WOE Chapter 7

Regional Nature of Ozone Transport

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Abstract

The transport of ozone into and within the State of Maryland above the nocturnal boundary layer has been examined using a combination of aircraft and ground-based measurements. The evidence from both the aircraft and the station ozone data clearly points to the importance of transport in the overall quality of Maryland's air. Ozone introduced to the surface after the breakdown of the nocturnal inversion can either be transported or derived from locally produced ozone, depending on nighttime residual layer wind speeds. The contribution of regional transport to afternoon boundary layer ozone has been quantified using ozone profile data obtained on aircraft flights. When the source regions lay over the Ohio River Valley (~59% of the profiles), transport accounted for 69-82% of the afternoon boundary layer ozone. When winds were weak (~27% of the profiles), transport only accounted for 58% of the afternoon boundary layer ozone. The ground level ozone data obtained from MDE monitoring stations has also been examined for evidence of downward mixing. On days when the transported ozone is low, peak ozone occurs at about 15:00 EST. However when the transported ozone is large, an earlier peak occurs at about 10:00 EST, corresponding to the breakdown of the nocturnal boundary layer. The rate of increase of ozone within this peak is about four times greater than that due to pure photochemistry. A study was made of the relative contribution of transported and local photochemistry to the ozone data for six 8-hour exceedance days in August, 2002. The results show that if local photochemistry were the only source of ozone, none of the 6 days examined would have exceeded the 8 hour ozone standard. The effect of the transported ozone is to add ozone early in the day and hence to expand the time interval over which the ozone level exceeds 85 ppbv. This directly affects the 8-hour ozone averages.

Introduction

Land surfaces are far more efficient at radiating heat than the atmosphere above them, hence on a cloudless night, the Earth's surface cools more rapidly than the air. That temperature drop is then conveyed to the lowest few hundred feet of the atmosphere. The air above this altitude cools more slowly, and a temperature inversion forms only a few hundred feet above the ground. The inversion, known as the nocturnal inversion, divides the atmosphere into two layers which do not mix. Below the nocturnal inversion the surface winds are weak, and any pollutants emitted overnight accumulate beneath the inversion. Above the nocturnal inversion, winds continue throughout the night and can become even stronger as the inversion isolates the winds from the friction of the rough ground surface. This situation is especially prevalent when a high pressure system exists, which is the hallmark of high pollution events along the East coast. It should be noted that the time used throughout this section is Eastern Standard Time (EST, or UTC-5).

In the morning, the sun warms the Earth's surface, and conduction and convection transfer heat upward. This warms the air near the surface more effectively than higher up; and by about 10:00 EST the temperature of the air above the surface has risen sufficiently to remove the nocturnal inversion. As a result, the ozone and its precursors that were above the inversion mix down to the surface. This mixing can either lower or increase the air pollution levels at the surface, depending on whether the air above the nocturnal inversion is cleaner or more polluted than the air at the surface. When wind speeds above the nocturnal boundary layer are brisk over night, and the area where the air mass originated had high ozone levels the previous day, the ozone and precursors that are mixed down in the central Mid-Atlantic region can be referred to as transported ozone. However, when wind speeds are weak above the nocturnal boundary layer overnight, the ozone produced in the central Mid-Atlantic area during the previous day can become decoupled from the surface with the formation of the nighttime inversion, remain in place over the region, and be mixed down the following day after the breakdown of the nocturnal boundary layer. This added ozone can be referred to as yesterdays local recirculated ozone. Vukovich and Scarborough (2005) have modeled the effect of this transported ozone and precursors using the aircraft data obtained by the University of Maryland (Dodderidge et al, 1995). They found a mixed response. On some days there was a large increase in the local recirculated ozone, indicating an increase in the chemical production of ozone, but on other days, the increase in local ozone was due only to the transported ozone mixed down from above the nocturnal inversion.

Results from aircraft measurements.

From 1997 to 2003, aircraft measurements of ozone were made, from the surface to 3 km, during summertime air pollution episodes over the Mid-Atlantic U.S. as part of the University of Maryland's Regional Atmospheric Measurement, Modeling, and Prediction Program (RAMMPP). Morning flights (before 12 noon EST) were generally made upwind of urban centers over locations such as Luray, Winchester, and Cumberland (Figure 1). Afternoon flights (after 12:00 EST) over locations such as Hartford and Easton were made downwind of urban centers (Figure 1). Boundary layer ozone measured in the afternoon was generally greater than that measured in the morning, though the lower free tropospheric ozone showed little variance (Taubman et al., 2006). The increased afternoon ozone is explained by three factors: (1) longer time periods of daylight that allow for photochemical buildup, (2) afternoon meteorology that allows for mixing of transported ozone, and (3) the location of the flights.

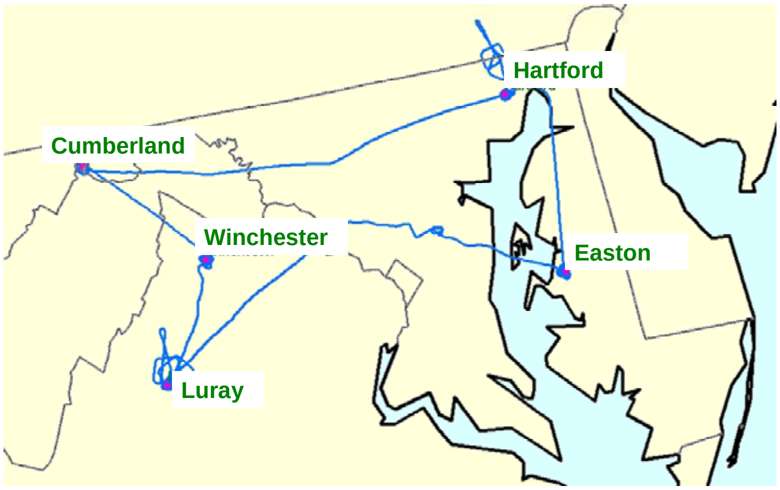

Figure 1. A typical flight path made by University of Maryland research aircraft. Morning spirals were made in Cumberland, Winchester, and Luray, all upwind of the Baltimore-Washington corridor. Afternoon spirals were made in Hartford and Easton, downwind of the Baltimore-Washington corridor

Taubman et al., 2006 used a cluster analysis of back trajectories in conjunction with the vertical profile data to identify source regions and characteristic transport patterns during summertime pollution episodes. Four of those clusters representing different meteorological regimes are discussed below.

Cluster 1 labeled as Moderate Northwesterly flow (Figure 2a) has large amounts of ozone (Figure 3), a large SO_2/CO ratio, large, highly scattering particles, and a large aerosol optical depth (AOD). These values are indicative of aged point source pollution. The greatest trajectory density lies over the northern Ohio River Valley where there are several large NO_x and SO_2 sources. Fresh NO_x and SO_2 emissions from these sources have had ample opportunity under a moderate flow regime to produce ozone and secondary aerosols en route to the Mid-Atlantic.

Cluster 2 shows wind directions similar to cluster 1 (Figure 2b), but with faster wind speeds (Fast Northwesterly flow). The greatest trajectory density also lies mainly over the northern Ohio River Valley and extends into the Great Lakes region. The particles are also large and highly scattering, but the AOD has less magnitude. The ozone values associated with this cluster are smaller than those in Cluster 1 (Figure 3). Clusters 1 and 2 are both associated with northwesterly flow bringing in point source pollution from the northern Ohio River Valley. The smaller ozone values associated with cluster 2 likely result from the faster wind speeds associated with this cluster. Faster winds inhibit local photochemical ozone production and increase ventilation of urban mobile source pollution.

Cluster 3 is typified by Slow Southerly flow (Figure 2c). The greatest air parcel density is found over the central Mid-Atlantic region. Ozone values, particularly in the afternoon are large (Figure 3). These large ozone values likely result from the previous day's ozone being brought down from the nocturnal boundary layer where it combines with the current day's ozone. The previous day's ozone, which was decoupled from the surface with the formation of the nighttime inversion, remained in place over the central

Mid-Atlantic region until being reintroduced to the surface layer the next day upon breakdown of the nocturnal boundary layer. The previous day's ozone could have been transported ozone or locally grown ozone. Figure 2c shows that there are few large NO_x and SO_2 sources in the area of greatest trajectory density. The particle property values are moderate and the CO values are large. These values, together with the weak winds associated with cluster 3, indicate local, urban pollution dominated by mobile sources.

The transport pattern identified by cluster 4 is characterized as Moderate Southwesterly flow and the greatest trajectory density lies over the southern Ohio River Valley. For the most part, this cluster is associated with little pollution loading, which suggests that there are fewer point sources located farther south along the Ohio River. Figure 2d shows no large NO_x or SO_2 sources in the area of greatest trajectory density, although many do encircle this area. Also, the afternoon ozone values are particularly small (Figure 3), and not much larger than the morning values indicating there was little photochemical production during transport of the air parcels.

The contribution of regional transport to afternoon boundary layer ozone is quantified as follows. The percent of the afternoon ozone boundary layer column content for each cluster that can be accounted for by regional transport was estimated with the following equation:

$$\%\ Ozone\ transported = \left(\frac{RL}{MBL}\right) \times \left(\frac{MBL}{ABL}\right) \times 100 \qquad (1)$$

RL: The residual layer column content defined as the layer between 500 m and 2000 m in the morning profiles

MBL: The morning boundary layer column content defined as the layer between 100 m and 2000 m in the morning profiles

ABL The afternoon boundary layer column content defined as the layer between 100 m and 2000 m in the afternoon profiles

The equation simplifies to the ratio of *RL*/*ABL* after the *MBL*s cancel out. Assuming the *RL* ozone was transported to the morning spiral location from an upwind regional source and subsequently transported to the afternoon spiral location where it mixed with the locally produced ozone to give the *ABL* ozone column content, the equation should provide the relative contribution of regionally transported ozone to the afternoon boundary layer column content. The accuracy of this method depends upon the Lagrangian nature of the morning and afternoon profiles from each cluster. Because flight plans were designed in a Lagrangian manner, where morning flights were upwind of afternoon flights (Figure 1), the estimate should be accurate. When the greatest cluster trajectory density lay over the Ohio River Valley (~59% of the profiles), transport accounted for 69-82% of the afternoon boundary layer ozone. When winds were weak (~27% of the profiles), transport only accounted for 58% of the afternoon boundary layer ozone.

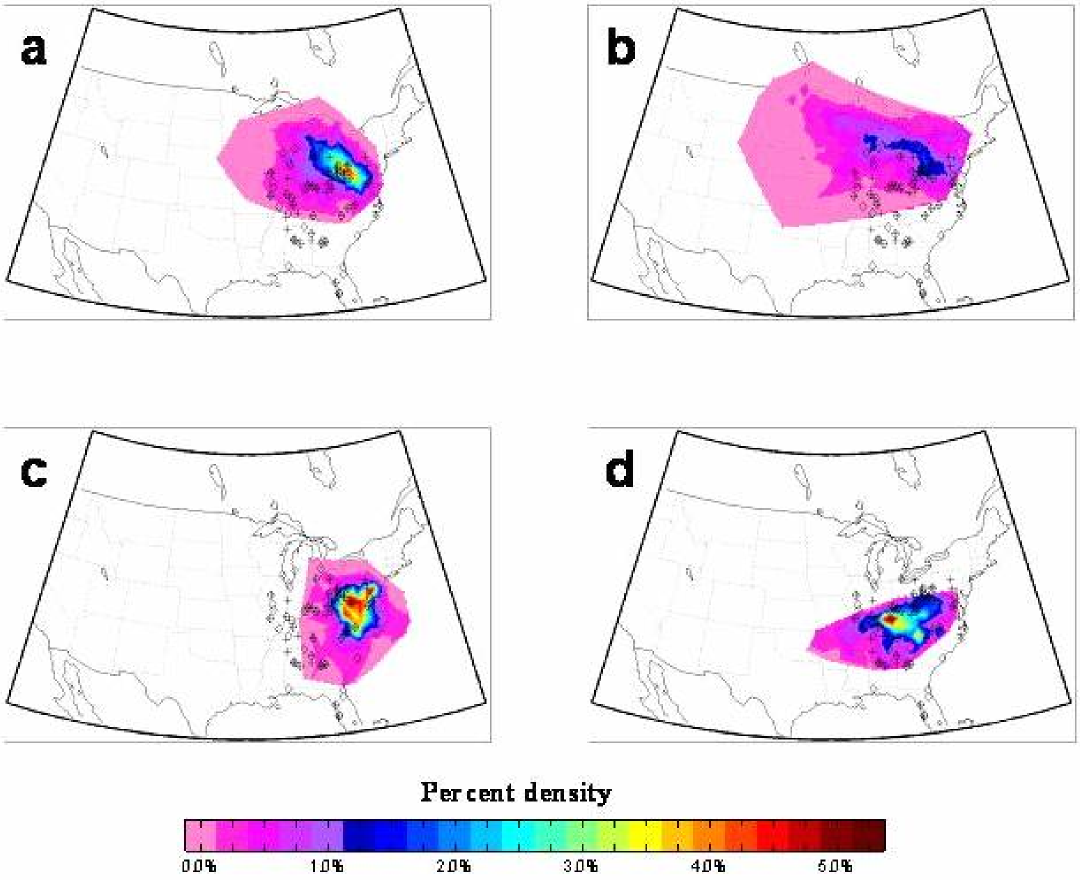

Figure 2. Trajectory density maps for back trajectory clusters with a) Moderate Northwesterly flow (Cluster 1), b) Fast Northwesterly flow (Cluster 2), c) Slow Southerly flow (Cluster 3), and d) Moderate Southwesterly flow (Cluster 4). The plots were generated using a linear interpolation method between the trajectory end points. They indicate the relative density (%) of air parcels over the total area described by the spaghetti plots. Also pictured are the locations of the top 0.3% emitters annually of NO_x (diamonds) and SO_2 (crosses) in the eastern United States.

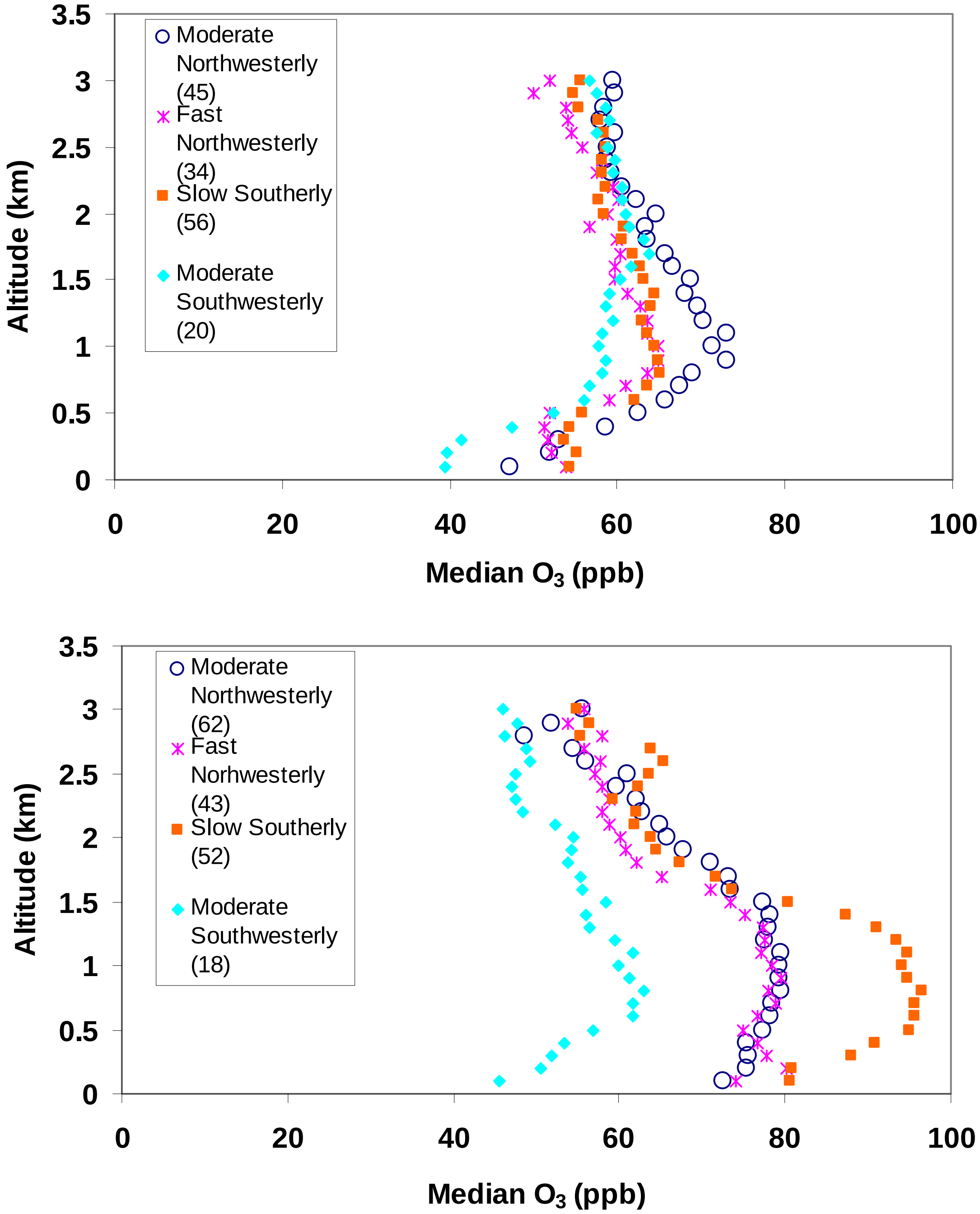

Figure 3. The median morning (a) and afternoon (b) profiles for back trajectory clusters with Moderate Northwesterly flow (Cluster 1), Fast Northwesterly flow (Cluster 2), Slow Southerly flow (Cluster 3), and Moderate Southwesterly flow (Cluster 4).

Results from Ground level Ozone Measurements

Figure 4 shows the hourly ozone measurements made at the Fort Meade air monitoring site for the first 9 days of August 2002, a month when there were many ozone episodes which led to 8-hour ozone exceedances. The hourly ozone data for August 2nd and August 8th show different slopes between 10:00 EST and 15:00 EST. This is shown more clearly in Figure 5 where the two days are plotted on top of one another.

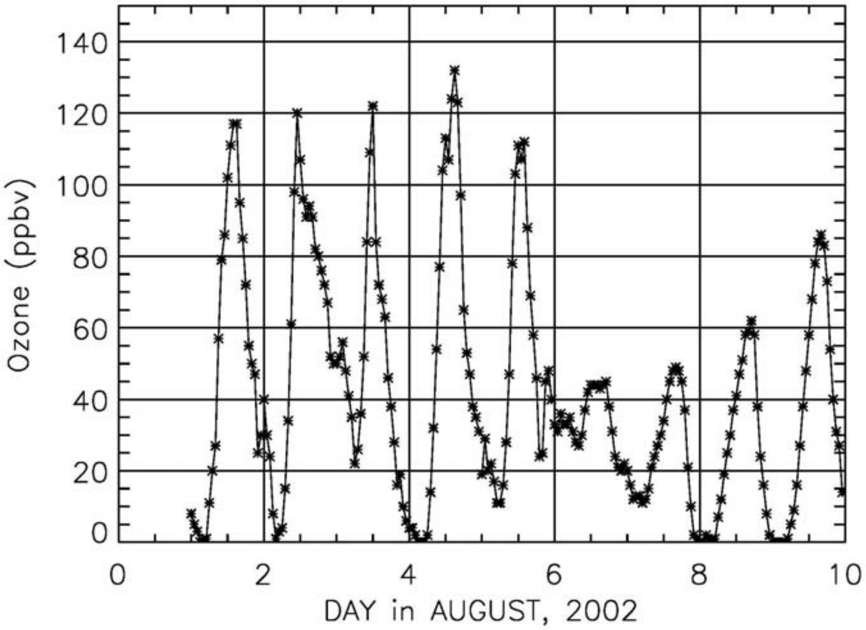

Figure 4. Ground based ozone measurements made at the Fort Meade station for August 1 to August 9, 2002.

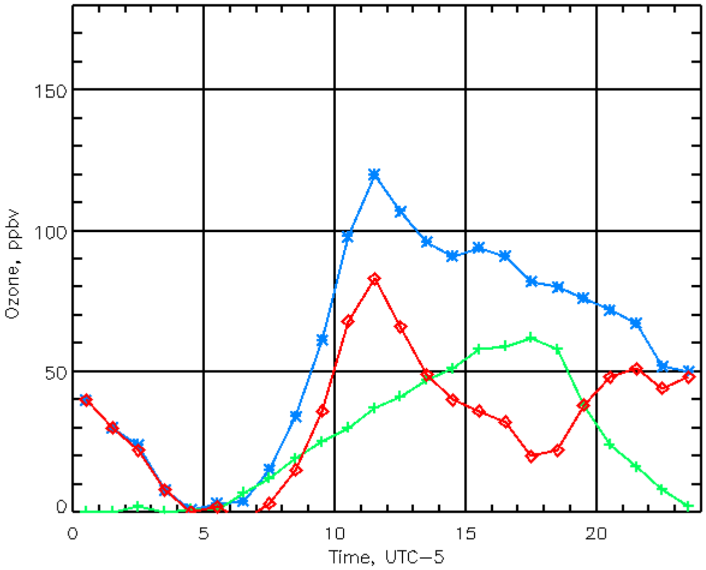

Figure 5. Ozone data for August 2nd (blue asterisks) and August 8th (green crosses) as a function of time (EST, UTC_5). The red diamonds are the difference between the two ozone curves

The data for August 8 is typical for local photochemical production of ozone. Emissions occur early in the morning, and as the solar radiation and ground temperature increase, the ozone climbs to a maximum at about 15:00 EST. The surface temperature maximum occurs simultaneously. The red curve on Figure 5 is the difference between the data for August 2nd and August 8th. The most striking feature of the difference plot is the peak of ozone centered at about 11:00 EST. Figure 6 is the same as Figure 5 except that the ozone data for August 8th ($O_3(8)$) has been multiplied by a normalization factor of 1.3 (the ratio of the measured ozone at 15:00 EST on August 2nd ($O_3(2,1500)$)and August 8th ($O_3(8,1500)$, that is:

$$O_{3rev}(8) = O_3(8) * O_3(2,1500)//O_3(8,1500)$$

This factor accounts for the fact that the ground temperature on August 8th is lower than the ground temperature on August 2nd. The difference curve (red) now shows a more pronounced peak. The modified August 8 data in Figure 6 can be interpreted as the local photochemical curve for August 2nd. The sudden increase in the rate of production of ozone starting at about 8:00 EST on August 2 is about a factor of four larger than the rate due solely to photochemistry. This remarkable increase is the product of ozone and its precursors being brought down from aloft as the nocturnal inversion slowly erodes and eventually breaks down at about 10:00 EST (Vukovich and Scarborough (2005)). The timing of the 11 EST peak in Figure 6 and the 10 EST peak found by Vukovich is remarkably similar given the limited data employed for the single case study presented here.

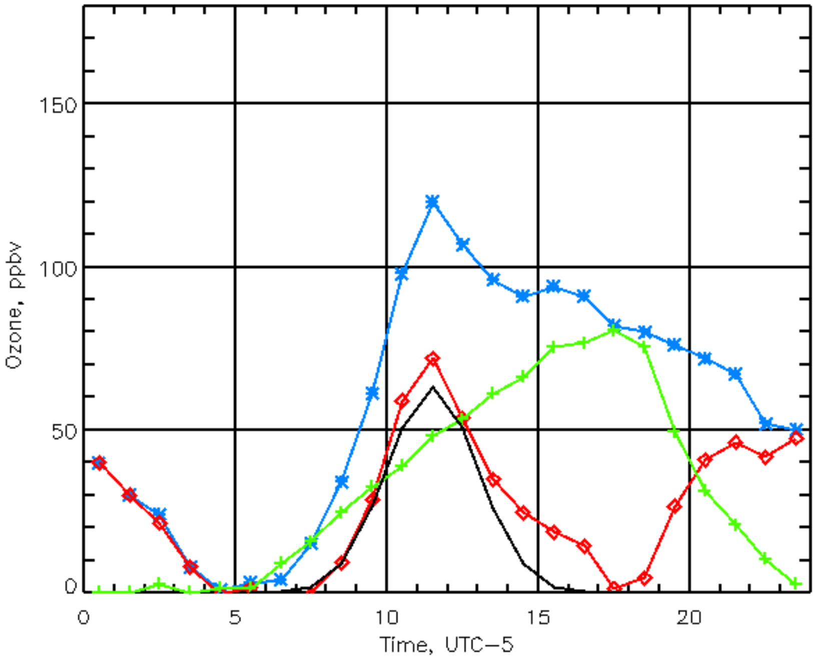

Figure 6. Ozone data for August 2nd (blue asterisks) and August 8th (green crosses) normalized to the August 2nd data at 17:00 EST (UTC-5). The red diamonds are the difference between these two curves. The solid black curve is a representative Gaussian curve**.**

Another inference of the difference between the ozone data on August 2nd and August 8th is that there is no transported ozone evident on August 8th. The reason for this can be seen if one compares the back trajectories of air parcels for these two days that have reached Baltimore at 10:00 EST. These are shown in Figure 7. On August 2nd the upper level parcels of air come from Eastern Pennsylvania. The air which reaches Baltimore at the 500 meter level has been lifted from an altitude of 200m 15 hours earlier, and one can expect that lower altitudes will have come from close to the ground. This transported air will be polluted. However on August 8th the air parcels have arrived from Canada accompanied by strong subsidence. These air parcels will have picked up little pollution.

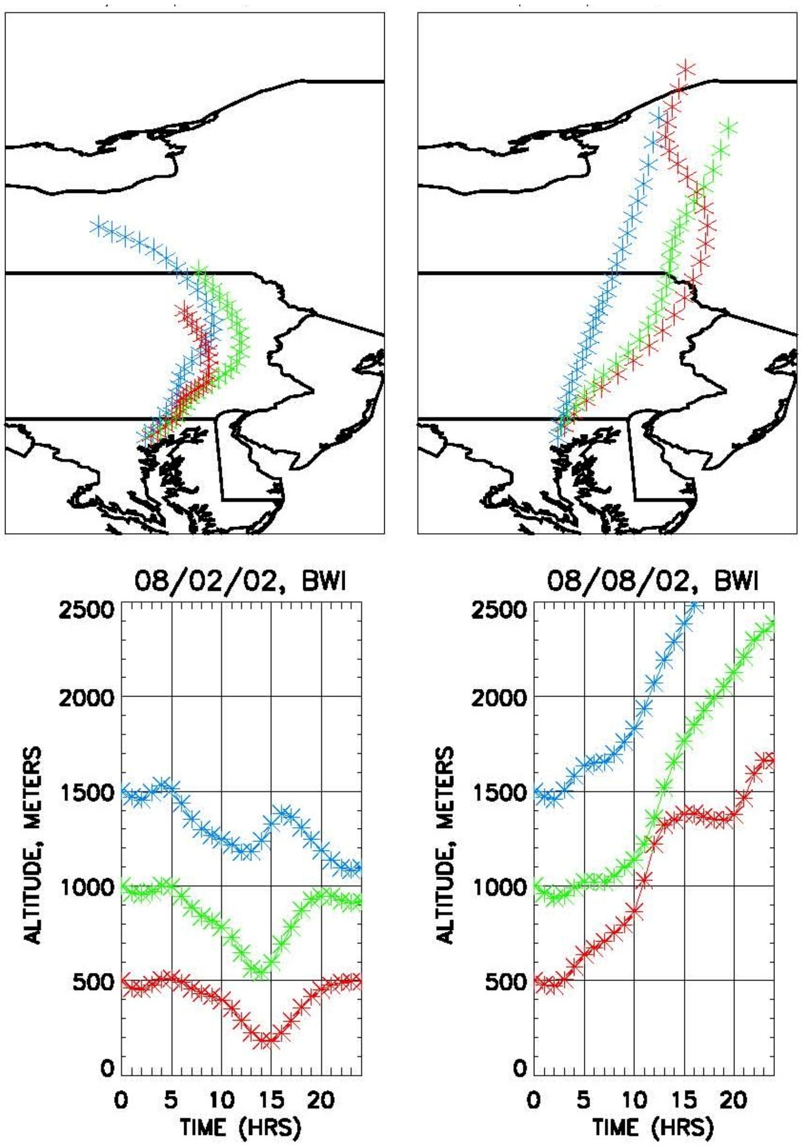

Figure 7. 24 hour back trajectories for August 2nd and August 8th ending at 10:00 EST. Red asterisks are for back-trajectories that begin at Baltimore at an altitude of 500 meters AGL. The green asterisks are for 1000 meters AGL, and the blue asterisks are for 1500 meters AGL.

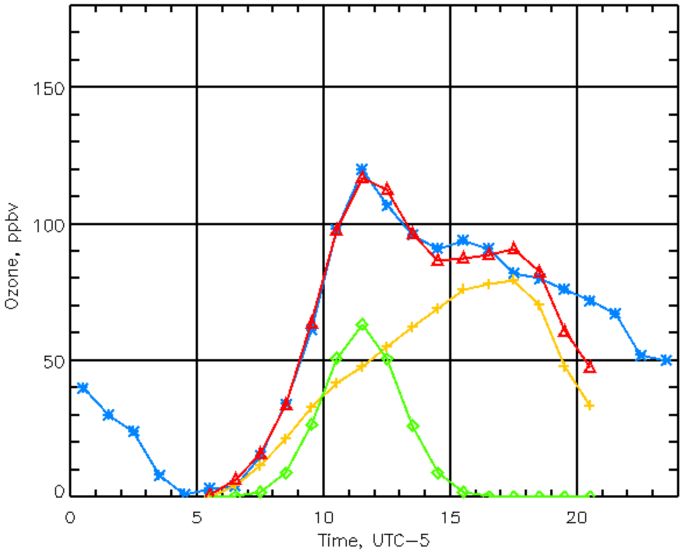

Figure 8. Calculated results for the transported and local photochemistry for August 2nd, 2002 with time in EST (UTC-5). The blue asterisks are the measured ozone data. The orange crosses are the best fit to the local photochemistry. The green diamonds are the transported ozone, and the red triangles are the best fit to the overall data

If one assumes that the effect of the transported ozone shown in Figure 6 can be approximated by a Gaussian curve, then one can fit the overall ozone data between 6:00 EST to 18:00 EST by a combination of a Gaussian curve and the ozone data for August 8th multiplied by a constant. The Gaussian curve is a function of three constants, the amplitude, the width, and the time of the peak. The overall data are fit to these four constants using a non-linear least squares procedure (Press et al., 1986). The result of such a fit for August 2nd is shown in Figure 8. The green curve represents the effect of the transported ozone, the blue curve is the local photochemical curve, and the red curve is the sum of these two. The best fit for six days in August 2002 (2, 4, 11, 12, 13, and 19) when Maryland exceeded the 8-hour ozone standard are shown in Figure 9. The back trajectories for these same days are given in Figure 10. They cover a wide range of wind directions.

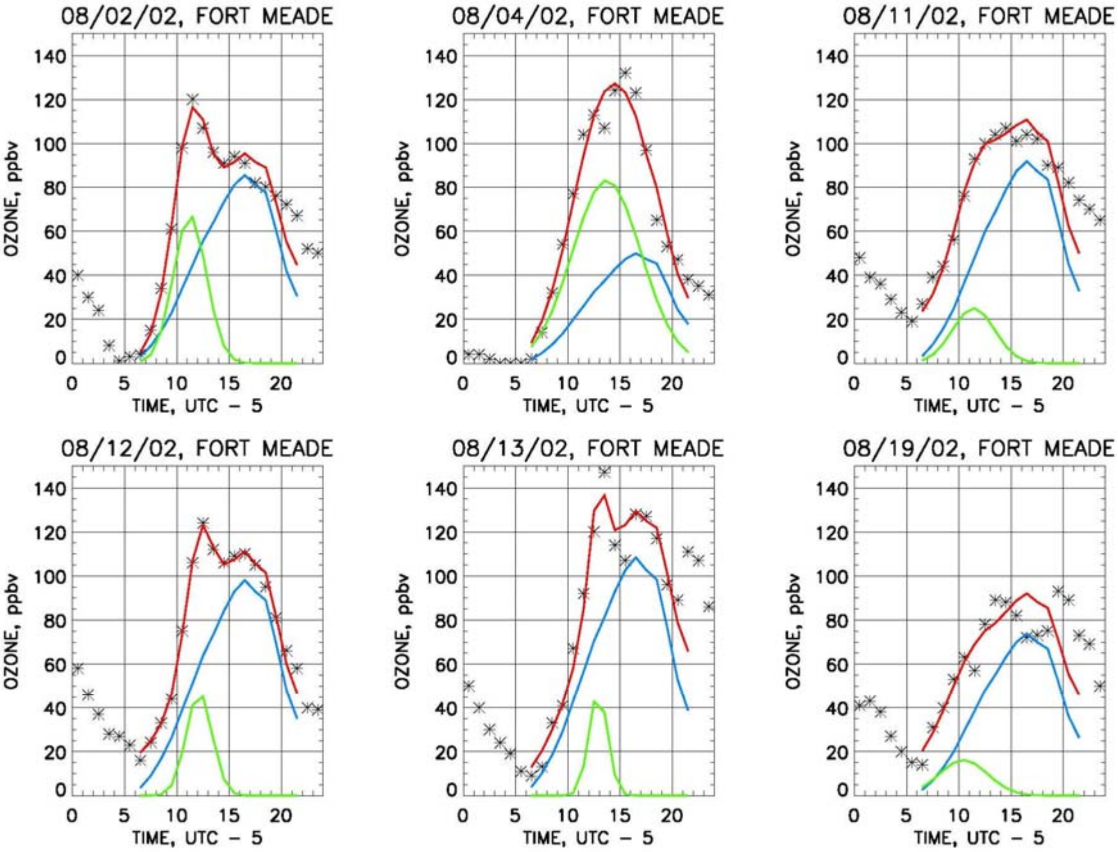

Figure 9. Best fit for the transported and local photochemical ozone for selected days (days that exceeded the 8 hour rule) in August 2002. The color scheme is the same as for Figure 8 and time is in EST (UTC-5).

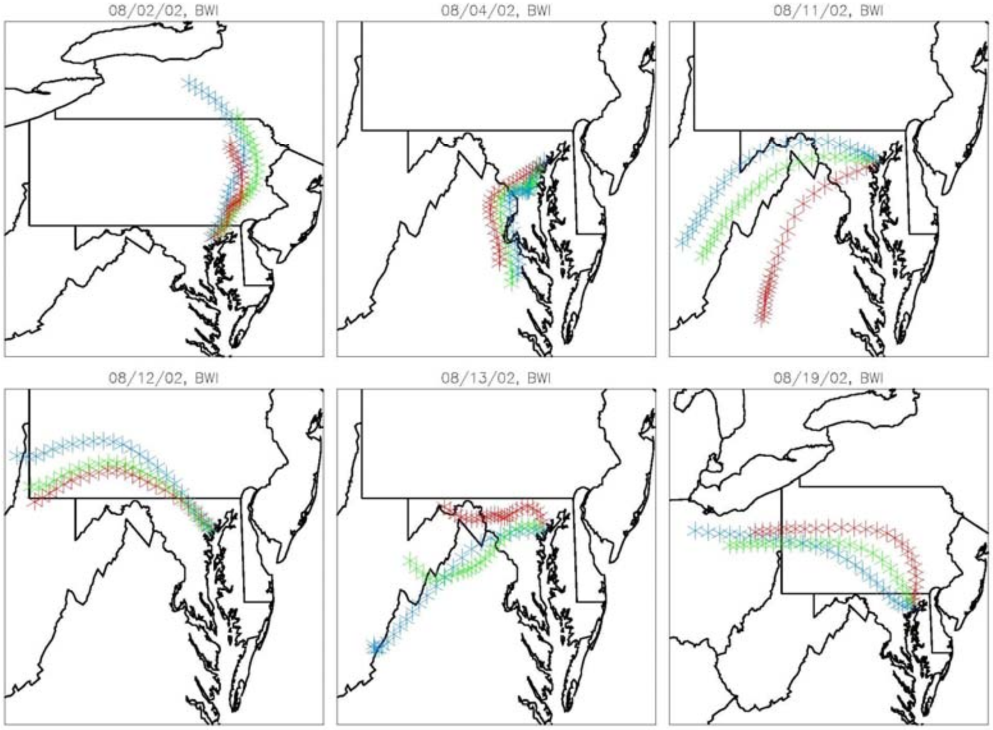

Figure 10. 24-hour back-trajectories for the days shown in Figure 9. Red asterisks are for back-trajectories that end at 10:00 EST at Baltimore at an altitude of 500 meters AGL. The green asterisks are for 1000 meters AGL, and the blue asterisks for 1500 meters AGL.

Conclusions

The evidence from both the University of Maryland aircraft and the Fort Meade ozone data clearly highlight the importance of transport to the overall air quality in the State of Maryland. However one point that comes out of the study is that the transport need not be fast, and that ozone introduced to the surface after the breakdown of the nocturnal inversion can either be transported or derived from the previous days locally produced ozone, dependent on nighttime residual layer wind speeds. The contribution of regional transport to afternoon boundary layer ozone has been quantified using ozone profile data obtained on aircraft flights. When the source regions lay over the Ohio River Valley (~59% of the profiles), transport accounted for 69-82% of the afternoon boundary layer ozone. When winds were weak (~27% of the profiles), transport only accounted for 58% of the afternoon boundary layer ozone. The study of the relative contribution of transported and local photochemistry to the surface ozone data for six exceedence days in August, 2002, suggests that if local photochemistry were the only source of ozone, none of the 6 days examined would have exceeded the 8-hour ozone standard. The effect of the transported ozone is to add ozone early in the day and hence to expand the time interval over which the ozone levels may exceed 85 ppbv. Clearly, if the transported portion of the daily ozone content were removed from Maryland, all monitors within the state would be well below the 8-hour ozone NAAQS.

Future Work

The analysis of the station ozone data would have benefited from ozone data taken at shorter intervals than one hour. It is recommended that data be archived at every 5 minutes for this purpose. In this study only a few days were analyzed. It is clear that a more extensive analysis needs to be implemented, and that other species be considered for detailed monitoring.

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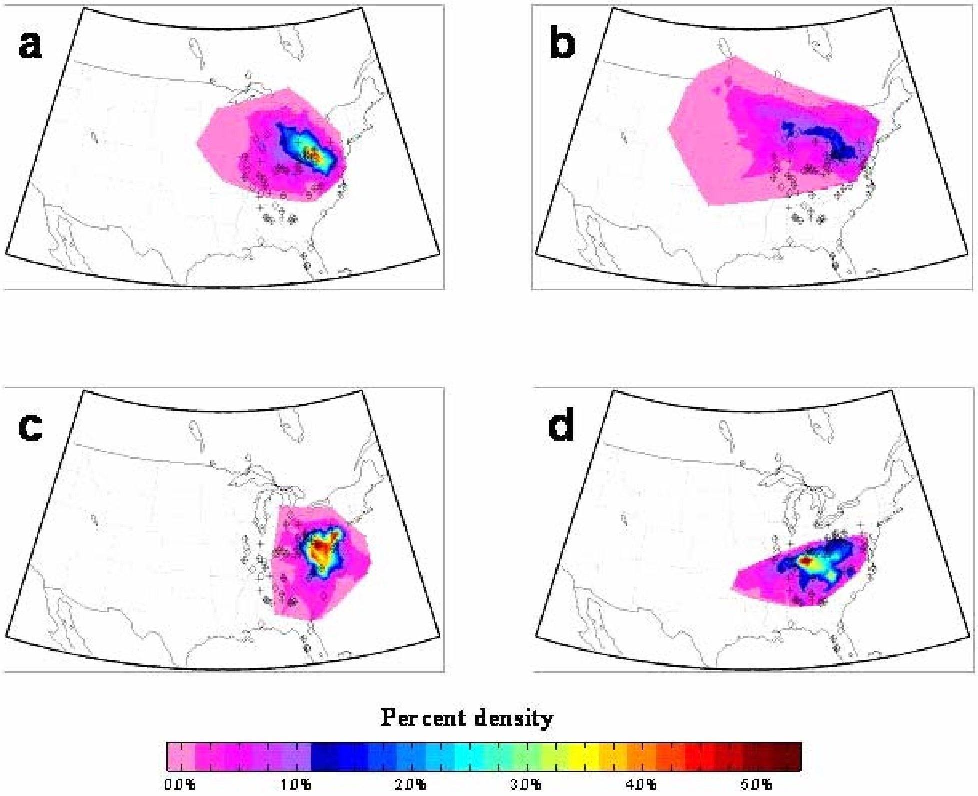

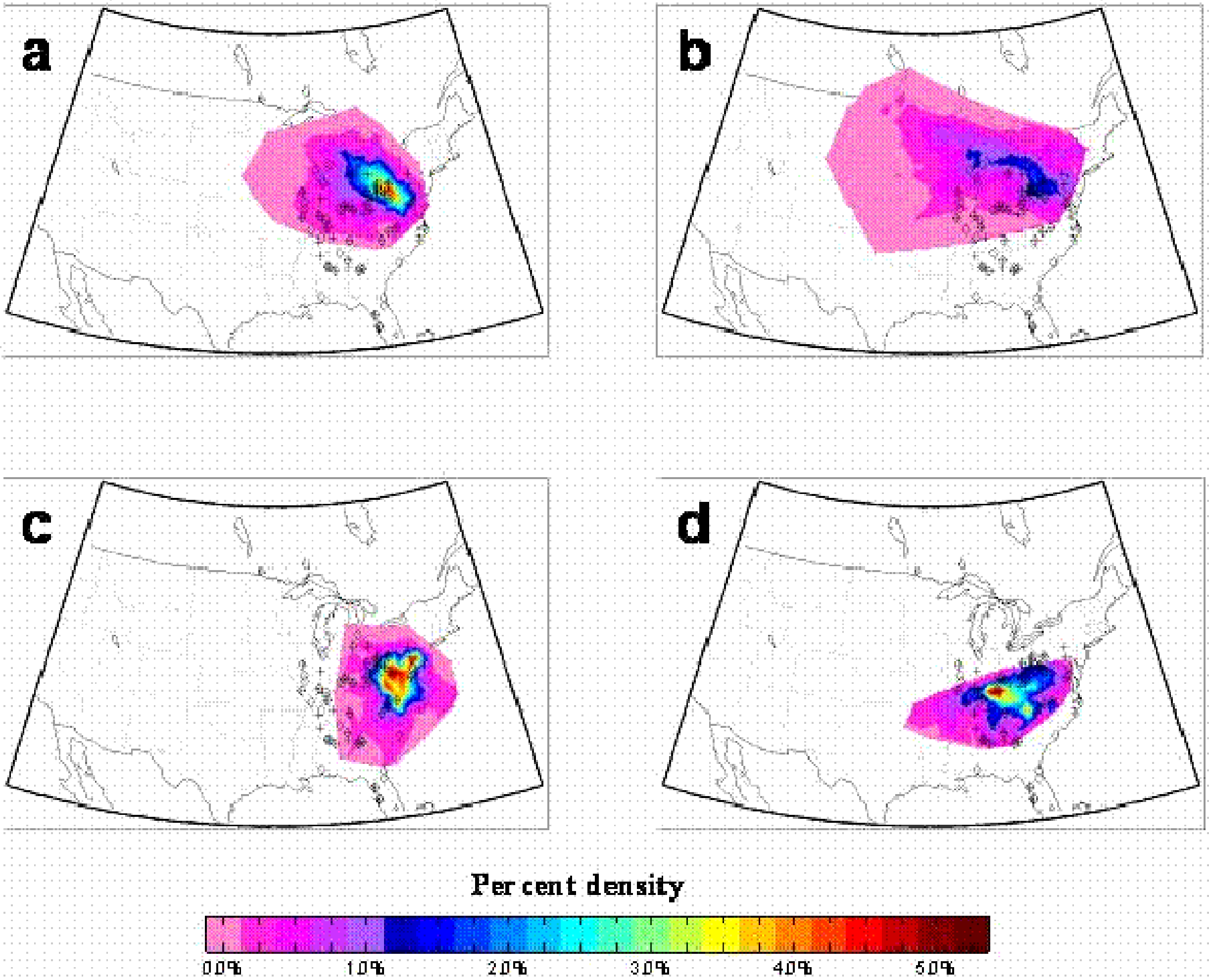
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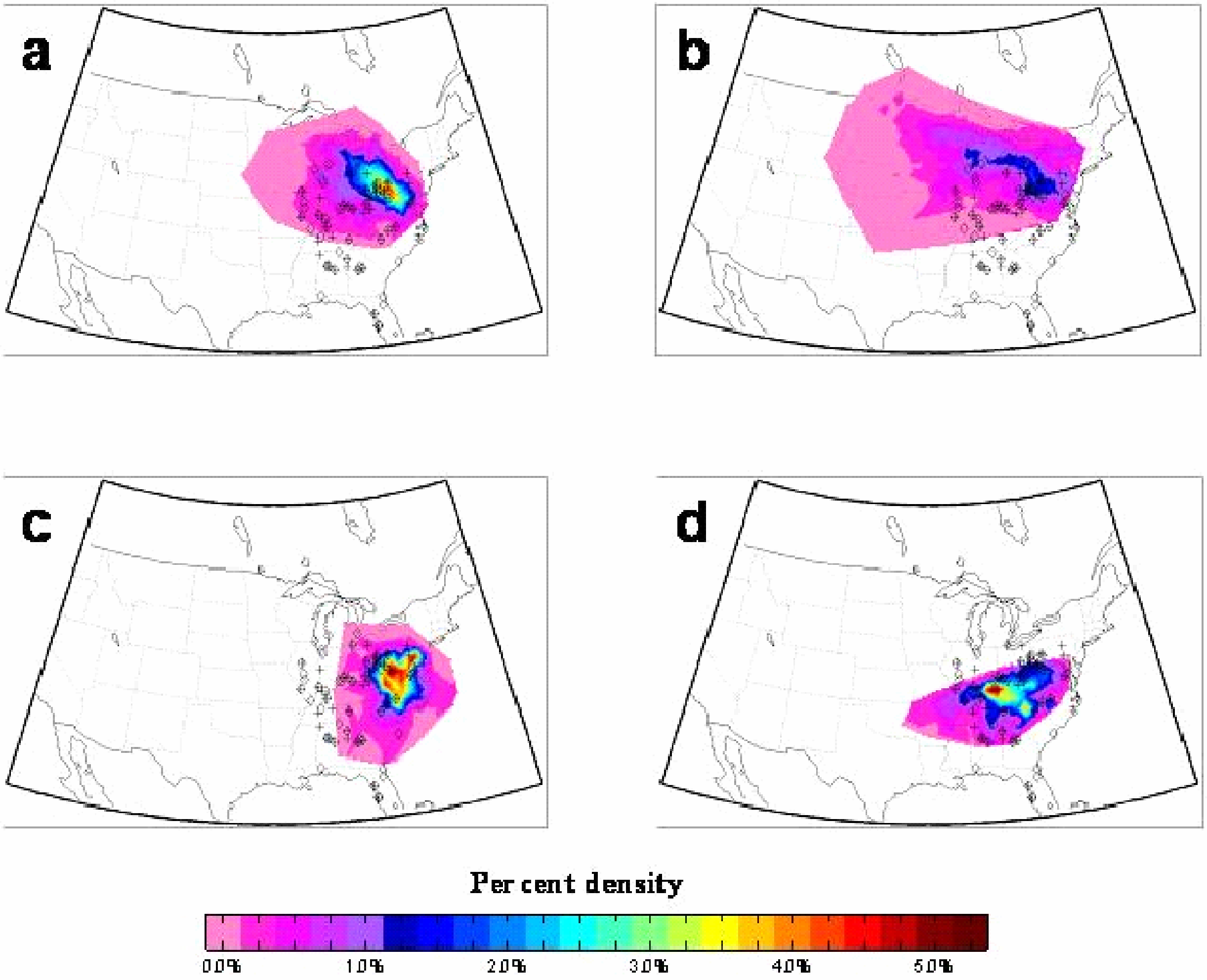
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