other shifts are apparent between coastal and interior areas.

This variability of the daily ozone pattern is tied to variations in the atmosphere's circulations over a range of scales, and how geographic features influence these

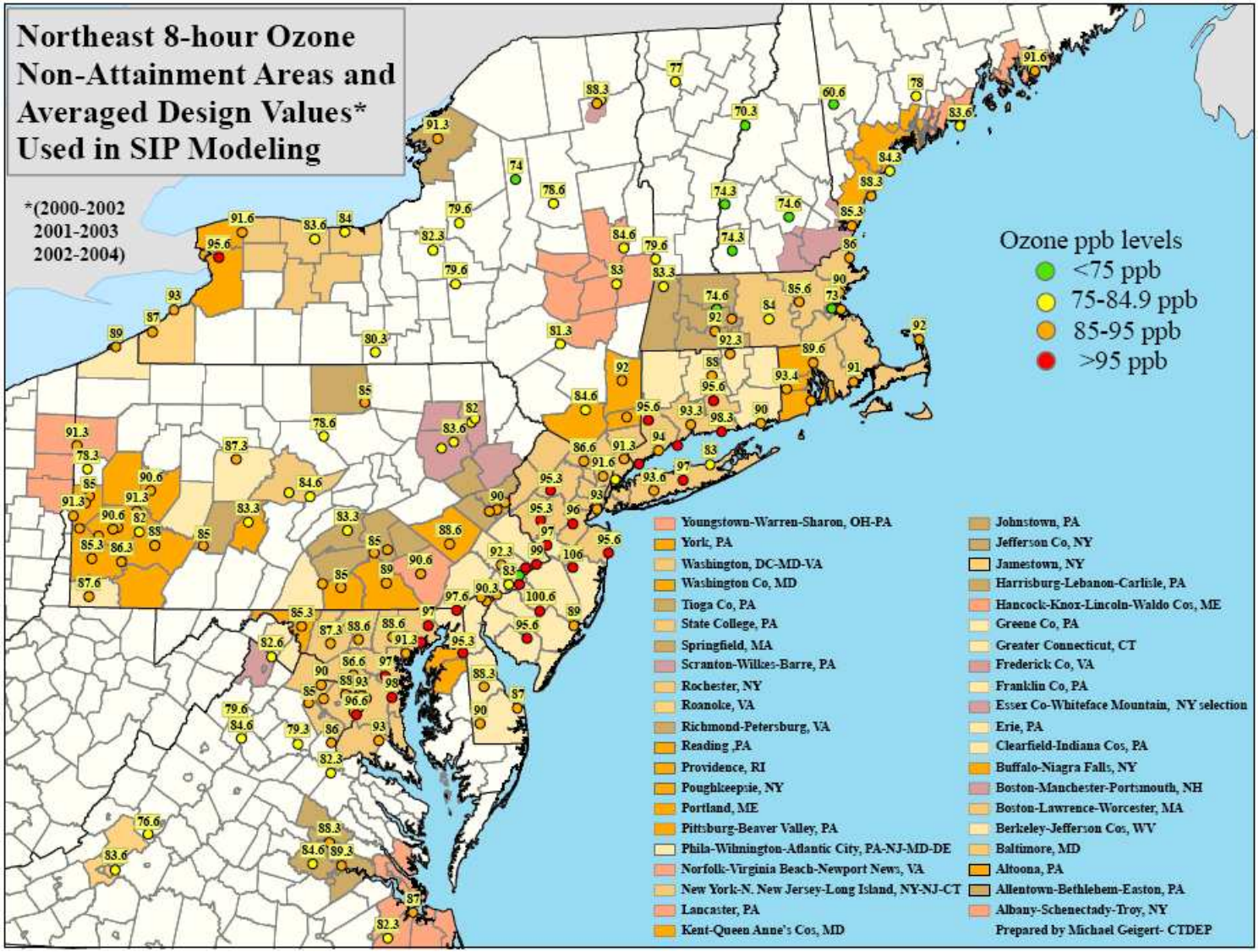
circulations. These features can include boundaries between land and sea, and the influence of the Appalachian Mountains on winds to their east over the Atlantic Coastal Plain.

For the OTR, Stoeckenius and Kemball-Cook (2005) have identified five general ozone patterns: (1) high ozone throughout the OTR; (2) high ozone confined to the extreme southeastern OTR; (3) high ozone along the I-95 corridor and northern New England; (4) high ozone in the western OTR; and (5) generally low ozone throughout the OTR. However, not all ozone episodes necessarily neatly fit into one of the five general patterns as daily conditions will vary and a given ozone episode may have characteristics that fall across several class types. These five general patterns, however, are a useful classification scheme for characterizing how representative an historical ozone episode is for possible use in air quality planning efforts. Appendix B presents the descriptions of the five general ozone patterns and their meteorological attributes as developed by Stoeckenius and Kemball-Cook (2005).

1.4. The regional extent of the ozone problem in the OTR

Air monitoring demonstrates that areas with ozone problems in the OTR do not exist in isolation. The map of Figure 1-2 shows an extensive pattern of closely adjacent ozone nonattainment in areas throughout the OTR. The 8-hour ozone baseline design values (defined in the figure caption) at the monitoring sites shown in the figure indicate extensive areas throughout the OTR with many monitors having values above the 8-hour ozone NAAQS of 0.08 ppm. In practice, this corresponds to levels equal to or greater than 0.085 ppm (equivalent to 85 ppb). The map also shows that many monitors outside the designated nonattainment areas of the OTR also record elevated ozone concentrations approaching the 8-hour ozone NAAQS (i.e., 75-84.9 ppb), even if not violating it. The many monitoring locations across that OTR measuring elevated ozone levels that approach or exceed the 8-hour ozone NAAQS give a strong indication of the regional nature of the OTR’s ozone problem.

Figure 1-2. Map of 8-hour ozone baseline design values in the OTR

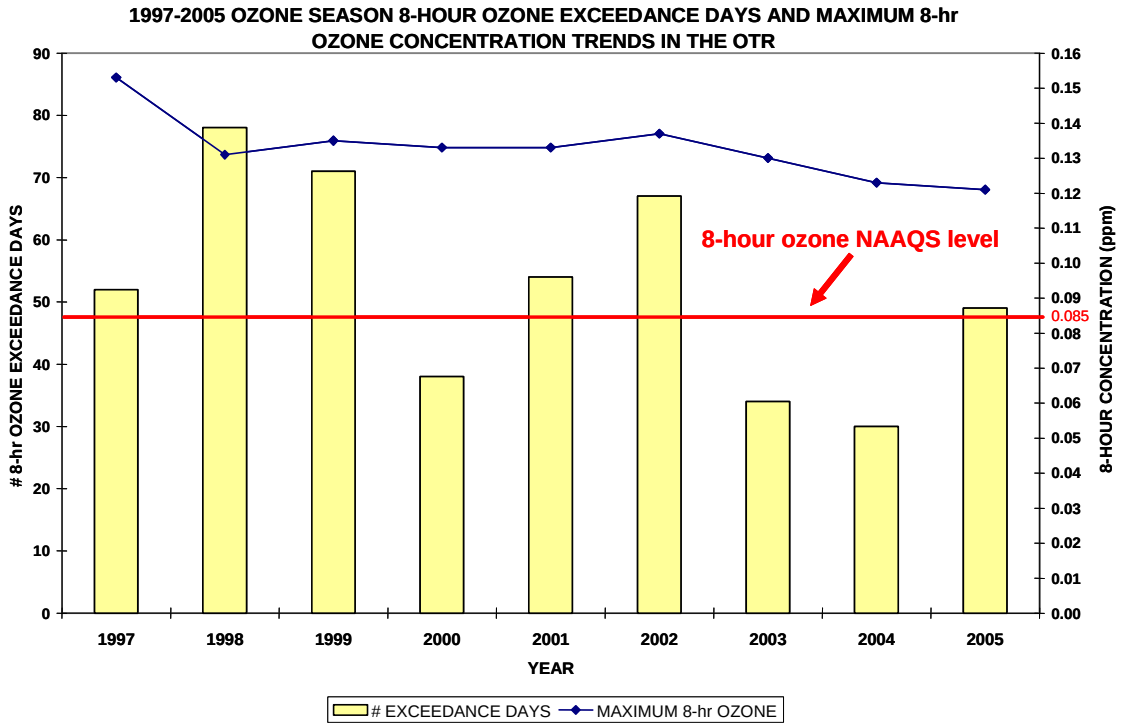


Note: A monitor's baseline design value is the average of the three design values (3-year averages of the 4th maximum 8-hour ozone level) for the set of years 2000-2002, 2001-2003, and 2002-2004. The figure shows the regional nature of ozone levels in the OTR, with a number of closely adjacent nonattainment areas (baseline design values ≥ 85 ppb) along with a broader region of elevated regional ozone (e.g., baseline design values ≥ 75 ppb) (figure by Michael Geigert, Connecticut Department of Environmental Protection).

1.5. Ozone trends in the OTR

The number of 8-hour ozone exceedance days vary year-to-year in the OTR, which is largely driven by variations in meteorology. During warmer summers conducive for ozone formation, the number of exceedance days at individual monitors in nonattainment areas of the OTR has been frequent, typically with 10 or more days above the 8-hour ozone NAAQS during the course of the summer. Figure 1-3 displays the variation in exceedance days when collectively considering all monitoring sites across the OTR since 1997. The figure also includes a line indicating the trend in the maximum 8-hour ozone concentrations observed in the OTR each year. The variation in exceedance days from year-to-year makes it difficult to discern a clear trend, although there is some hint that the number of exceedance days may be declining in recent years. There appears to be a stronger indication of a declining maximum 8-hour ozone concentration in the OTR since 1997, although the maximum concentration remains well above the 8-hour ozone NAAQS. This reflects the impact of numerous control strategies implemented locally, regionally, and nationally to reduce emissions of the precursor pollutants that contribute to ozone formation in the atmosphere.

Figure 1-3. Trends in 8-hour ozone in the OTR 1997-2005



Note: The bars correspond to the number of 8-hour ozone exceedance days per year. The upper blue line indicates the trend in maximum 8-hour ozone concentrations in the OTR during 1997-2005. The lower red horizontal line indicates the level of the 8-hour ozone NAAQS (functionally 0.085 ppm). (Figure created by Tom Downs, Maine Dept. of Environmental Protection.)

The tables in Appendix C contain the frequency of ozone exceedance days for individual monitors in the OTR states from 1997 to 2005. Appendix D contains tables for the 8-hour ozone design values recorded at ozone monitors in the OTR during 1997-

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2. METEOROLOGY AND EVOLUTION OF OZONE EPISODES IN THE OZONE TRANSPORT REGION

The following sections describe current knowledge of the factors contributing to ozone episodes in the OTR. The general description of weather patterns comes mainly from the work of Ryan and Dickerson (2000) done for the Maryland Department of the Environment. Further information is drawn from work by Hudson (2005) done for the Ozone Transport Commission and from a mid-Atlantic regional air quality guide by MARAMA (2005). The regional nature of the observed ozone episodes in the OTR is reinforced in modeling studies by the USEPA for the Clean Air Interstate Rule.

2.1. Large-scale weather patterns

Ryan and Dickerson (2000) have described the general meteorological features conducive to ozone formation and transport that are pertinent to the OTR. On the local scale, meteorological factors on which ozone concentrations depend are the amount of available sunlight (ultraviolet range), temperature, and the amount of space (volume) in which precursor emissions mix. Sunlight drives the key photochemical reactions for ozone and its key precursors and the emissions rates of many precursors (isoprene for example) are temperature dependent. Emissions confined within a smaller volume result in higher concentrations of ozone. Winds in the lowest 2 km of the atmosphere cause horizontal mixing while vertical temperature and moisture profiles drive vertical mixing. High ozone is typically associated with weather conditions of few clouds, strong temperature inversions, and light winds.

The large-scale weather pattern that combines meteorological factors conducive to high ozone is the presence of a region of upper air high pressure (an upper air ridge) with its central axis located west of the OTR. The OTR east of the axis of the high-pressure ridge is characterized by subsiding (downward moving) air. This reduces upward motion necessary for cloud formation, increases temperature, and supports a stronger lower level inversion. While the upper air ridge is located west of the OTR, surface high pressure is typically quite diffuse across the region. This pattern occurs throughout the year but is most common and longer lived in the summer months (Ryan and Dickerson, 2000).

The large, or synoptic, scale, weather pattern sketched above has important implications for transport into and within the OTR. First, the persistence of an upper air ridge west of the OTR drives generally west to northwest winds that can carry ozone generated outside the OTR into the OTR. A key point from this wind-driven transport mode is that stagnant air is not always a factor for high ozone episodes in the OTR. Second, the region in the vicinity of the ridge axis, being generally cloud free, will experience significant radiational cooling after sunset and therefore a strong nocturnal inversion will form. This inversion, typically only a few hundred meters deep, prevents ozone and its precursors from mixing downward overnight. Above the inversion layer, there is no opportunity for destruction of the pollutants by surface deposition, thus increasing the pollutants' lifetimes aloft and consequently their transport distances. Third, with diffuse surface high pressure, smaller scale effects can become dominant in the

lowest layers of the atmosphere. These include bay and land breezes, the Appalachian lee side trough, and the development of the nocturnal low level jet. Nocturnal low-level jets are commonly observed during high ozone events in the OTR (Ryan and Dickerson, 2000).

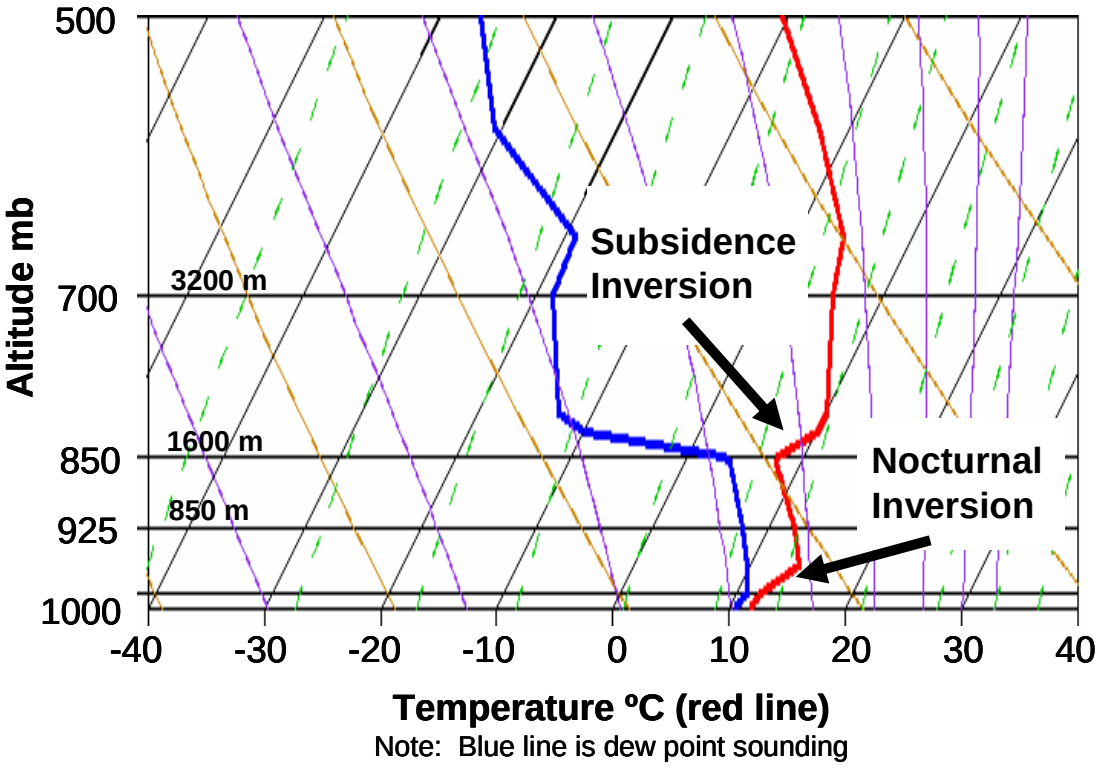
As previously mentioned in Section 1, Stoeckenius and Kemball-Cook (2005) have identified five ozone patterns in the OTR as a guide to an historical ozone episode's representativeness for air quality planning purposes. They also described the meteorological conditions that are generally associated with each of these patterns. Appendix B presents the five types with the additional meteorological detail.

2.2. Meteorological mixing processes

An important element in the production of severe ozone events is the ability of the atmosphere through temperature inversions to inhibit the mixing processes that under normal conditions would lead to dilution of the emitted pollutants. For the purposes of this discussion, we focus on two major classes of temperature inversions, (1) nocturnal (radiative) and (2) subsidence.

Figure 2-1 shows an example of nocturnal and subsidence inversions in a temperature profile taken over Albany, NY, on September 1, 2006 at 7 a.m. eastern standard time. The figure shows two distinct temperature inversions – the ground-based nocturnal inversion and an inversion at about 1600 meters caused by the sinking motion (subsidence) of the atmosphere in a high pressure system.

Figure 2-1. Temperature profile taken over Albany, NY, on September 1, 2006 at 7 a.m. eastern standard time



2.2.1. Nocturnal inversions

Land surfaces are far more efficient at radiating heat than the atmosphere above, hence at night, the Earth's surface cools more rapidly than the air. That temperature drop is then conveyed to the lowest hundred meters of the atmosphere. The air above this layer cools more slowly, and a temperature inversion forms. The inversion divides the atmosphere into two layers that do not mix. Below the nocturnal surface inversion, the surface winds are weak and any pollutants emitted overnight accumulate. Above the inversion, winds continue through the night and can even become stronger as the inversion isolates the winds from the friction of the rough surface.

In the morning, the sun warms the Earth's surface, and conduction and convection transfer heat upward to warm the air near the surface. By about 10:00 – 11:00 a.m., the temperature of the surface has risen sufficiently to remove the inversion. Air from above and below the inversion can then mix freely. Depending on whether the air above the inversion is cleaner or more polluted than the air at the surface, this mixing can either lower or increase air pollution levels.

2.2.2. Subsidence inversions

Severe ozone events are usually associated with high pressure systems. In the upper atmosphere, the winds around a high pressure system move in a clockwise direction. At the ground, friction between the ground and the winds turns the winds away from the center of the system and "divergence" occurs, meaning that air at the surface moves away from the center. With the movement of air horizontally away from the center of the high at the surface, air aloft moves vertically downward (or "subsides") to replace the air that left. Thus, the divergence away from the high pressure system gives rise to subsidence of the atmosphere above the high. The subsiding motion causes the air to warm as it moves downward and is compressed. As the warmer air meets the colder air below, it forms an inversion. A subsidence inversion is particularly strong because it is associated with this large scale downward motion of the atmosphere. The subsidence inversion caps pollution at a higher altitude in the atmosphere (typically from 1200 to 2000 meters), and it is far more difficult to break down than the nocturnal inversion. Hence the subsidence inversion limits vertical mixing in the middle of the day during an air pollution episode, keeping pollutants trapped closer to the ground.

2.3. Meteorological transport processes

2.3.1. Introduction

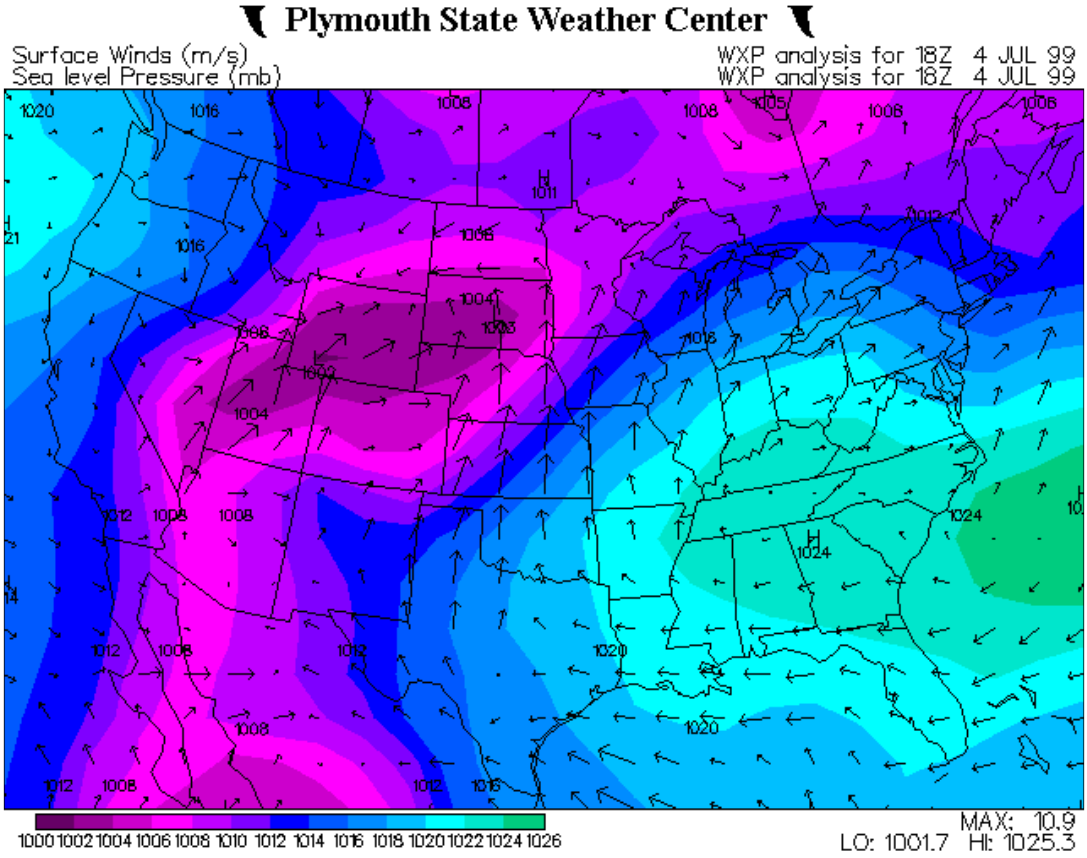
Figure 2-2 shows the classic synoptic weather pattern at the Earth's surface associated with severe ozone episodes within the OTR. A quasi-stationary high pressure system (the Bermuda high) extends from the Atlantic Ocean westward into interior southeastern U.S., where a second weaker high is located. Surface winds, circulating clockwise around the high, are especially light in the vicinity of the secondary high. Farther north, a southwesterly flow strengthens toward New York and southern New England. This situation illustrates two circulation regimes often existing in OTR ozone episodes: more stagnant conditions in southern areas and a moderate transport flow in the OTR from southwest to northeast. In addition, as discussed previously, high pressure

systems exhibit subsidence, which results in temperature inversions aloft, and cloud free skies.

Closer to the surface, the Appalachian Mountains induce changes in the wind field that also play important roles in the formation and transport of ozone in the OTR. The mountains act as a physical barrier confining, to some degree, pollution to the coastal plain. They also induce local effects such as mountain and valley breezes, which, in the case of down-slope winds, can raise surface temperatures thereby increasing chemical reactivity. In addition, mountains create a lee side trough, which helps to channel a more concentrated ozone plume, and contribute to the formation of nocturnal low level jets, the engine of rapid nighttime transport.

The Atlantic Ocean also plays a strong role during ozone episodes where sea breezes can draw either heavily ozone-laden or clean marine air into coastal areas.

Figure 2-2. Schematic of a typical weather pattern associated with severe ozone episodes in the OTR



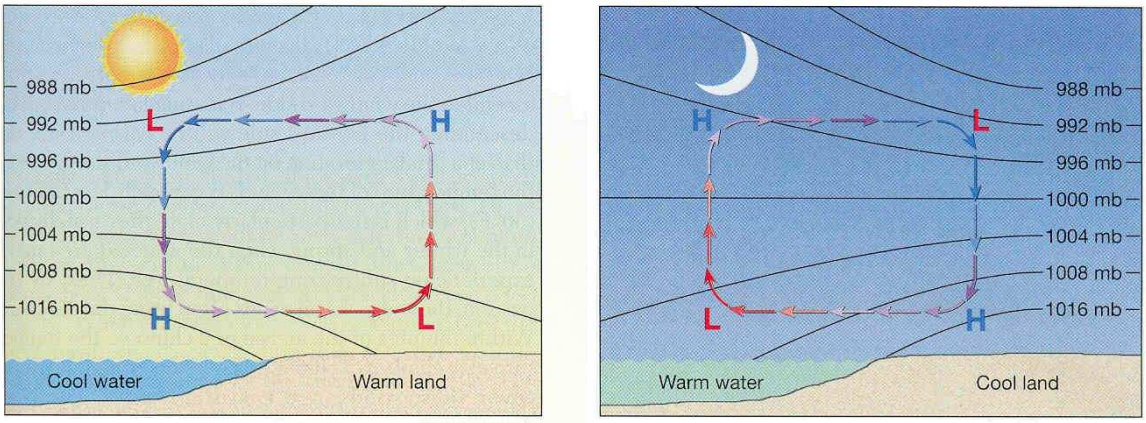
Meteorological processes that transport ozone and its precursors into and within the OTR can roughly be broken down into three levels: ground, mid and upper. The following sections discuss the three wind levels associated with meteorological transport processes in more detail.

2.3.2. Ground level winds

Land, sea, mountain, and valley breezes

In the OTR, land and sea breezes, and mountain and valley breezes can have an important influence on local air quality. These local winds are driven by a difference in temperature that produces a difference in pressure. Figure 2-3 shows a schematic of the formation of a sea breeze. The sea breeze forms in the afternoon when the land is considerably hotter than the ocean or bay. Air then flows from the high pressure over the ocean toward the low pressure over land. At night, the opposite may happen as the land cools to below the ocean's temperature, and a land breeze blows out to sea. Because the nighttime land and water temperature differences are usually much smaller than in the day, the land breeze is weaker than the sea breeze. Sea breezes typically only penetrate a few kilometers inland because they are driven by temperature contrasts that disappear inland.

Figure 2-3. Illustration of a sea breeze and a land breeze



a) Sea Breeze **b) Land Breeze**

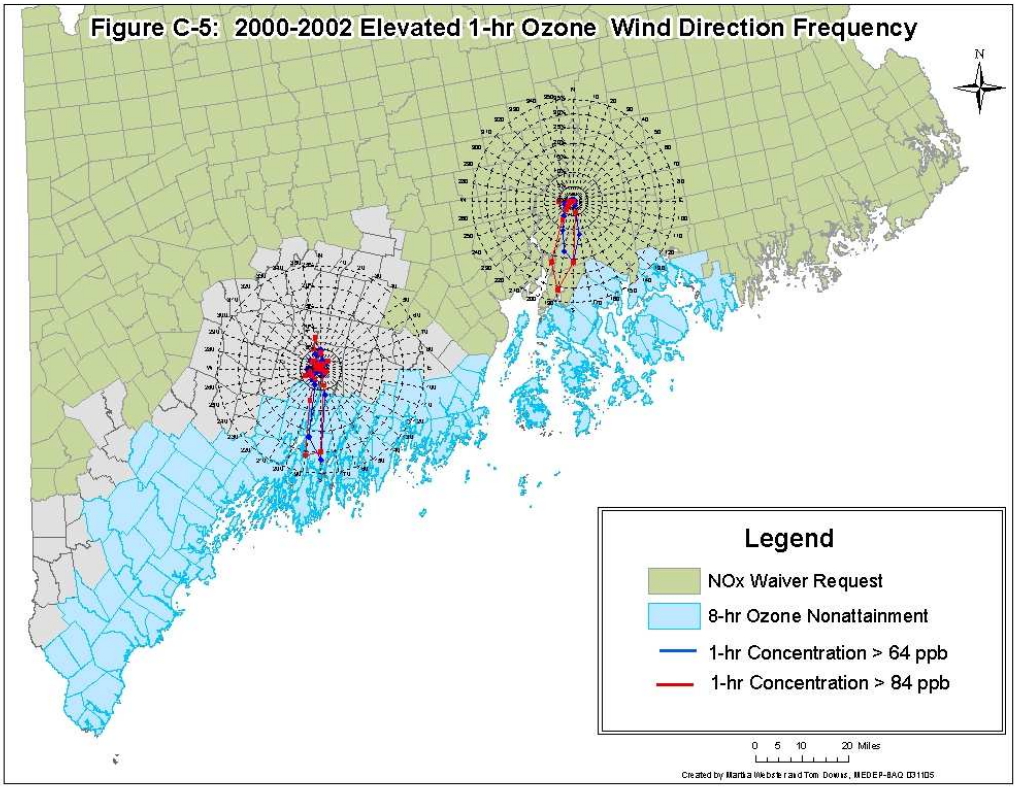
Figure from *Lutgens & Tarbuck*, 2001.

Along coastlines, such as coastal New England, sea breezes bring in air pollution transported near the surface over water from urban locations located to the southwest. Figure 2-4 shows the average 2000-2002 wind direction frequency for elevated 1-hour ozone in the vicinity of the Kennebec and Penobscot Rivers in Maine. There is a clear maximum of pollution in the direction of the sea breeze. These sites are located many miles upriver from the coast, and receive ozone transported over water from the sea up through the coastal bays and rivers.

In other cases, sea breezes can affect air quality in coastal cities because, under stagnant synoptic-scale winds, a city's emissions may be recirculated or pushed back over land after having drifted out over the sea earlier. Before sea breeze circulation begins, air pollution from a coastal city can move out over the water. In the absence of a shift in winds due to a sea breeze, the city's air pollution will be blown away. When a sea breeze circulation sets up, however, the polluted air is pushed back toward the city. The sea breeze only pushes a few miles inland, which is where the barrier to mixing lies. Later in the day, the air may be quite clean on the ocean side of the city, but the air is

usually quite dirty on the inland side. The city suffers from its own recirculated pollution, and also from the sea breeze that does not allow pollution from the city to flow away from it. Appendix E presents more detailed information on sea breezes and flow over the ocean that contribute to ozone transport in parts of the OTR.

Figure 2-4. Average 2000 – 2002 wind direction frequency associated with elevated one-hour ozone levels in coastal Maine



The bay breeze is a shallow circulation over large inland bays, and may only extend a couple hundred meters above the surface. For example, bay breezes from the Chesapeake Bay often make Baltimore's summertime air quality particularly poor. Air from the city cannot escape directly across the Bay. On the other hand, a few miles closer to the Bay, conditions are often considerably cleaner, since no fresh emissions have gotten into the air there since earlier that morning. Polluted air from the west side of the Bay can still mix upward, where it meets the stronger winds aloft, pass over the Bay breeze circulation and come back down on the east side of the Bay.

Mountain and valley breezes are also driven by a temperature contrast. In the daytime, the side of the mountain will heat up more quickly than the valley, and hence a flow from the valley to the mountain results. At night this flow is reversed as the mountain side cools more quickly than the valley. As a result of these differences in cooling and heating, during the day, warm winds blow up toward the peaks from the valley below, while at night, cool air sinks and flows down the valley, settling in the lowest points. Local topography is very important in generating this phenomenon, making the breeze unique to a particular area.

Mountains and valleys also serve to isolate air in the valleys, while air at the mountaintops may be coming from very far away. Mountain winds, inversions, and mixing are quite complex. On a quiet night, the mountaintop may be in the free troposphere, open to long-range transport, while the valley below is usually capped by a nocturnal inversion, isolating pollution in the valley. Air quality measurements taken during plane flights in the Shenandoah River Valley have shown that the air pollutants in the valley may be rather different from the air at the nearby peaks. Cities on the western side of the mountains will find that the Appalachians are capable of damming pollution up against them (MARAMA, 2005 at pp. 42-43).

Appalachian lee side trough

The Appalachian lee side trough forms on the leeward (downwind) side of the Appalachian Mountains. In a sense, it is the daytime companion to the nocturnal low level jet, discussed below, because it forms under similar stagnant conditions; however, the mechanism for its formation is different. In the OTR, a lee side trough forms when winds blow over the Appalachian Mountains and down the lee side of the mountain range to the coastal plain. As the column descends down the lee side, it stretches vertically and spins faster, pulling up air and creating low pressure, thus rotating the winds to the southwest. Because the air is typically rather dry, and the trough itself is rather weak, it does not usually lead to showers and thunderstorms the way a trough associated with other weather systems would. It does cause winds to shift their direction, so a wind that comes over the mountains from the west will turn and blow from the southwest along the coastal plain. Therefore, when surface winds on the coastal plain are from the southwest, if the Appalachian lee side trough is in place, it may be that the air actually came from the west, descended, and turned. The implication for air quality policy is straightforward. Pollution making its way over the mountains from the west will turn once it reaches the coastal plain and come from the southwest. Because surface winds are then from the southwest, when the Appalachian lee side trough is in place, the limits of a nonattainment area's airshed will be expanded farther south and west than they might otherwise be (MARAMA, 2005 at pp. 41-42). Studies have observed high ozone levels in the OTR associated with a lee side trough east of the Appalachian Mountains and aligned with the Northeast Corridor (Gaza, 1998; Kleinman *et al.*, 2004).

2.3.3. Mid-level winds: Nocturnal low level jets

The nocturnal low level[c] jet is a localized region of rapid winds in the lower atmosphere (typically 500-1500 m above the ground level) that form at night under the same calm conditions often present in a pollution episode. Forming just above the nighttime temperature inversion mentioned previously, the nocturnal low level jet depends on the isolation from the surface provided by the inversion. It is primarily a nocturnal phenomenon that occurs more frequently during the spring and summer seasons.

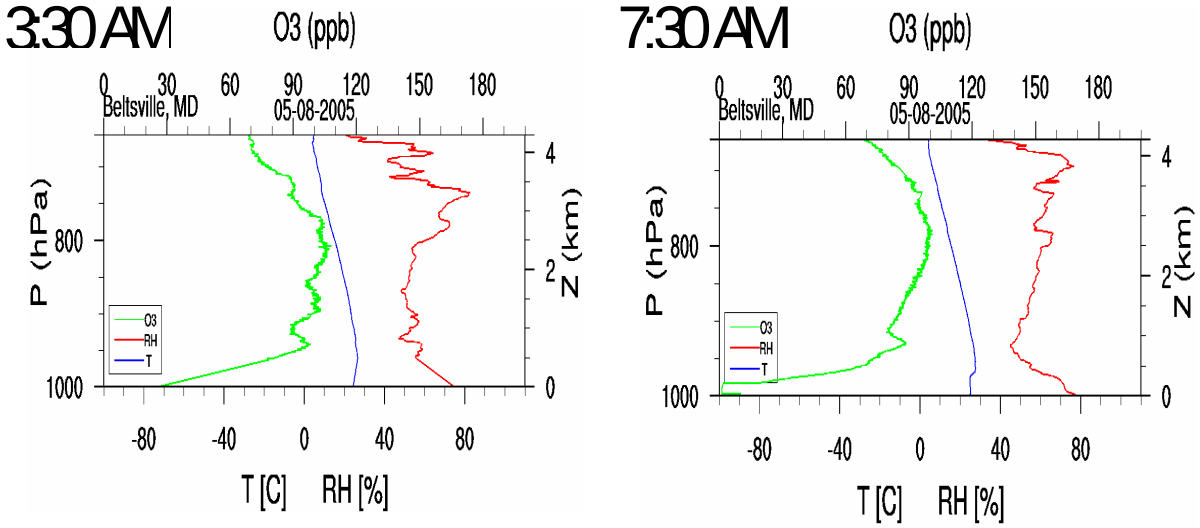
[c] "Low level" in this instance is relative to upper level jets occurring in the upper troposphere to lower stratosphere at heights of 10-15 km above the ground level. It is not a "ground level" phenomenon of the types described in the previous section.

A nocturnal low level jet is generally found where a range of mountains meets a flat plain. There is a particularly strong nocturnal low level jet in the Great Plains of the central United States on the eastern side of the Rocky Mountains. On the Eastern Seaboard, nocturnal low level jets develop along the Atlantic Coastal Plain located to the east of the Appalachian Mountains and to the west of the Atlantic Ocean. While the typical wind speed minimum of a nocturnal low level jet is often defined as more than 12 meters per second (m s^{-1}), Ryan (2004) has proposed a weaker minimum speed criterion of 8 m s^{-1} in the East because of the expected weaker terrain-induced forcing in this region. The mid-Atlantic nocturnal low level jet has a width of 300-400 km (to its half peak value) and a length scale of more than 1500 km, following closely the orientation of the Appalachian Mountains.

The nocturnal low level jet forms when fronts and storm systems are far away. Surface winds are parallel to the terrain, which in the case of the OTR is southwest running over the Atlantic Coastal Plain in front of the Appalachian Mountains. The nocturnal low level jet forms because land cools quicker than the air above it at night. The quickly cooling land results in the air closest to the surface cooling quicker than the air higher above. This creates a temperature inversion that separates the atmosphere into layers. The warmer air above the inversion layer (~200-800 m above ground) loses the frictional effect of the surface and increases in speed. In the eastern United States, the nocturnal low level jet has been observed in Georgia, the Carolinas and Virginia (Weisman, 1990; Sjostedt *et al.*, 1990) in addition to the OTR (NARSTO, 2000). Appendix F describes a specific example of an observed nocturnal low level jet occurring over the length of the OTR during a period of high ozone in July 2002.

Upper air studies have observed ozone being transported overnight in nocturnal low level jets in the OTR (Woodman *et al.*, 2006). The Maryland Department of the Environment (MDE) operates an upper air profiler at the Howard University (HU) site located in Beltsville, Maryland. On August 5, 2005, two helium-filled balloons carrying ozone sensors (called "ozonesondes") were launched at the HU – Beltsville site in the early morning hours. Using the upper air profiler, a nocturnal low level jet of 15 m s^{-1} was observed between approximately midnight and 7:30 a.m. One ozonesonde was launched at 3:30 a.m. and measured an ozone concentration of approximately 95 ppb at about 600 meters, which is within the nocturnal low level jet. Another ozonesonde was launched at 7:30 a.m. and measured an ozone concentration of approximately 90 ppb at about 1,000 meters (Figure 2-5). Each of the ozone concentrations was observed at approximately the same height as the nocturnal temperature inversion as indicated by the kink in the temperature profile. The observations indicated that elevated ozone concentrations are within the nocturnal low level jet.

Figure 2-5. Ozonesonde measurements on August 5, 2005 of elevated ozone concentrations in a nocturnal low level jet above Beltsville, MD



2.3.4. Upper level winds: Ozone and precursors aloft

Theoretical and numerical model simulations have suggested for some time that there is a strong regional component to urban air quality in the northeastern United States (Liu *et al*., 1987; Sillman *et al*., 1990; McKeen *et al*., 1990). Since 1992, over 300 aircraft flights have been made to measure vertical profiles of ozone, the nitrogen oxides, carbon dioxide, sulfur dioxide, and more recently aerosol particles during high ozone episodes.[d] Figure 2-6 shows the results of profiles taken over central Virginia on July 15, 1995, at about 9:00 am on the last day of a four day severe ozone episode. During this episode, winds measured at Sterling, Virginia (IAD) in the 500-3000 m layer, where ozone was at a maximum, were consistently from the west to the north. This was particularly true on July 15. There were no periods of stagnation or reversal of wind direction during this period. Figure 2-6 shows that the ozone mixing ratio above the boundary layer is much larger than that at the ground, peaking at about 1200 meters.

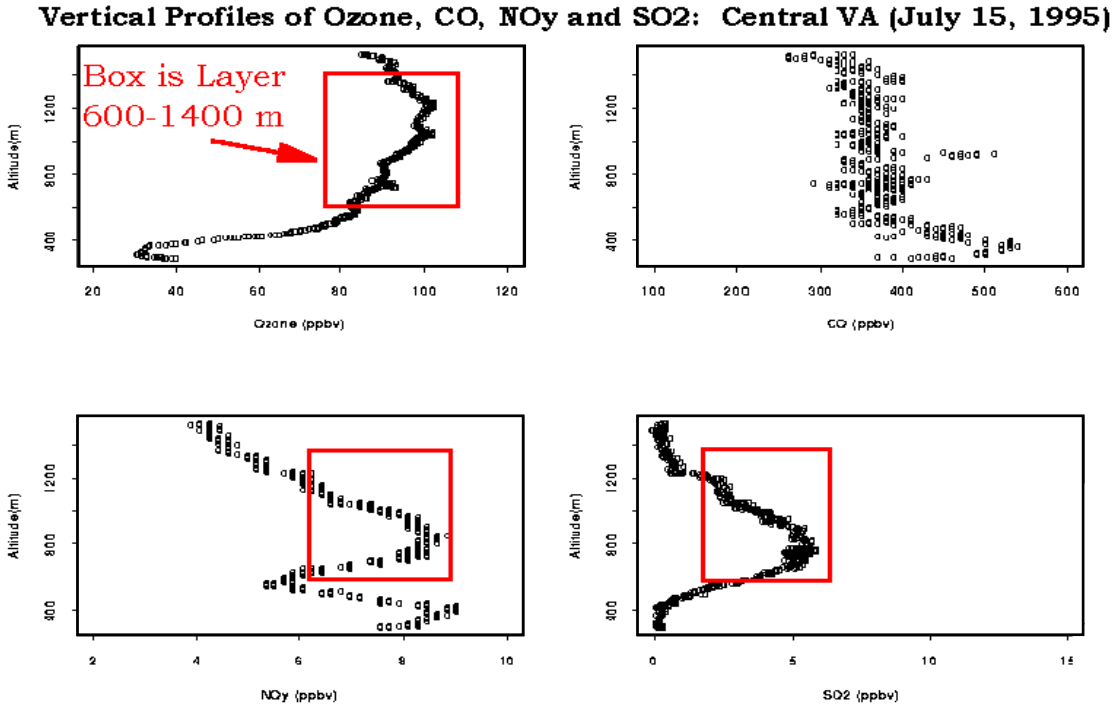
An examination of the various pollutant data in Figure 2-6 helps to identify possible sources of the elevated ozone. It should be noted that while both automobiles and power plants emit NO_X, automobiles emit carbon monoxide (CO) but not sulfur dioxide (SO_2), while power plants emit SO_2 but not CO. The CO profile is not correlated well with the ozone data, indicating that the source of the ozone is not from local sources, i.e., automobiles. The peak in the NO_Y[e] profile at around 800 meters is an indication of "aged air" (hence transport) as a number of studies have found a strong relationship between increasing ozone and NO_Y in photochemically aged air masses (Trainer *et al.*,

[d] These measurements were made as part of the University of Maryland's RAMMPP (Regional Atmospheric Measurement, Modeling, and Prediction Program) under the sponsorship of ARMA, MARAMA (Mid-Atlantic Regional Air Management Association), VADEQ (Virginia Department of Environmental Quality), and NCDEQ (North Carolina Department of Environmental Quality).

[e] NO_Y = NO + NO_2 + all other oxidized nitrogen products of NO_X, excluding N_2O.

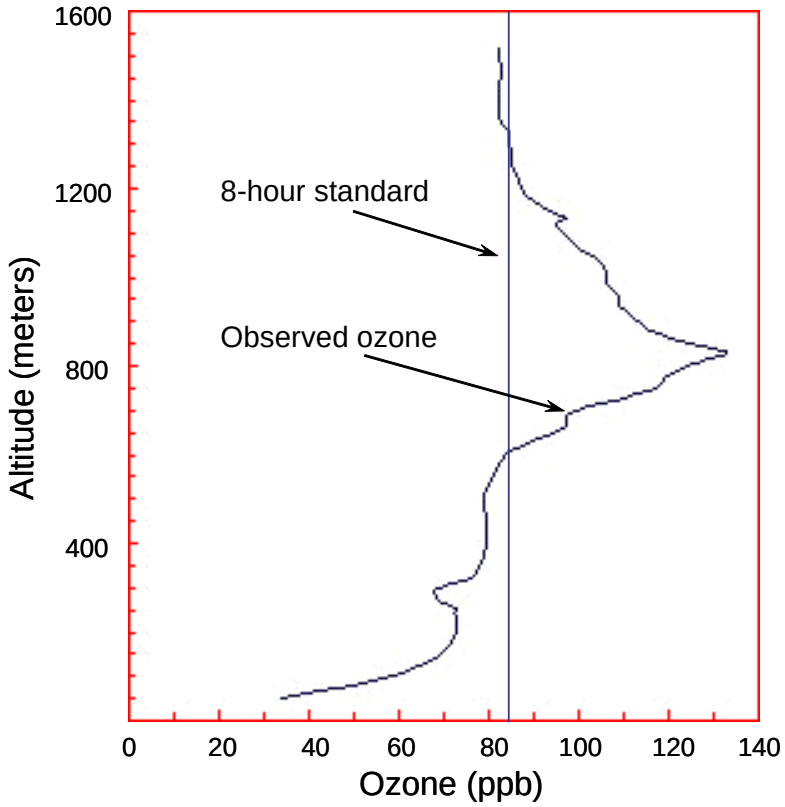
1993; Kleinman *et al.*, 1994; Olszyna *et al.*, 1994). Finally, the peak in the SO_2 profile, which occurs above the nocturnal inversion, is unlikely to come from local sources. Indeed the presence of the SO_2 leads to the conclusion that the air is coming from power plants west of the Appalachian Mountains.

Figure 2-6. Altitude profiles for ozone, carbon monoxide, NO_Y, and SO_2 taken on July 15, 1995



During the same July 1995 period, measurements aloft in other parts of the OTR also recorded high ozone overnight in layers 500 m or higher above the surface. Ozone aloft concentrations above Poughkeepsie, NY and New Haven, CT approached levels of 120 ppb or greater on the night of July 14 (Zhang & Rao, 1999). Figure 2-7 displays the aircraft measurements above Poughkeepsie, NY around 4 a.m. EST.

Figure 2-7. Observed vertical ozone profile measured above Poughkeepsie, NY at about 4 a.m. EST on July 14, 1995



Note: The figure includes a vertical line at 85 ppb for comparing aloft measurements with the 8-hour ozone NAAQS (observed ozone data from Zhang & Rao, 1999).

The aircraft measurements since 1992 reinforce the previously mentioned observations by Clarke and Ching (1983) during the summer of 1979, in which aircraft measurements recorded aloft ozone concentrations of about 90 ppb transported overnight from eastern Ohio and entering into the Northeast Corridor over a region stretching from the lower Hudson River Valley north of New York City down across eastern Pennsylvania and into Maryland just west of Baltimore. The measurements also observed NO_X aloft during the overnight hours that could contribute to additional ozone formation in the OTR as it mixed down to the surface in the morning.

The presence of high levels of ozone and precursors aloft across a large spatial region gives rise to the concept of an "ozone reservoir" existing at night just above the nocturnal inversion boundary. The pollutants in this reservoir are not subject to destruction at the surface, and can be transported long distances in the wind flows created by the synoptic scale weather patterns conducive to ozone formation and transport.

2.4. Atmospheric modeling of regional ozone transport

Modeling results by the USEPA for the Clean Air Interstate Rule (CAIR) further underscore the regional nature of ozone transport into and within the OTR through the

various pathways described in the above sections. Based on ozone air quality modeling results, the USEPA tabulated the percent contribution to 8-hour ozone nonattainment in a number of OTR counties. The USEPA modeled the contributions for the base year 2010, which included implementation of the NO_X SIP Call and other existing and promulgated control programs. Table 2-1 shows the CAIR results for the OTR counties (USEPA, 2005, from Table VI-2).

Table 2-1. USEPA CAIR modeling results of percent contribution to 8-hour ozone nonattainment in OTR counties in 2010 due to transport from upwind states

2010 Base Nonattainment Counties	2010 Base 8-Hour Ozone (ppb)	Percent of 8-Hour Ozone due to Transport
Fairfield CT	92	80 %
Middlesex CT	90	93 %
New Haven CT	91	95 %
Washington DC	85	38 %
Newcastle DE	85	37 %
Anne Arundel MD	88	45 %
Cecil MD	89	35 %
Harford MD	93	31 %
Kent MD	86	47 %
Bergen NJ	86	38 %
Camden NJ	91	57 %
Gloucester NJ	91	62 %
Hunterdon NJ	89	26 %
Mercer NJ	95	36 %
Middlesex NJ	92	62 %
Monmouth NJ	86	65 %
Morris NJ	86	63 %
Ocean NJ	100	82 %
Erie NY	87	37 %
Richmond NY	87	55 %
Suffolk NY	91	52 %
Westchester NY	85	56 %
Bucks PA	94	35 %
Chester PA	85	39 %
Montgomery PA	88	47 %
Philadelphia PA	90	55 %
Kent RI	86	88 %
Arlington VA	86	39 %
Fairfax VA	85	33 %

From USEPA, 2005 (Table VI-2)

The CAIR modeling by the USEPA also provides information on the upwind areas (by state) contributing to downwind nonattainment in the OTR counties. Table 2-2 presents the upwind states significantly contributing to 8-hour ozone nonattainment in counties within the OTR, according to significance criteria used by the USEPA (USEPA, 2005, from Table VI-5). The states listed in the table as significantly contributing to

downwind ozone nonattainment in the OTR counties include states outside of the OTR, indicating the broad regional scale of the ozone transport problem.

Table 2-2. USEPA CAIR modeling results of upwind states that make a significant contribution to 8-hour ozone in downwind OTR nonattainment counties

Downwind State/County		Upwind States									
CT	Middlesex	MA	NJ	NY	OH	PA	VA				
CT	New Haven	MD/DC	NJ	NY	OH	PA	VA	WV			
CT	Fairfield	MD/DC	NJ	NY	OH	PA	VA	WV			
District of Columbia		MD/DC	OH	PA	VA						
DE	New Castle	MD/DC	MI	NC	OH	PA	VA	WV			
MD	Harford	NC	OH	PA	VA	WV					
MD	Kent	MI	NC	OH	PA	VA	WV				
MD	Cecil	MI	OH	PA	VA	WV					
MD	Anne Arundel	MI	NC	OH	PA	VA	WV				
NJ	Ocean	DE	MD/DC	MI	NY	OH	PA	VA	WV		
NJ	Bergen	MD/DC	MI	OH	PA	VA	WV				
NJ	Gloucester	DE	MD/DC	MI	OH	PA	VA	WV			
NJ	Morris	DE	MD/DC	MI	NY	OH	PA	VA	WV		
NJ	Middlesex	DE	MD/DC	MI	NY	OH	PA	VA	WV		
NJ	Hunterdon	DE	MD/DC	OH	PA	VA	WV				
NJ	Camden	DE	MD/DC	MI	OH	PA	VA	WV			
NJ	Mercer	DE	MD/DC	MI	NY	OH	PA	VA	WV		
NJ	Monmouth	DE	MD/DC	MI	NY	OH	PA	VA	WV		
NY	Erie	MD/DC	MI	NJ	PA	VA	WI				
NY	Westchester	MD/DC	NJ	OH	PA	VA	WV				
NY	Richmond	MD/DC	MI	NJ	PA	VA	WV				
NY	Suffolk	CT	DE	MD/DC	MI	NC	NJ	OH	PA	VA	WV
PA	Montgomery	DE	MD/DC	NJ	OH	WV					
PA	Philadelphia	DE	MD/DC	MI	NJ	OH	VA	WV			
PA	Chester	DE	MD/DC	MI	NJ	OH	VA	WV			
PA	Bucks	DE	MD/DC	MI	NJ	OH	VA	WV			
RI	Kent	CT	MA	NJ	NY	OH	PA	VA			
VA	Arlington	MD/DC	OH	PA							
VA	Fairfax	MD/DC	OH	PA	WV						

From USEPA, 2005 (Table VI-5). States are listed alphabetically and not according to order of influence.

While the USEPA modeled 40 eastern U.S. counties as in nonattainment of the 8-hour ozone NAAQS in the 2010 base year (including counties not in the OTR), it projected that only three of those 40 counties would come into attainment by 2010 with the additional NO_X reductions of CAIR (USEPA, 2005, p. 58). The USEPA modeling does predict that ozone will be lower in the remaining nonattainment counties by 2010 due to CAIR, with additional counties coming into attainment by 2015. The CAIR reductions, therefore, will bring the OTR nonattainment counties closer to attainment by 2010, but will not result in attainment for a large majority of OTR counties predicted to be in nonattainment in 2010 prior to implementation of CAIR.

2.5. Summary

This section has summarized current knowledge of the meteorological processes that affect local ozone levels within the OTR. A conceptual description of transport within the OTR can be divided into three principle components: ground level transport at the surface, transport by the nocturnal low level jet, and transport aloft. All three modes of transport depend on the location of the high pressure system. Ground level transport is the result of interaction between the synoptic flow and local effects, such as the sea breeze and the Appalachian lee side trough. Transport within the OTR can occur by the nocturnal low level jet that forms late at night or in the very early morning hours. This phenomenon is a result of the differential heating of the air between the Appalachian Mountains and the Atlantic Ocean. It has been observed throughout the Eastern Seaboard from Georgia to Maine. The nocturnal low level jet can transport ozone that formed within the OTR or was transported into the OTR from outside the region. Transport aloft is dominated by the anti-cyclonic flow around a high pressure system, which can lead to transport of an ozone reservoir into the OTR created by emissions in areas that lie outside the OTR. Local emissions within the OTR add to the polluted air mixing down from above that arrived from more distant locations.

Atmospheric modeling by the USEPA underscores the observations that the OTR's ozone problem has contributions from outside and upwind of the region. Pollution sources in the Ohio River Valley and the Southeast significantly contribute to ozone nonattainment problems in various portions of the OTR.

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3. OZONE-FORMING POLLUTANT EMISSIONS

The pollutants that affect ozone formation are volatile organic compounds (VOCs) and nitrogen oxides (NO_X). The emissions dataset presented for the OTR in the first section below is from the 2002 MANE-VU (Mid-Atlantic/Northeast Visibility Union) Version 2 regional haze emissions inventory. MANE-VU is the regional planning organization (RPO) for the mid-Atlantic and Northeast states coordinating regional haze planning activities for the region. While the context of the MANE-VU inventory is regional haze, it includes inventories of NO_X and VOCs that also inform air quality planners on sources important to ozone formation.[f] To provide a fuller context of precursor emissions contributing to regional ozone affecting the OTR, the section following the MANE-VU information presents NO_X and VOC emissions information from the 2002 National Emissions Inventory (NEI) for states in adjacent RPOs.

3.1. Emissions inventory characteristics in the OTR

3.1.1. Volatile organic compounds (VOCs)

Existing emission inventories generally refer to VOCs as hydrocarbons whose volatility in the atmosphere makes them particularly important in enhancing ozone formation in the presence of NO_X.

As shown in Figure 3-1, the VOC inventory for the OTR is dominated by mobile and area sources. Most VOC emissions in the OTR, however, come from natural sources, which are not shown in the figure. Among the human-caused VOC emissions, on-road mobile sources of VOCs include exhaust emissions from gasoline passenger vehicles and diesel-powered heavy-duty vehicles as well as evaporative emissions from transportation fuels. VOC emissions may also originate from a variety of area sources (including solvents, architectural coatings, and dry cleaners) as well as from some point sources (e.g., industrial facilities and petroleum refineries).

Naturally occurring (biogenic) VOC emissions are caused by the release of natural organic compounds from plants in warm weather. Many natural VOCs that contribute to ozone formation are highly reactive. Isoprene, for example, is a highly reactive five-carbon natural VOC emitted from mostly deciduous trees (e.g., oaks) that plays an important role in enhancing regional ozone formation across the eastern U.S. (Trainer *et al.*, 1987; Chameides *et al.*, 1988). Because biogenic VOC emissions are large and reactive, they are the most important part of the VOC inventory for understanding and predicting ozone formation. Biogenic VOCs are not included in Figure 3-1, but nationally, they represent roughly two-thirds of all annual VOC emissions (USEPA, 2006a). Modeling biogenic emissions can be difficult as it requires simulating biological responses to a range of environmental conditions, such as leaf temperature and the amount of sunlight reaching a leaf surface.

[f] The description of OTR state inventories discussed in the first section does not include the portion of Virginia in the Washington, DC metropolitan area. Information for Virginia is in the following section and comes from the 2002 National Emissions Inventory.

Figure 3-1. 2002 MANE-VU state VOC inventories in the OTR

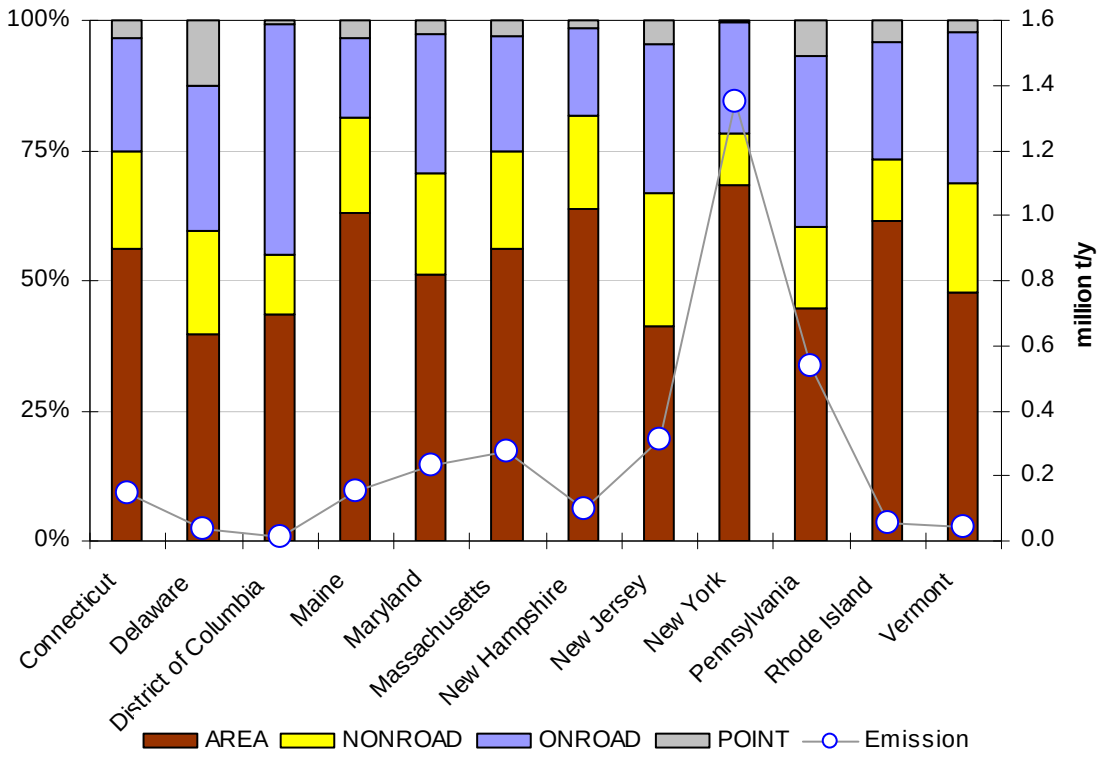


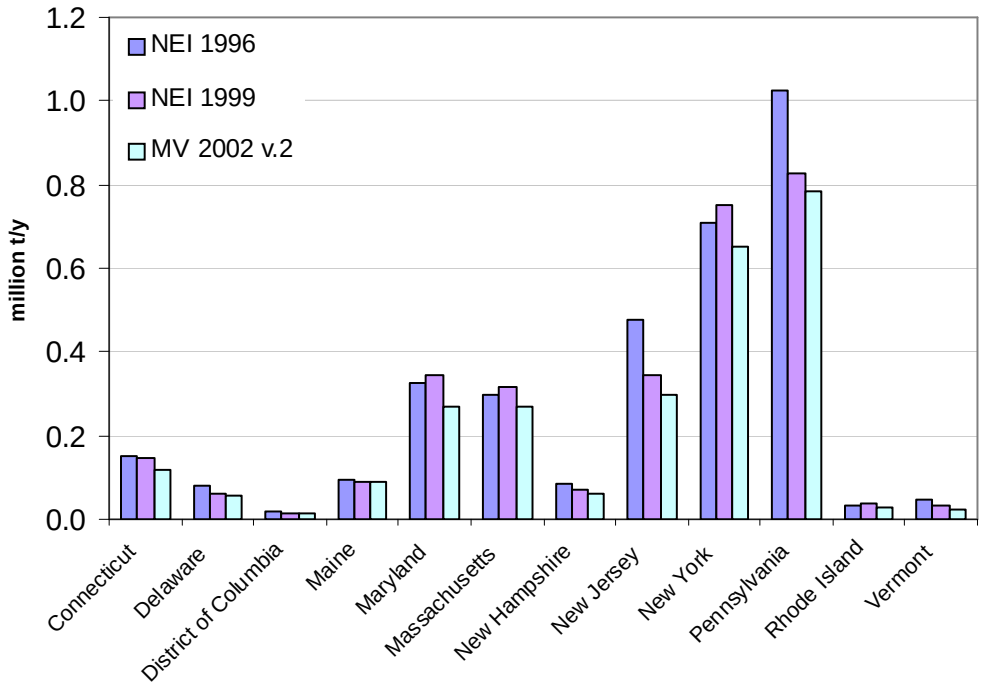
Figure key: Bars = Percentage fractions of four source categories; Circles = Annual emissions amount in 10^6 tons per year. The Virginia portion of the Washington, DC metropolitan area is not shown in the figure.

3.1.2. Oxides of nitrogen (NO_X)

NO_X emissions are a fundamental necessity for the atmospheric formation of ozone. Without NO_X, ozone formation during warm summer days would virtually cease, regardless of the amount of reactive VOCs present. By contrast, without VOCs, NO_X would still produce ozone in the presence of sunlight, albeit at a much diminished efficiency.

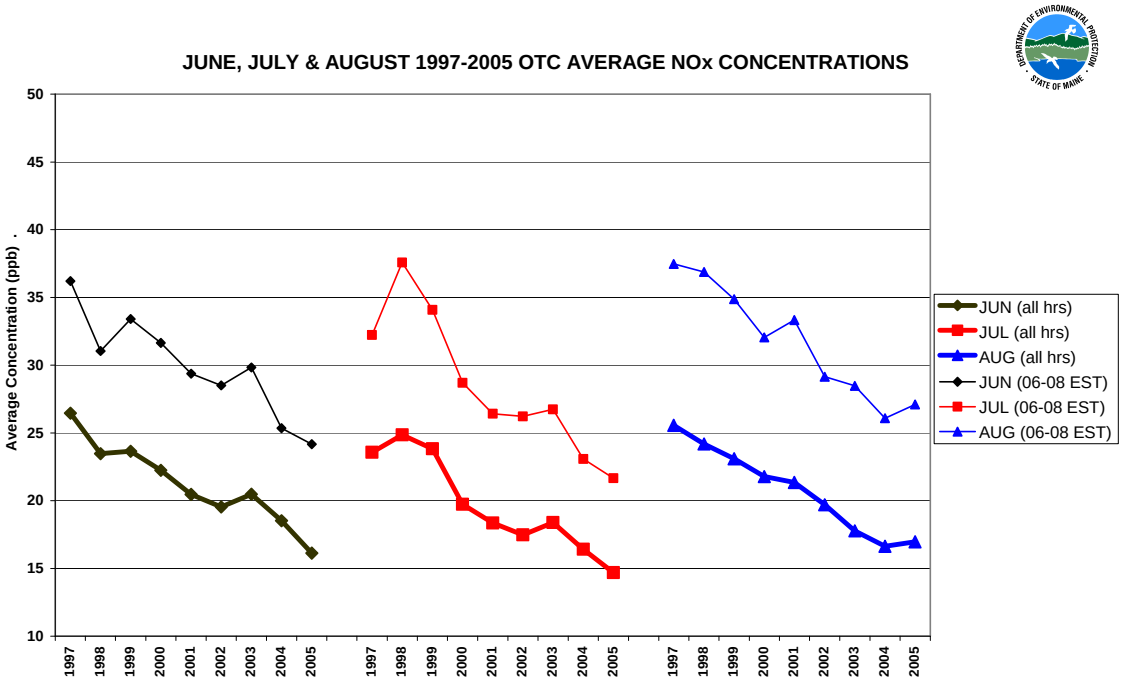
Figure 3-2 shows NO_X emissions in the OTR at the state level. Since 1980, nationwide emissions of NO_X from all sources have shown little change. In fact, emissions increased by 2 percent between 1989 and 1998 (USEPA, 2000). This increase is most likely due to industrial sources and the transportation sector, as power plant combustion sources have implemented modest emissions reductions during the same time period. Most states in the OTR experienced declining NO_X emissions from 1996 through 2002, except Massachusetts, Maryland, New York, and Rhode Island, which show an increase in NO_X emissions in 1999 before declining to levels below 1996 emissions in 2002.

Figure 3-2. State level nitrogen oxides emissions



Monitored ambient NO_X trends during the summer from 1997 to 2005 corroborate the downward trend in NO_X emissions seen in the emissions inventories for the OTR. As seen in Figure 3-3, the 24-hour (lower trend lines) and 6 a.m.-8 a.m. (upper trend lines) NO_X concentrations indicate decreases in NO_X over this time period in the OTR. The NO_X reductions likely come from decreasing vehicle NO_X emissions due to more stringent motor vehicle standards as well as NO_X reductions from the OTR NO_X Budget Program and the NO_X SIP Call (mainly power plants).

Figure 3-3. Plot of monitored NO_X trends in OTR during 1997-2005



Note: Upper trend lines correspond to ambient NO_X measured from 0600-0800 EST in the morning. Lower trend lines correspond to NO_X measured over entire day (created by Tom Downs, Maine Department of Environmental Protection).

Power plants and mobile sources generally dominate state and national NO_X emissions inventories. Nationally, power plants account for more than one-quarter of all NO_X emissions, amounting to over six million tons. The electric sector plays an even larger role, however, in parts of the industrial Midwest where high NO_X emissions have a particularly significant power plant contribution. By contrast, mobile sources dominate the NO_X inventories for more urbanized mid-Atlantic and New England states to a far greater extent, as shown in Figure 3-4. In these states, on-road mobile sources — a category that mainly includes highway vehicles — represent the most significant NO_X source category. Emissions from non-road (i.e., off-highway) mobile sources, primarily diesel-fired engines, also represent a substantial fraction of the inventory.

Figure 3-4. 2002 MANE-VU state NO_X inventories in the OTR

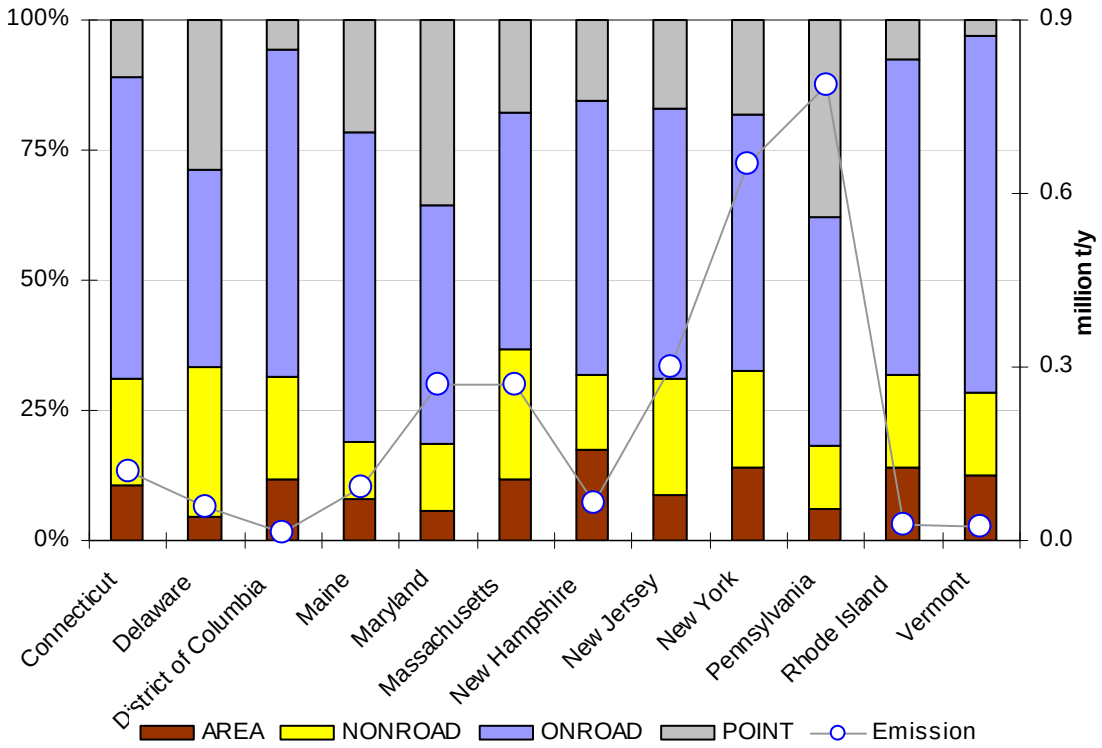


Figure key: Bars = Percentage fractions of four source categories; Circles = Annual emissions amount in 10^6 tons per year. The Virginia portion of the Washington, DC metropolitan area is not shown in the figure.

3.2. Emissions inventory characteristics outside the OTR

NO_X and VOC emissions in the OTR are only one component of the emissions contributing to ozone affecting the OTR. As regional modeling for the NO_X SIP Call and CAIR have shown, emission sources, primarily of NO_X, located outside the OTR can significantly contribute to ozone transported into the OTR. Here we present regional emissions information grouped by the three eastern RPOs – MANE-VU, VISTAS (Visibility Improvement State and Tribal Association of the Southeast), and the MWRPO (Midwest RPO). Table 3-1 lists the states in each RPO.

The inventory information is extracted from the USEPA final 2002 National Emissions Inventory (NEI). For consistency, the MANE-VU information here also comes from the 2002 NEI rather than from the MANE-VU Version 2 regional haze emissions inventory described above. The differences between the inventories are not great, as the NEI and the MANE-VU Version 2 inventory are both based on the same inventory information provided by the states.

Table 3-1. Eastern U.S. RPOs and their state members

RPO	State
MWRPO	Illinois
MWRPO	Indiana
MWRPO	Michigan
MWRPO	Ohio
MWRPO	Wisconsin
MANE-VU	Connecticut
MANE-VU	Delaware
MANE-VU	District of Columbia
MANE-VU	Maine
MANE-VU	Maryland
MANE-VU	Massachusetts
MANE-VU	New Hampshire
MANE-VU	New Jersey
MANE-VU	New York
MANE-VU	Pennsylvania
MANE-VU	Rhode Island
MANE-VU	Vermont
VISTAS	Alabama
VISTAS	Florida
VISTAS	Georgia
VISTAS	Kentucky
VISTAS	Mississippi
VISTAS	North Carolina
VISTAS	South Carolina
VISTAS	Tennessee
VISTAS	Virginia
VISTAS	West Virginia

Table 3-2 presents VOC emissions by source sector and RPO for the eastern United States. The NO_X emissions by source sector and RPO are presented in Table 3-3. Regionally, NO_X emissions are more important with respect to regional ozone formation and transport. NO_X emissions in combination with abundant naturally occurring VOC emissions from oaks and other vegetation have been shown to be important sources of regional ozone in the eastern U.S. (Trainer et al. 1987; Chameides et al. 1988).

Table 3-2. VOC emissions in eastern RPOs

RPO	Point	Area	On-road	Non-road	Total
MWRPO	234,938	1,182,186	660,010	492,027	2,569,160
MANE-VU	93,691	1,798,158	793,541	494,115	3,179,504
VISTAS	458,740	2,047,359	1,314,979	609,539	4,430,617

Table 3-3. NO_X emissions in eastern RPOs

RPO	Point	Area	On-road	Non-road	Total
MWRPO	1,437,284	184,790	1,290,178	723,844	3,636,096
MANE-VU	680,975	268,997	1,297,357	534,454	2,781,783
VISTAS	2,094,228	266,848	2,160,601	812,615	5,334,293

3.3. Are NO_X or VOC control strategies most effective at reducing ozone?

The effectiveness of a NO_X-focused or VOC-focused control strategy to reduce ozone is not constant by location or emissions; rather it is a changing chemical characteristic of an air parcel affecting a particular location. As a result, the effectiveness of a NO_X or VOC-focused control strategy can vary within an air parcel as it dynamically evolves over time with transport, dispersion, and photochemical aging (NARSTO, 2000).

On a regional basis, OTAG, CAIR and other modeling studies have consistently shown that NO_X reductions have the greatest impact on regional ozone concentrations, while VOC reductions have more local impacts. This is largely a result of significant naturally occurring VOC emissions (especially isoprene) in large forested regions of the eastern U.S. Real-world results from regional NO_X reductions at power plants (i.e., the NO_X SIP Call) are now indicating that significant ozone reductions are occurring on a regional basis as a result of regional NO_X strategies. A recent USEPA report finds a strong association between areas with the greatest NO_X emission reductions due to the NO_X SIP Call and downwind sites exhibiting the greatest improvement in ozone in 2005 (USEPA, 2006b).

As a general rule, VOC reductions may be effective at reducing urban-scale ozone pollution in lieu of or in combination with local NO_X reductions, while regional NO_X controls are most effective at reducing regional ozone. While a general rule can be outlined in evaluating the potential effectiveness of NO_X and VOC-focused control strategies, the optimal strategy for a specific location will depend on the particular circumstances of that location. Exceptions to a VOC-only strategy for an urban area can occur when the urban area has large natural VOC emissions, ozone is transported from upwind, or there is recirculation of aged local pollution (e.g., sea breeze effect). Furthermore, because the conditions causing individual ozone episodes can vary, a given urban area may change in sensitivity between a NO_X and VOC-focused strategy depending on a particular episode's conditions (NARSTO, 2000). Therefore, the appropriate combination of VOC and NO_X controls at the local level depends on local circumstances with the realization that a single approach focusing on NO_X or VOC-only controls is not necessarily effective for all episode types. It is clear, however, that regional NO_X reductions provide regional ozone reductions, and this will influence ozone levels being transported into local urban areas.

3.4. Summary

There are large emissions of VOCs and NO_X within and outside the OTR that contribute to local and regional ozone problems. Naturally occurring VOC emissions play an important role in combination with human-caused NO_X emissions in forming regional ozone across large sections of the eastern U.S. Regional NO_X control strategies are demonstrating success in reducing regional ozone. On a more local scale, some combination of VOC and NO_X controls may be needed, with the specific combination dependent upon local circumstances.

References

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USEPA. *National Air Quality and Emission Trends Report, 1998*, EPA 454/R-00-003, available online: http://www.epa.gov/oar/aqtrnd98/, 2000.

USEPA. *2002 Final National Emissions Inventory (NEI)*, available online: ftp://ftp.epa.gov/EmisInventory/2002finalnei/, 2006a (accessed October 10, 2006) [The 2002 NEI reports national annual emissions for total anthropogenic VOC emissions as 16.8 million tons, and total biogenic VOC emissions as 41.8 million tons].

USEPA. *NO_X Budget Trading Program 2005 Compliance and Environmental Results*, EPA430-R-06-013, available online: http://www.epa.gov/airmarkets/fednox/, 2006b.

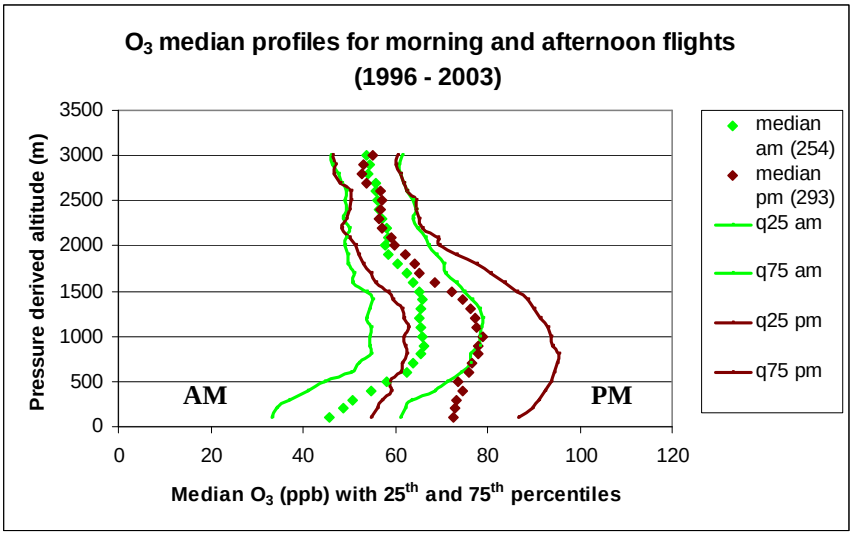
4. WHAT WILL IT TAKE TO CLEAN THE AIR? – LINKING THE SCIENCE TO POLICY

4.1. The three phases of a bad ozone day and the ozone reservoir

With the atmospheric chemistry, meteorology, and air emission inventory elements presented in the previous sections, a conceptual description emerges of ozone problem in the OTR. Consider a typical "day," defined as starting at sunset, for a severe ozone event associated with a high pressure system. Conceptually, a bad ozone day can be considered as occurring in three phases. During phase one, a nocturnal inversion forms as the temperature of the earth drops following sunset, isolating the surface from stronger winds only a few hundred feet overhead. Ozone near the surface cannot mix with ozone above and is destroyed as it reacts with the Earth's surface. In a city, fresh NO_X emissions react with ozone, further reducing its concentration, so that by morning, very little ozone is left below the nocturnal inversion. At this time, the nocturnal inversion is at its strongest, and winds at the surface are typically calm.

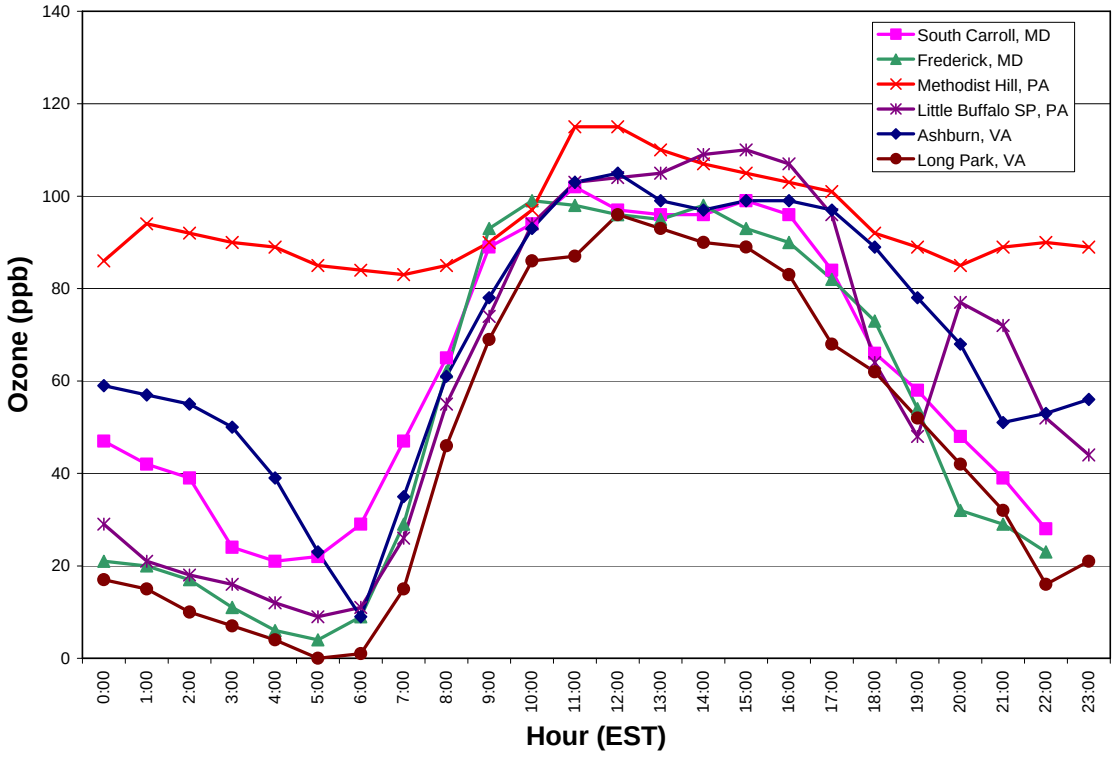
Above the nocturnal inversion, the situation is quite different. Ozone and its precursors, both from the previous day's local emissions and from transport, remain largely intact. There are no surfaces to react with the ozone and a large reservoir of ozone remains above the inversion. During phase two of a bad ozone day, the nocturnal inversion breaks down at mid-morning, with the result that the ozone and precursors above the inversion can now mix with the air near the surface. The result of this mixing is a sudden change in ozone. Figure 4-1 shows median ozone profiles for morning and afternoon aircraft flights from 1996 – 2003. One can clearly see the breakdown of the nocturnal inversion throughout the day (Hudson, 2005).

Figure 4-1. Median ozone profiles for morning and afternoon flights from 1996 – 2003



In phase three of a bad ozone day, ozone concentrations reach their highest levels in the afternoon through the combined accumulation of local pollution produced that day mixed with the transported regional pollution load brought in overnight from the ozone reservoir. Figure 4-2 shows this graphically for the southern OTR. The ozone monitor at Methodist Hill, PA is a high elevation site located at 1900 ft in altitude in south central Pennsylvania, and is above the nocturnal inversion. In the early morning hours of August 12, 2002 (e.g., 5 a.m.), it recorded ozone concentrations above 80 ppb, which was much higher than what other lower elevation monitors in the region were recording (e.g., Little Buffalo State Park, PA, South Carroll County, MD, Frederick, MD, Ashburn, VA, Long Park, VA). Due to the lack of sunlight necessary to produce ozone photochemically during nighttime hours, the high ozone levels seen at Methodist Hill, PA indicate the presence of a significant ozone reservoir above the nocturnal inversion layer produced during daylight hours at some earlier point in time and transported into the region. With the break up of the nocturnal inversion after sunrise (e.g., starting about 7 a.m.), ozone concentrations at the lower elevation monitors show a rapid increase. This reflects the mixing down of the ozone reservoir from higher altitude to the surface in combination with local ozone production near the surface now that the sun has begun inducing its photochemical production.

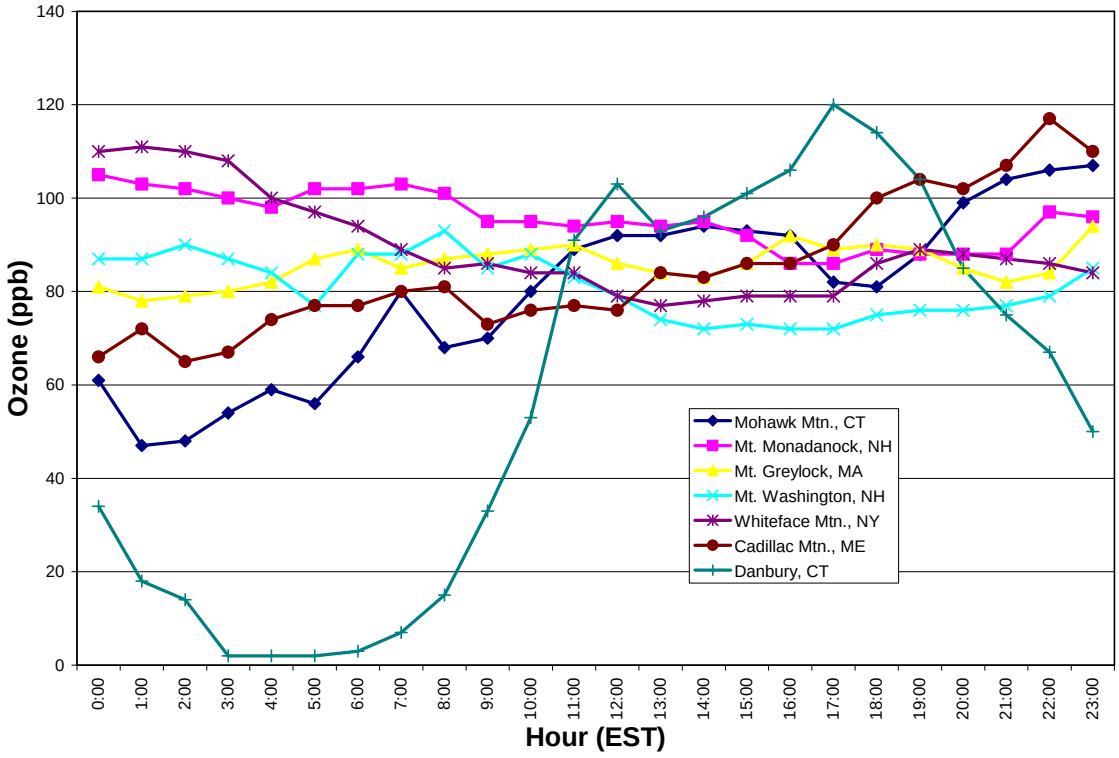
Figure 4-2. Hourly ozone profiles in the southern OTR, August 12, 2002



The ozone reservoir extends across the OTR, as seen on the same night in high elevation ozone monitoring sites in the northern OTR. Figure 4-3 shows the hourly ozone concentrations measured on August 12, 2002 at Mohawk Mountain, CT, Cadillac Mountain, ME, Mt. Greylock, MA, Mt. Monadanock, NH, Mt. Washington, NH, and

Whiteface Mountain, NY. As with Methodist Hill, PA on this day, these sites show elevated ozone concentrations during nighttime hours, as compared to lower elevation sites below the nocturnal inversion (e.g., Danbury, CT). By mid-day, however, the nocturnal boundary layer has broken down, mixing the transported ozone from the reservoir above into the locally produced ozone below. Appendix G provides more detail on contributions to the ozone reservoir within and outside the OTR.

Figure 4-3. Hourly ozone profiles in the northern OTR, August 12, 2002



Data provided by Tom Downs, Maine Department of Environmental Protection.

4.2. Chronology of an ozone episode – August 2002

The chronology of an historical ozone episode occurring in the OTR from August 8 to August 16, 2002 provides a real-world example that pieces together the elements of the ozone conceptual description given in this document. Surface maps from the period provide a synoptic overview of major weather systems that were influencing air quality across the OTR during that time. Meteorological insights combined with ozone concentration information provide a picture of the evolving ozone episode on a day-by-day basis. Figure 4-4, Figure 4-5, and Figure 4-6, respectively, show eight-panel displays of surface weather maps, back trajectories, and 8-hour maximum ozone concentrations from each day. The daily progression shows the formation of high ozone that shifts from west to east, and ultimately northward, during successive days of the episode according to local ozone formation and transport shaped by wind patterns within and outside of the OTR.

The August 2002 episode began with a slow-moving high pressure system centered over the Great Lakes initiating a northerly flow over the OTR on August 8. Over

the next several days, the high drifted southeastward and became extended across a large part of the eastern U.S., bringing high temperatures to the region. Calm conditions west of the OTR on August 10 were pivotal for the formation of ozone, which first began building in the Ohio River Valley. Over the next four days, 8-hour ozone concentrations climbed well above the 85 ppb (0.08 ppm) NAAQS over a wide area of the OTR. Large parts of the heavily populated Northeast Corridor experienced 8-hour ozone levels above 100 ppb during the height of the episode, which far exceeded the 85 ppb NAAQS.

The following chronology provides a day-by-day evolution of the August 2002 ozone episode. Parts of this description are taken from Ryan (2003).

August 8: A high pressure system over the Great Lakes produces NW-N prevailing surface winds (~4-8 mph) throughout the region. Maximum daily temperatures approach or exceed 80º F.

August 9: Wind speeds fall off but the direction remains NW-N as the high moves into the Pennsylvania-New York region. Temperatures rise as cloud cover declines. Background ozone levels begin to build in the Ohio River Valley with 8-hour maximum concentrations reaching the 60-80 ppb range.

August 10: High pressure is directly over the mid-Atlantic. With dew points still in the mid-50º's F, the skies are extraordinarily clear throughout the day. Temperatures (except in northern-most areas) approach 90º F while surface-level winds turn to more southerly directions. With high pressure overhead, the back trajectories suggest very light winds and recirculation. Calm conditions through the morning hours in the lower Ohio River Valley promote increasingly higher levels of ozone noted in surface observations – now reaching above the 85 ppb 8-hour ozone NAAQS over much of Indiana, Ohio, and other states along the Ohio River, as well as states around Lake Michigan and large portions of the southeastern U.S. Ozone levels above the 8-hour NAAQS now begin appearing for the first time in the western and southern parts of the OTR.

August 11: Surface high pressure drops slowly southeastward across the mid-Atlantic with the center in western North Carolina drifting to coastal South Carolina during the day. The upper level ridge has also moved east and is located over the mid-Atlantic. Circulation around the high becomes well established. A surface-level trough descends from north of the Great Lakes during the day, passes eastward through the Ohio River Valley and stalls over the Allegheny Mountains and southward. Peak temperatures are in the low to mid-90º's F. Morning winds are low-to-calm in the area east of the Mississippi – the area of ozone now reaches from eastern Wisconsin to Tennessee and eastward to Georgia up through the Carolinas into the OTR, covering most of Pennsylvania, New York, New Jersey, Connecticut, Rhode Island and Massachusetts. Winds are generally south to southwest as is reflected in the boundary layer back trajectories. The key factor driving local ozone production appears to be a very stable boundary layer. The 8 a.m. sounding at the Washington-Dulles airport shows a very strong low-level inversion from 950-900 mb with a deep residual layer beneath a continuing strong subsidence inversion – now based at 760 mb.

August 12: The upper level ridge remains quasi-stationary with its axis over the mid-Atlantic. The center of high pressure at 850 mb is over North Carolina and Georgia. At the surface, the characteristic Appalachian lee side trough forms. Temperatures exceed

90º F throughout the OTR except in coastal Maine. Winds are fairly strong from the northwest. This is reflected in the back trajectories that show a shift to westerly transport. Elevated upwind ozone concentrations at 11 a.m. on August 11 occur in the vicinity of the origin of the back trajectories, on the order of 78-86 ppb. Ozone concentrations fall this day west of the Appalachians but increase markedly across the mid-Atlantic. The area of highest ozone has pushed eastward and now extends from southern Maine across central Pennsylvania down through Maryland into the Carolinas, Georgia, and eastern Tennessee. Ozone builds throughout the day as circulation forces it to channel northeast between the stalled trough and a cold front approaching from the Midwest. Some of the highest 8-hour concentrations occur through the central to southern OTR on this day.

August 13: Calm conditions prevail as the trough reaches coastal New Jersey by 8 a.m. Generally clear skies allow temperatures to reach the mid-90º's F everywhere except in coastal Maine. Dew points, which had been rising since August 8, reach the upper 60º's F. A morning sounding at the Washington-Dulles airport showed a continuing strong low level inversion with a residual mixed layer to 850 mb ending just beneath a weak secondary inversion. The cap aloft has lifted to ~ 630 mb and the sounding is more unstable compared to previous day's between the two inversion layers. The Appalachian lee side trough continues in place from late on August 12. As is typically the case, the highest ozone concentrations are found in proximity to this boundary. The highest 8-hour ozone concentrations are along the eastern portions of the OTR from northeastern Virginia through New Jersey, Long Island, Connecticut, and into eastern Massachusetts. By 8 p.m., showers associated with the approaching cold front have reached into Ohio.

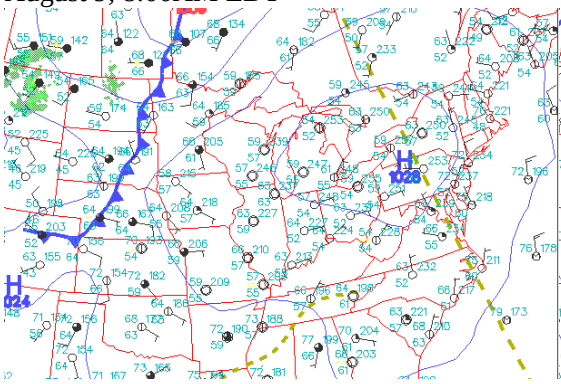
August 14: By 8 a.m., the trough has dissipated and the high is moving offshore, resulting in an increasing southerly wind component, which pushes maritime air northward. Dew points remain in the upper 60º's F and peak temperatures reach into the 90º's F everywhere and top 100º F in several locations. Ozone concentrations build again, with the highest levels concentrated in the central OTR from eastern Pennsylvania across to Massachusetts. A "hotspot" of ozone appears in upstate New York at the eastern end of Lake Ontario, and may be the result of transport from the west across the lake. Ozone concentrations decrease south and west of Baltimore and along coastal New Jersey as cleaner maritime air pushes in from the south.

August 15: This episode ends in a very different manner than the standard high ozone episode. Instead of the passage of a sharp cold front, this episode ends gradually as cleaner air sweeps north, winds increase, and the atmosphere steadily destabilizes. Ozone concentrations fall across the middle and lower OTR as low level flow becomes more southeast and the Bermuda high fills in westward. The highest levels, still exceeding the 8-hour ozone NAAQS, now occur in the northern reaches of the OTR in upstate New York, Vermont, New Hampshire, and Maine.

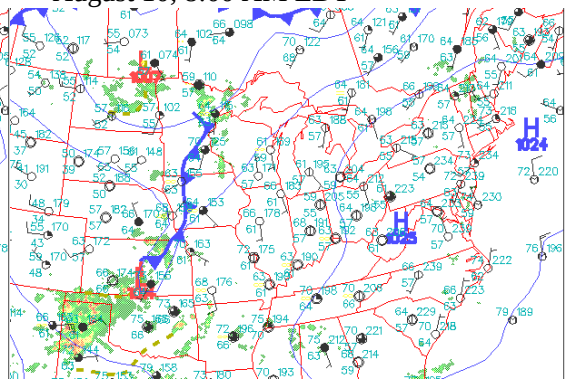
August 16: Cloud cover spreads over the region with ozone falling further. The new high building into the upper Midwest pushes the remains of the showers out of the Northeast. A spot of high ozone persists in central New Jersey. This is the last exceedance day in a string of seven exceedance days within the OTR during this extended episode.

Figure 4-4. Surface weather maps for August 9-16, 2002

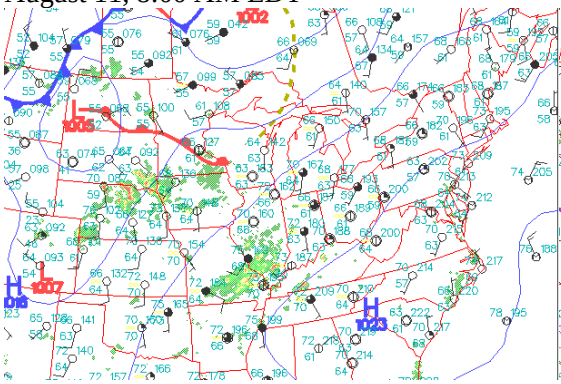
August 9, 8:00AM EDT



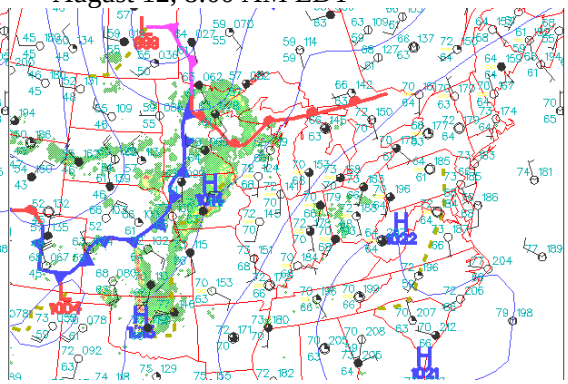
August 10, 8:00 AM EDT



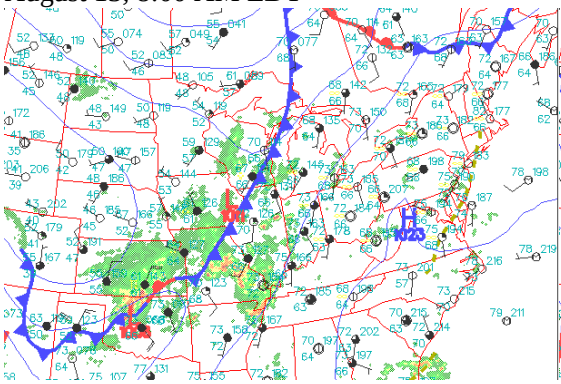
August 11, 8:00 AM EDT



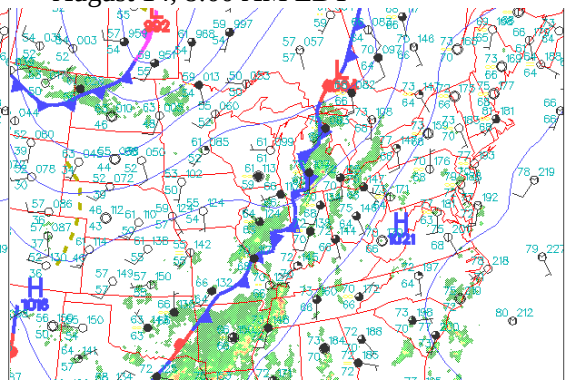
August 12, 8:00 AM EDT



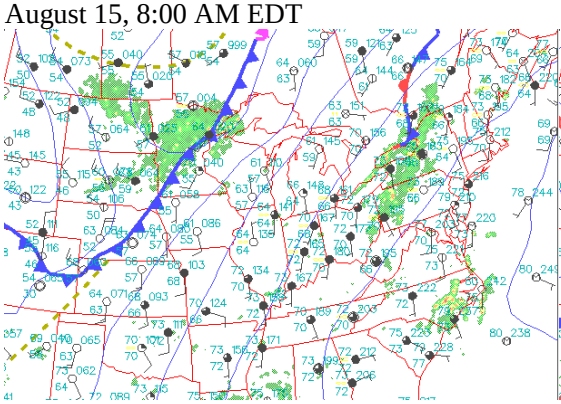
August 13, 8:00 AM EDT



August 14, 8:00 AM EDT



August 15, 8:00 AM EDT



August 16, 8:00 AM EDT

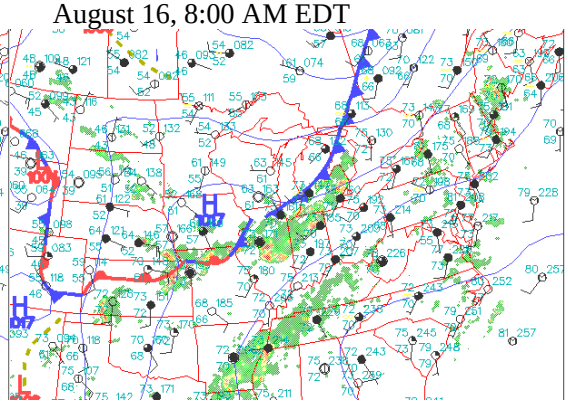
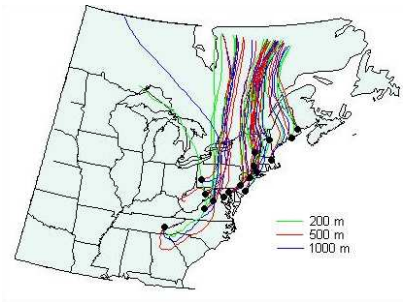
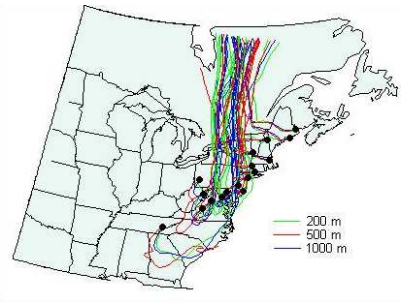


Figure 4-5. HYSPLIT 72-hour back trajectories for August 9-16, 2002

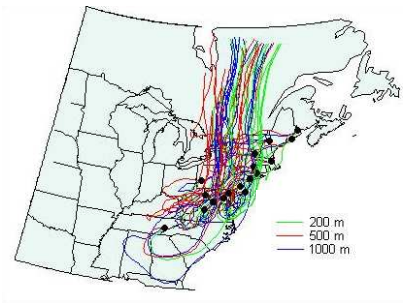
Aug 9, 2002 8 am EDT



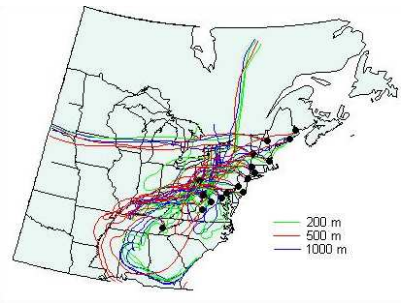
Aug 10, 2002 8 am EDT



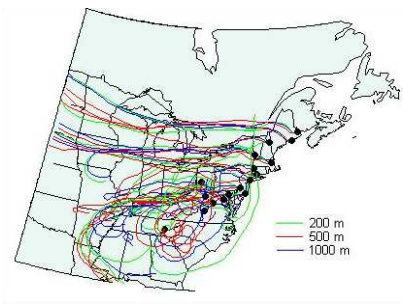
Aug 11, 2002 8 am EDT



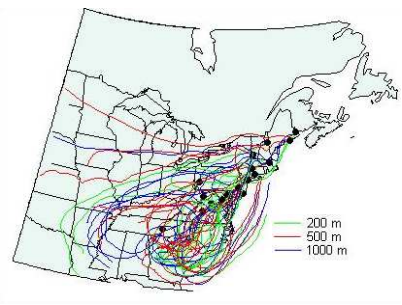
Aug 12, 2002 8 am EDT



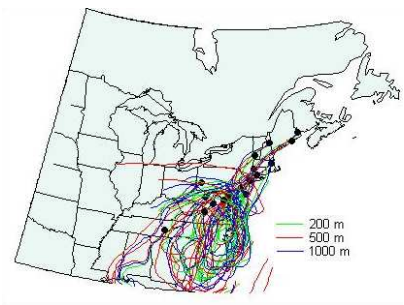
Aug 13, 2002 8 am EDT



Aug 14, 2002 8 am EDT



Aug 15, 2002 8 am EDT



Aug 16, 2002 8 am EDT

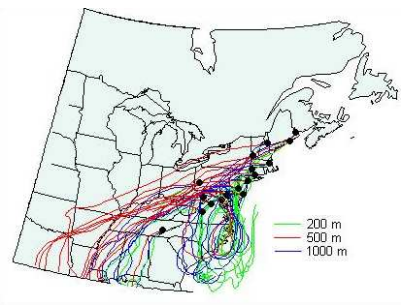


Figure 4-6. Spatially interpolated maps of maximum 8-hour surface ozone concentrations August 9 – 16, 2002