Ozone Levels at Mammoth Cave National Park: An Investigation into the Potential Source Areas Affecting High Ozone Levels at the Park

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INTRODUCTION

Under the National Park Service (NPS) Organic Act and the federal Clean Air Act, the NPS has the responsibility to protect the natural resources contained within NPS lands from the adverse effects of air pollution. Of the numerous air pollutants that are emitted directly from industrial and mobile sources, or are formed as a result of these emissions, ozone has been found to be the most prevalent, and, perhaps, one of the most injurious to vegetation including crops. The United States Environmental Protection Agency (USEPA) acknowledges that high ozone levels not only affect human populations but may also result in forest and ecosystem damage. According to the USEPA, ozone is responsible for annual agricultural crop yield losses in the billions of dollars in the U.S. and causes noticeable foliar damage in many crops and tree species.[1] In order to protect human health and welfare from the adverse effects of ozone, the USEPA has established primary and secondary national ambient air quality standards, respectively, for this pollutant. Currently the primary and secondary standards for ozone are set at 0.12 parts per million (ppm), or equivalently at 120 parts per billion (ppb). There is a growing debate, however, whether the level and/or form of the present standard is sufficient to prevent injury to vegetation and crops. Thus, the NPS has a responsibility to assess the levels of air pollutants within park boundaries and survey park resources for damage or injury due to these pollutants regardless of the level or existence of ambient standards.

Ozone exposure, even at low chronic levels, has been found to affect plant processes.[2] For example, ozone has been shown to inhibit photosynthesis, reduce growth, increase mortality (particularly in seedlings and young trees), and reduce the reproductive potential of some species.[3,4,5,6] Numerous visible symptoms of ozone exposure, which may not necessarily precede the above effects on plant processes, have also been documented in the scientific literature. These have been classified into six main categories[7]:

- Chlorosis or yellowing
- Tip burn
- Stippling
- Flecking
- Upper surface bleaching
- Necrosis or browning

McLaughlin et al.[8] have documented a common pattern to the decline in vigor of trees sensitive to ozone stress. Ozone exposure can lead to: (1) premature aging and loss of older leaves at the end of the growing season; (2) reduced storage capacity in the fall and in the spring to support new needle growth; (3) shorter leaves resulting in reduced photosynthesis; and, (4) reduced ability to repair chronically-stressed tissues.

It has been hypothesized that the above effects on plant processes can result in several ecosystem effects such as:[9]

- Elimination of sensitive species and reduction in species diversity;
- Selective removal of larger overstory plants and the favoring of smaller plants;
- Reduction of the standing crop of organic matter leading to the reduction in the nutrient levels within the living system;
- Increased activity of pests and some diseases leading to increases in mortality of some species and/or age classes.

Regardless of the extent and magnitude to which these effects from air pollutants may be occurring in national parks, air pollution injury to vegetation found in parks runs contrary to NPS fundamental resource protection and preservation mandates. At Mammoth Cave National Park (NP) previous studies have documented that injury to vegetation due to ozone is already occurring. Surveys of park vegetation conducted in 1985 and 1986 found dark stippling attributable to ozone on most tree species[10]. Injury was most common on white ash, green ash, redbud, sycamore, tulip poplar, wild grape, and milkweed, with less injury found in 1986 than in 1985. Thus, it is of interest to the NPS to document ambient levels of ozone within national parks and to examine the potential sources which may be contributing to any high levels observed, particularly if ozone effects have been noted.

This paper examines ozone levels measured at Mammoth Cave NP during the period 1985 through 1990, compares these levels with those measured at nearby urban areas and other national parks in the eastern U.S., and, finally, investigates the potential source areas affecting ozone levels at the park.

METHODS

Nearby urban centers currently not attaining the National Ambient Air Quality Standards for ozone (i.e., non-attainment areas) have a potential to influence ozone levels measured in national parks. These urban centers typically emit significant quantities of ozone precursor emissions, which when transported by winds, can result in the production of elevated ozone levels in national parks often located at large distances from these urban centers. As can be seen from Figure 1, which identifies all ozone non-attainment areas in the U.S. as of 1988, Mammoth Cave NP is located near, and surrounded by, several of these areas, namely: Knoxville and Nashville, TN; Lexington, Louisville, Owensboro, and Paducah, KY; and, Cincinnati and Dayton, OH. In order to explore the influence of these non-attainment areas on ozone levels

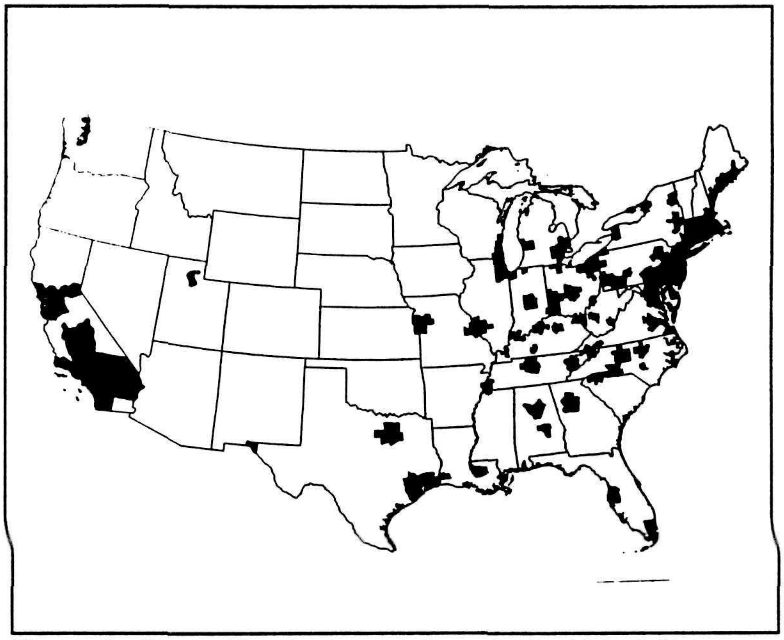


Figure 1. Ozone Non-Attainment Areas in the United States

measured at Mammoth Cave NP, the correlations between ozone levels measured at Mammoth Cave NP and at these urban centers were calculated. Using surface meteorological data collected at Mammoth Cave NP, days were stratified on the basis of wind persistence from these areas and the correlations were recomputed and sector means calculated. Finally, a back-trajectory modeling technique was also employed to identify further the potential source areas of high and low ozone levels measured at the park.

Correlation Analysis

One way to examine the influence of nearby urban centers on ozone levels in parks is to employ the use of linear correlation techniques and the stratification of days by wind direction. Although these techniques alone may be insufficient to establish definitive cause-effect relationships, they may uncover interesting relationships among the variables being investigated. For this paper, we focus on the correlation between the ozone daily maximum at Mammoth Cave NP and the daily maxima at each of the nearby urban areas listed previously. Additionally, the daily maximum is compared to the daily maxima measured two and three days prior in these cities in an attempt to ascertain the likely duration of the ozone transport time into the Mammoth Cave area. Linear correlation coefficients were computed in two ways. The first analysis considered all days regardless of wind direction. In this case all daily maxima measured during the period 1987-1990 at each location were considered and correlation coefficients computed for each year separately. The second analysis was wind direction dependent and considered the direction from which the wind was blowing as indicated by the surface winds measured at the Mammoth Cave station. This analysis considered only 1989 and 1990 data since these were the only years for which meteorological data were available. Forty-five degree sectors were defined for each urban area with the azimuth from the park to the urban area serving as the center for each sector. Because Cincinnati, Dayton, Lexington, and Louisville are all NE of the park, all of these cities were grouped into one 80° sector ("Ohio Valley"). For each day the wind was said to persist from a given sector if the resultant direction for more than 6 hours during the hours of 0600 to 1700 was contained within the sector. The sectors defined were as follows:

Ohio Valley	0 - 80°
Knoxville	119 - 164°
Nashville	183 - 228°
Paducah	245 - 290°
Owensboro	290 - 335°

The mean of the daily maxima measured at Mammoth Cave was calculated for each sector when the wind persisted from these sectors. In addition two other sectors were considered. An "Other" sector was defined as containing those days when the wind persisted (as defined above) from the sectors other than those listed above. A "Non-Persistent" sector represented those days when the wind did not persist from any of the previously defined sectors or the "Other" sector.

Back-Trajectory Analysis

Atmospheric back-trajectories were computed using the ARL-ATAD model.[11] This is a Lagrangian parcel model which uses a single transport layer which can be of either fixed or variable depth. Upper level winds and temperatures are interpolated both in time and space, and are obtained from all available radiosonde stations. The model does not consider complex terrain, as in mountainous regions; however, in the case of a variable-depth transport layer, the bottom of the layer is always a minimum of 300 meters above the surrounding surface at each radiosonde station. The top of a variable-depth layer is determined by the model, as it looks for some critical inversion in the radiosonde data. In the case of a fixed-depth transport layer, the bottom and top of the layer are specified. For this study, the two model runs were made using two different transport layers. One was a "low-level" transport layer and the other was a "mid-level" transport layer. The low-level layer is always based at the surface and the top is always 300 meters above the surface. The mid-level layer is a variable-depth layer.

Trajectories begin at the park at six-hour intervals, and air parcel positions, or endpoints, are computed at three-hour intervals, backwards in time and for up to five days in duration. Trajectory endpoint positions are calculated at one-hour intervals by interpolating linearly between two three-hour positions, so for a full five-day trajectory, 120 endpoint positions are known. Trajectories are truncated before five days if the air parcel passes into a region void of data, such as the ocean, or where radiosonde data are missing.

Trajectory analysis includes the calculation of a high source contribution function (HSCF) and a high conditional probability function (HCPF) by considering days associated with high ozone concentrations above a pre-determined maximum. The analysis can be extended to also include days on which ozone concentrations at a location were below a pre-determined minimum in which case a low source contribution function (LSCF) and a low conditional probability function (LCPF) can also be computed. The HSCF analysis method is well-documented[12-14] and will be discussed only in brief here. HSCF analysis begins by partitioning the area around a park into 1° latitude by 1° longitude grid squares. The limits of the grid used for Mammoth Cave were: 25 to 50° N. latitude and 70 to 115° W. longitude (the Onyx Meadow monitoring station at Mammoth Cave is at 37.22° N, 86.07° W.). Then, the number of back-trajectory endpoints falling into each grid square, when the trajectory terminated at the park and was associated with a high ozone concentration, is counted. A high ozone concentration for this analysis is defined as one standard deviation above the geometric mean for the period of analysis. The number of endpoints in each grid square is then proportional to the total time that all air, arriving at the park when ozone concentrations were high, passed over, or resided, in that grid square. This is termed the high concentration residence time.

Because all back-trajectories begin at the park, the highest residence time values are centered around the park since all of the trajectories must pass through the grid square containing the park. While high concentration residence time is useful in indicating atmospheric pathways that are dominant when ozone concentrations at the park are high, source regions can be better defined if this central tendency is removed. Removal of this central tendency is accomplished by assuming that an air parcel can arrive at the park from any direction with equal probability. While this assumption is not realistic, it is still quite useful in illustrating frequently passed over areas, and therefore the dominant atmospheric transport pathways associated with high ozone concentrations, as well as the relative contribution of one source area as compared with another. The probability of an air parcel passing through a given grid square decreases with and is proportional to the inverse of the distance of the grid square from the park. Therefore, the high concentration residence time values for each grid square are multiplied by that square's distance from the park, and the new field with central tendency removed is termed the HSCF.

HCPF analysis is accomplished by dividing the number of endpoints in each grid square when the ozone concentrations at the park were high by the total number of endpoints having fallen in that grid square. This resultant field is a probability field for the entire analysis period, providing the percentage of total time that air, having passed through a specific grid square, was associated with a high ozone concentration at the park. It should be noted here that a high potential of a specific region for contribution to high ozone concentrations at a park is only realized if a sufficiently high number of air masses actually pass over this region. Therefore, a region having a high probability of being associated with high ozone concentrations at the park may be less of an influence than a region with a lower probability, if transport from the lower probability region occurs more often.

Merging of Ozone Measurements and Back-Trajectory Endpoints

Since back-trajectories begin at the parks at six-hour intervals, the hourly ozone concentrations were averaged over six-hour periods. The six-hour ozone average is then matched to the trajectory beginning at the park at the start of the six-hour period. Thus, a trajectory beginning at 00 GMT is matched with the six-hour ozone average for the period 00-05 GMT. The six-hour averages of ozone concentrations are the statistics used for determining the overall mean and minimum high ozone concentration for the period in question.

DATA

Ozone Measurements

The National Park Service operates an extensive air pollution monitoring network throughout the U.S. which includes ozone monitoring at 41 stations located in 33 national parks, as shown on Figure 1. Mammoth Cave NP has been a part of this network since late 1984 when the State of Kentucky's Air Pollution Control Division deployed the Onyx Meadow station under a cooperative agreement with the NPS. Since 1988, the station has been operated by NPS personnel with the assistance of several monitoring support contractors. The station at Mammoth Cave uses a Dasibi ultra-violet (UV) photometric analyzer to record hourly ozone concentrations which are stored on site using a SumX Corporation Model SX-444 data logger. The NPS polls the Mammoth Cave station on a weekly basis and the data are entered into a centralized database maintained in Lakewood, CO, for later processing and validation.

The data collected at NPS stations meet the USEPA's monitoring regulations applicable to State and local monitoring stations (40 CFR 58). Data obtained from NPS sites is stored in the NPS Environmental Database Management System and is later archived in the USEPA's Aerometric Information Retrieval System (AIRS).

Ozone levels measured at nearby urban centers were obtained from USEPA's AIRS data base. Where possible, data collected at sites designated as National Air Monitoring Stations (NAMS) were employed in our analysis. The AIRS identification number and the location of each of the sites used in this analysis are given in Table 1.

Table 1. Urban Area and NPS Monitoring Sites

Location	AIRS Identification No.
Lexington, Fayette Co., KY	*21-067-0001*
Lexington, Fayette Co., KY	*21-067-0012*
Louisville, Jefferson Co., KY	*21-111-1021*
Louisville, Jefferson Co., KY	*21-111-0027*
Mammoth Cave NP, Edmonson Co., KY	*21-061-0500*
Owensboro, Daviess Co., KY	*21-059-0005*
Paducah, McCracken Co., KY	*21-145-1024*
Cincinnati, Hamilton Co., OH	*39-061-0006*
Dayton, Montgomery Co., OH	*39-113-0019*
Knoxville, Knox Co., TN	*47-093-0021*
Knoxville, Knox Co., TN	*47-093-1020*
Nashville, Davidson Co., TN	*47-037-0011*

Meteorological data used in our analysis were obtained from two sources. Since 1988, surface meteorological data from a 10-meter tower have been collected at the Onyx Meadow site in Mammoth

Cave NP. These data were used for the correlation analysis performed. Upper air meteorological data used for the back-trajectory model were obtained from the National Climatic Data Center, Asheville, NC.

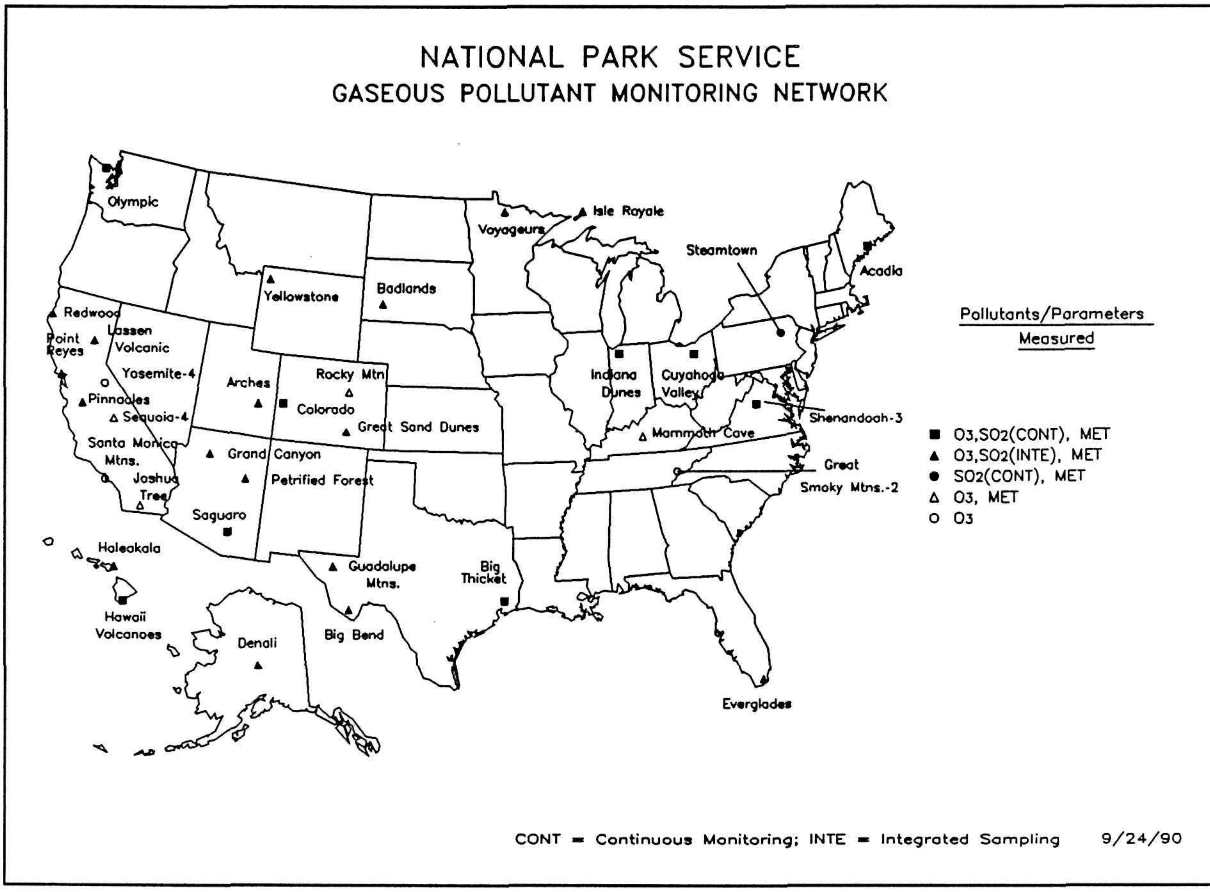


Figure 2.

RESULTS AND DISCUSSION

Mammoth Cave NP Ozone Levels

Table 2 summarizes the ozone levels measured at each of the locations listed in Table 1. From this data summary we note that the annual maximum hourly ozone concentration measured at the park is generally lower than at any of the surrounding cities. This can be seen graphically in Figure 3, which plots the annual maximum hourly concentration measured at each of these locations for the period 1987-1990. Figure 3 also shows that most of these locations recorded their highest levels during 1988 which had an exceptionally hot and dry summer. The pattern of annual maxima at the park during the period 1987-1990 closely resembles (and is almost identical) to the pattern of annual maxima recorded at Nashville, Owensboro, and Paducah, suggesting that ozone levels at the park may be more closely associated with those at these locations. From the data presented in Table 2 several observations can be made. We note that in 1989 and 1990, almost all sites in the region did not exceed the national ambient standard for ozone, and in general, there has been an overall decrease in ozone levels since 1988. Over the four-year period, cumulative exposures >= 60 ppb can vary by as much as a factor of ten at a given site, as well as among sites within a given year, although variation by a factor of 2 to 4 is more common. We note further that levels in 1987 and 1988 were significantly higher than the two-year period 1989-1990.

Table 2. Ozone Summary Statistics (April-October) for Mammoth Cave NP and Nearby Urban Centers[1]

Location	Annual Maximum	No. Days >NAAQS[2]	Exposure[3] >=60ppb (ppb-hr)	Exposure[3] >=80ppb (ppb-hr)	7-h Mean (ppb)	12-h Mean (ppb)
Lexington (21-067-0001)						
1987	139	1	13786	2070	52	49
1988	117	0	13622	2738	52	48
1989	118	0	9922	2059	50	46
1990	118	0	3994	352	43	40
Louisville (21-111-1021)						
1987	125	1	9509	1458	46	40
1988	158	3	12244	3384	46	41
1989	119	0	4426	850	32	35
1990	106	0	3166	284	38	33
Mammoth Cave NP						
1987	108	0	11017	1416	**56**	**50**
1988	140	**5**	13710	3703	**56**	**50**
1989	95	0	6348	443	50	45
1990	109	0	6269	572	50	46
Owensboro						
1987	132	1	13177	2856	53	49
1988	158	4	16182	5289	55	**50**
1989	107	0	5898	568	49	44
1990	114	0	6304	929	45	41
Paducah						
1987	118	0	9585	1522	51	45
1988	139	1	9458	1683	52	46
1989	96	0	3386	167	47	41
1990	102	0	5119	465	46	41
Cincinnati						
1987	**174**	2	12889	3449	48	43
1988	146	**5**	**17226**	**6273**	49	45
1989	126	1	6482	1144	44	40
1990	132	1	6174	1330	41	38
Dayton						
1987	124	0	8355	1276	44	39
1988	129	1	12440	3675	47	43
1989	99	0	3006	267	39	35
1990	119	0	5340	1032	39	35
Knoxville (47-093-0021)						
1987	105	0	9109	957	47	45
1988	145	**5**	12691	3728	41	41
1989	95	0	1283	83	29	29
1990	135	1	11140	2891	42	40
Nashville						
1987	105	0	2232	152	36	32
1988	145	3	11514	3394	46	41
1989	100	0	1680	145	35	31
1990	110	0	4264	543	43	37

[1] Numbers in **bold** indicate maximum value for each statistic
[2] NAAQS= National Ambient Air Quality Standard
[3] Exposure adjusted to account for missing data

Where the daily maxima may serve well to assess attainment of the ambient standard, these concentrations alone are probably not the best indicators to relate ozone levels to vegetative injury. Lefohn and others[15] have suggested other indices that may be more relevant for relating ozone injury to crops and vegetation. These indices include the 7-hour (0900-1559h), the 12-hour (0700-1859h) arithmetic means averaged over the growing season (used to assess crop losses by the USEPA's National Crop Loss Assessment Network), and cumulative exposures above certain thresholds such as 60 and 80 ppb. The exposures given in Table 2 were calculated using the following formulae. Exposures above a specified threshold, t, are first determined using Equation 1 for each month (in this case April-October).

$$E_t=\sum_{i=1}^{N}(x_i-t),x_i\geq t \qquad (1)$$

where x_i is the hourly ozone concentration. The annual cumulative exposure is then adjusted by accounting for missing data using Equation 2. The adjusted annual cumulative exposure, $\hat{E}_t$, is defined as the sum of the adjusted monthly exposures as given by:

$$\hat{E}_t=\sum_{i=4}^{10}E_{t_i}\frac{N_i}{n_i} \qquad (2)$$

where:

$\hat{E}_t$ = Total adjusted annual exposure over a threshold, t,
E_{ti} = Observed exposure over a threshold, t, for month i,
N_i = Total number of hours for month i, and
n_i = Total number of hours measured for month i.

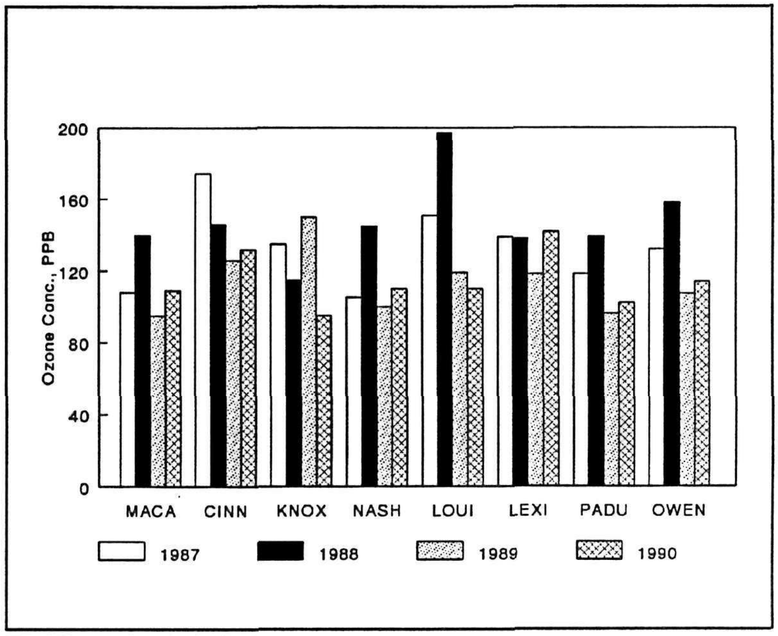


Figure 3. Annual Ozone Daily Maximum for Mammoth Cave NP (MACA) and Nearby Urban Centers, 1987-1990.

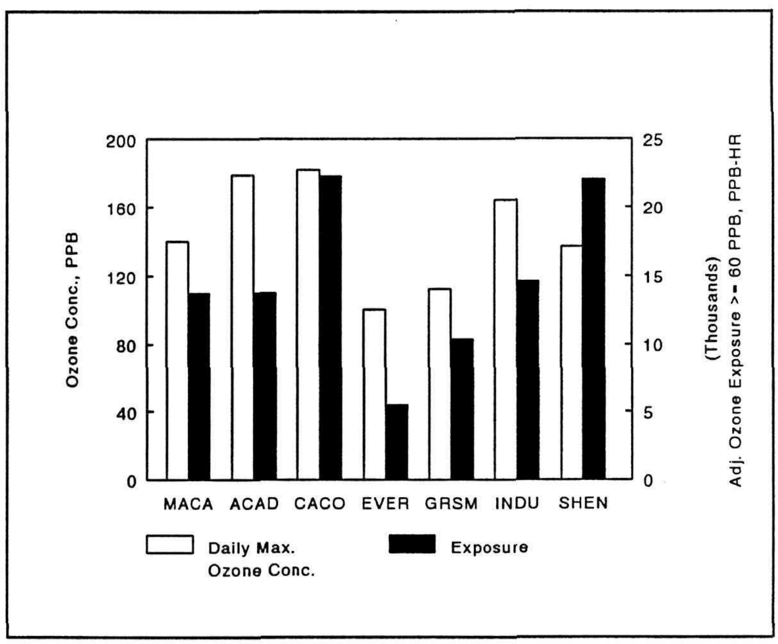


Figure 4. Annual Ozone Daily Maximum and Ozone Exposure >= 60 ppb at Mammoth Cave (MACA), Acadia (ACAD), Cape Cod (CACO), Everglades (EVER), Great Smoky Mts. (GRSM), Indiana Dunes (INDU) and Shenandoah (SHEN), 1988.

Referring to Table 2 again, one notes that the adjusted annual ozone exposure equal to or above the threshold level of 60 ppb measured at the park exceeds that measured at most urban areas. In contrast the adjusted annual exposure equal to or above 80 ppb is typically lower at Mammoth Cave. This indicates that although rather high levels tend to persist at the park, peak concentrations tend to be slightly lower than in most urban areas. However, exposure levels and 7-hour and 12-hour means at Mammoth Cave have been consistently higher than those measured in Louisville, Nashville, and Paducah. This may suggest that vegetation (as well as the general public) is more at risk to ozone effects at the park than in these urban centers (discounting, of course, the synergistic effects of other air pollutants). The 7-hour (0900-1559h) and 12-hour (0700-1859h) means averaged for the growing season (assumed to be April through October), likewise are higher at Mammoth Cave than at most of the surrounding urban centers. With respect to other NPS areas in the midwestern and eastern U. S., ozone levels at Mammoth Cave are intermediate. Figure 4 compares the ozone daily maxima and exposure levels (> =60 ppb) at Mammoth Cave with those at other NPS locations. As can be seen from this figure, levels at Mammoth Cave during 1988 were higher than at Great Smoky Mountains NP, but the cumulative exposure > = 60 ppb was substantailly less at Mammoth Cave than at Shenandoah NP.

High exposure levels are not uncommon in national parks and result from ozone photochemistry and transport of ozone and its precursors into rural areas. Ozone formation is dependent not only on the mix of precursor emissions (principally, nitrogen oxides and volatile organic compounds), but also on strong solar insolation and high ambient temperature. This gives rise to the characteristic diurnal pattern observed in urban areas, as well as in rural areas impacted by these areas. Ozone photochemistry also accounts for higher levels sometimes being observed at some distance downwind of an urban area. Figure 5 compares the diurnal ozone pattern observed at Mammoth Cave with those at three nearby cities, 2 urban (Louisville and Nashville) and 1 rural (Paducah). These curves were obtained by averaging all observations occurring at a given hour for the period April through October 1988. As illustrated in the figure, ozone concentrations typically peak in the early to mid afternoon hours as a result of high solar insolation and ambient temperature. Ozone is at its minimum, oftentimes near zero in urban areas, during the early morning hours as a result of additional ozone scavenging by nitrogen oxide emissions in the absence of photolysis at night. As can be seen from the figure, ozone concentrations at Mammoth Cave are, on average, higher than the three cities considered and there appears to be less ozone scavenging occurring at the park. Note also that higher levels at the park persist through the late evening hours.

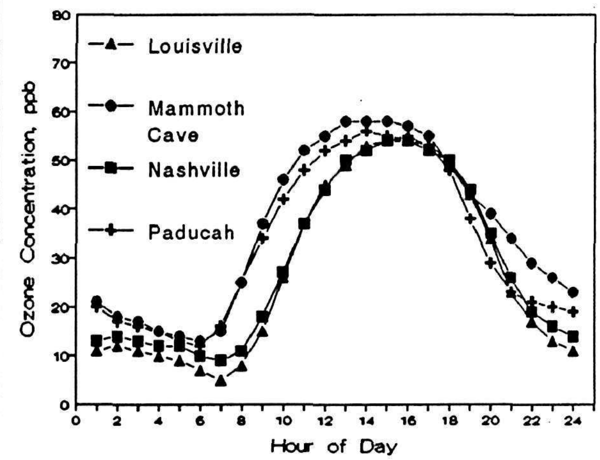


Figure 5. Ozone Diurnal Pattern for Mammoth Cave, Louisville, Nashville, and Paducah, April-October 1988.

In addition to the diurnal pattern, ozone concentrations also follow an annual pattern with peak concentrations typically occurring in the summer months when high solar insolation and ambient temperatures are present. This pattern is illustrated in Figure 6 where the monthly maxima and cumulative exposures greater than or equal to 60 ppb for the years 1985-1990 are plotted. Note the atypical peak values for both of these indices that occurred in 1988 as well as the month-to-month and year-to-year variability in these levels. Prior to 1988, the monthly maxima and exposures show somewhat of a consistent pattern with the highest levels occurring in the late spring and early summer. In 1988 and

1990, peak levels occurred later in the summer than in other years. The plot of the monthly maxima show that the annual maximum concentration, with the exception of 1988, have not varied greatly during this six year period. Monthly exposures equal to or above 60 ppb, on the other hand, show a greater variation with much lower exposures having occurred in 1989 and 1990. A better way of illustrating differences in ozone levels at the park is to look at the cumulative exposure on an annual basis. Figure 7 shows the cumulative exposure curves for Mammoth Cave for the years 1985 through 1990 using 60 ppb as the threshold value. From this figure one can more easily explore the actual differences in ozone levels at the park and how ozone exposure accumulates throughout the year. We note that ozone levels at the park were highest during 1987 and 1988, with 1990 having the lowest. Total exposure levels did not vary greatly for 1985, 1986, 1989, and 1990; although levels in 1990 show a relatively low exposure throughout most of the summer as stated earlier. With the exception of 1988, which showed dramatic increases in ozone exposure in June and July, most years are characterized by a gradual increase in cumulative exposure throughout the year. Based on these cumulative exposures one can hypothesize that park vegetation was most vulnerable to ozone injury during 1987 and 1988. Recall that injury surveys performed during 1985 and 1986 showed visible injury occurring on numerous species.

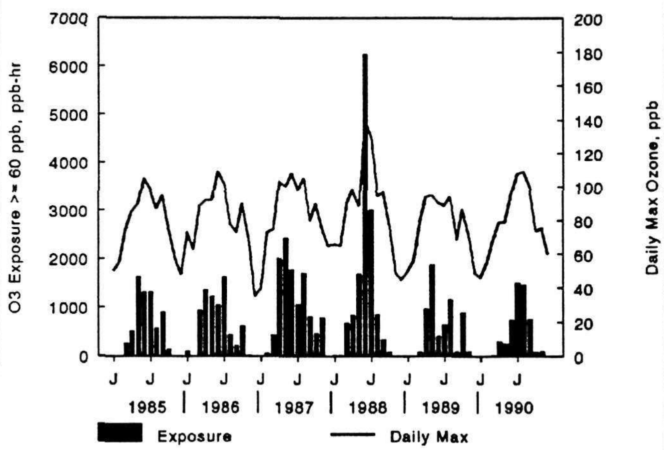


Figure 6. Monthly O_3 Exposure > = 60 ppb and Monthly Ozone Daily Maximum at Mammoth Cave NP, 1985-1990.

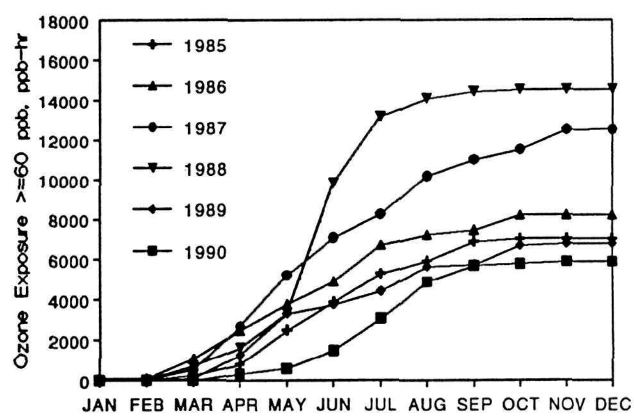


Figure 7. Adjusted Annual Ozone Exposure > = 60 ppb at Mammoth Cave NP, 1985-1990.

Correlations

Table 3 presents results of our wind independent correlation analysis. As can be seen from the table, ozone levels at Mammoth Cave NP are highly correlated with those observed at each of the surrounding cities, implying that levels in the area are likely the result of a regional scale phenomenon. Notwithstanding, ozone levels at the park are more highly correlated with those measured at Louisville and Nashville. Ozone levels in Nashville and Louisville are also highly correlated with each other. Although these high correlations do not allow us to assign causality for high ozone levels at the park, they

Table 3. Annual Correlation Coefficients Between Daily Maximum Ozone Concentrations at Mammoth Cave NP and Ozone Daily Maximum at Nearby Ozone Non-Attainment Areas 1987-1990 (Wind Direction Independent)

	Year			
Urban Center	**1987**	**1988**	**1989**	**1990**
Louisville (21-111-1021)	.66	.76	.79	.79
Louisville (21-111-0027)	.68	.80	.81	.77
Lexington (21-067-0001)	.75	.56	.57	.70
Lexington (21-067-0012)	.68	.70	.67	.64
Cincinnati	.54	.61	.52	.57
Dayton	.54	.57	.49	.52
Knoxville (47-093-0021)	.52	.65	.48	.57
Knoxville (47-093-1020)	.58	.61	.53	.63
Nashville	.73	.79	.81	.71
Paducah	.57	.64	.73	.60
Owensboro	.61	.72	.73	.71

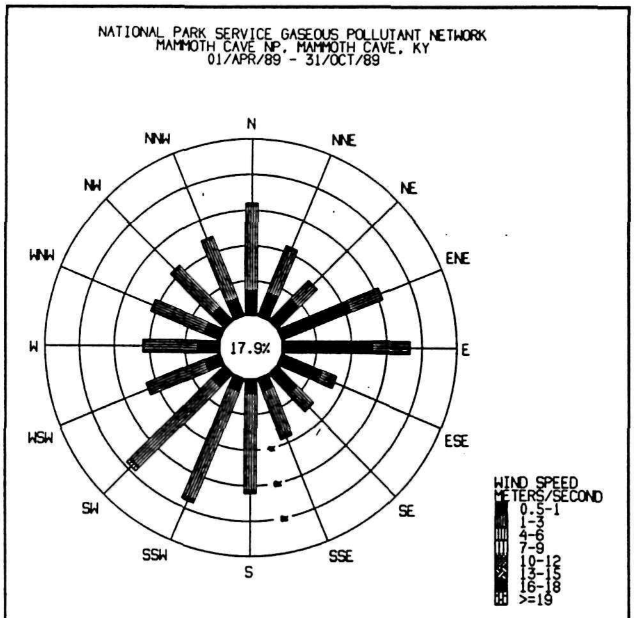


Figure 8. Wind rose for Mammoth Cave NP, April-October 1989.

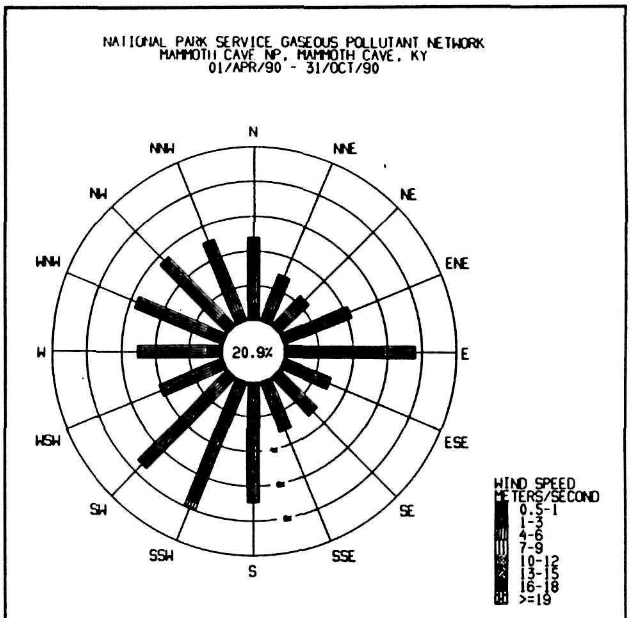


Figure 9. Wind rose for Mammoth Cave NP, April-October 1990.

are suggestive of the influence that these cities have on park levels. Nor can we say which of these two areas has a greater influence since both cities are approximately the same distance (90 miles) from the park, with Nashville being SSW of the park and Louisville NNE. However, we did find that the correlation between Louisville's daily maximum and Nashville's previous day daily maximum is slightly higher than vice versa. This suggests that Nashville may have a stronger influence on the ozone daily maximum observed at Mammoth Cave than Louisville. Although not presented in Table 3, our correlation analysis showed that the ozone daily maximum at Mammoth Cave is more highly correlated with the same day maximum at all cities rather than with the daily maximum measured one, two, or three days before. This may suggest that ozone transport from these cities occurs on the same day or that meteorological conditions were favorable for ozone formation on the same day.

Examining the surface wind roses for Mammoth Cave (see Figures 8 and 9) for the period April through October (1988 and 1989, respectively) we note a higher occurrence of winds from the S to SW sector than from the N to NE sector. Thus, air masses are more likely to be transported to the Mammoth Cave area from the Nashville area. This results in Mammoth Cave being downwind of the Nashville area most often and, consequently, one would expect a greater influence from the Nashville urban area than from the others.

The correlations discussed to this point were based on all observations recorded at each location without regard to surface wind direction. If surface wind measurements made at Mammoth Cave are indicative of surface layer transport winds, then one would expect higher correlations between Mammoth Cave and each of the cities if one computes these correlations using only those days when Mammoth Cave was downwind of these cities. To do this, we selected only those days for which the wind direction persisted from a 45° sector centered at each urban area for more than 6 hours between 0600 and 1400 hours. Because it was not possible to define non-overlapping 45° sectors for Cincinnati, Dayton, Louisville, and Lexington, only one 80° sector was defined as "Ohio Valley". As a result only 5 separate wind sectors were defined (see Methods section). In addition an "Other" sector defined those days when the wind persisted from directions other than from the 5 defined sectors. A "Non-Persistent" sector was also defined to represent those days when the winds did not persist from any of the defined sectors, including the "Other" sector.

The correlation coefficients re-computed for each of the above sectors are given in Table 4. The correlations given under the "Sector" column are those computed for days when the wind persisted from the identified wind sector. The number of days in which the wind persisted from each wind sector is given in parenthesis. When we compare the correlation coefficients in the Sector column with those in the Non-Persistent column we see that in all but the Knoxville wind sector (which had only 4 persistent days), the "Sector" correlations are higher than the "Non-Persistent" correlations. The increase in the correlation coefficient for Louisville, Lexington, Nashville, and Owensboro is statistically significant ($p<.01$). We also note that the sector average of the ozone daily maximum at Mammoth Cave is greatest when the winds persist from the Nashville sector. It is interesting to note that the second highest sector average is the one associated with Paducah, and that the Ohio sector average is substantially less than Nashville. In fact, if one considers the Non-Persistent sector average as the average day at Mammoth Cave, one would expect higher ozone daily maxima at the park on those days when the wind persisted from the Nashville and Paducah sectors, or generally when the winds are from the southwest. In contrast, we note that the ozone daily maximum at Mammoth Cave is, on average, lower when the winds persist from the northwest and southeast, or when Mammoth Cave is not persistently downwind from any of the urban centers considered in this analysis (the "Other" sector).

Table 4. Annual Correlation Coefficients Between Daily Maximum Ozone Concentrations at Mammoth Cave NP and Ozone Daily Maximum at Nearby Ozone Non-Attainment Areas 1987-1990 (Wind Direction Dependent)

Wind Sector	Urban Area	Correlation Coefficients *Sector*	*Other*	*Non-Persist.*	Sector Mean, O_3 Daily Max (ppb)
Ohio (0 to 80°)					56.9
(n=58)	Louisville (21-111-1021)	.82	.48	.63	
	Louisville (21-111-0027)	.86	.58	.65	
	Lexington (21-067-0001)	.73	.49	.52	
	Lexington (21-067-0012)	.67	.66	.63	
	Cincinnati	.68	.44	.49	
	Dayton	.64	.38	.44	
Knoxville (119 to 164°)					53.0
(n=4)	Knoxville (47-093-0021)	-.04	.64	.44	
	Knoxville (47-093-1020)	-.04	.67	.47	
Nashville (183 to 228°)					62.2
(n=53)	Nashville	.83	.71	.53	
Paducah (245 to 290°)					59.5
(n=19)	Paducah	.81	.52	.63	
Owensboro (290 to 335°)					50.6
(n=28)	Owensboro	.94	.79	.64	
Other (n=27)		--	--	--	54.6
Non-Persistent (n=164)		--	--	--	58.7

Back Trajectories

In a recent study, Dattore et al.[16] used a trajectory-based analysis to explore possible ozone source areas at five eastern U.S. national parks, including Mammoth Cave NP. A high ozone source contribution function (HSCF) was used to indicate the atmospheric transport pathways that are dominant when ozone concentrations at the parks were above a pre-defined minimum, and a high concentration conditional probability function (HCPF) was used to determine the probability that an air mass, having passed over a region, would be associated with a high concentration at a park. The combination of the HSCF and HCPF identifies possible source regions and transport pathways associated with high concentrations. Dattore found that high ozone levels at the park were associated most frequently with air masses which passed over the western halves of Tennessee and Kentucky, northeastern Arkansas, and northern Alabama. This paper extends Dattore's work by considering both low-level and mid-level winds to determine the HSCF and HCPF, where the earlier work considered only mid-level winds.

Figures 10-12 show the HSCF and HCPF maps for Mammoth Cave National Park. For each map, source contribution function values and conditional probabilities were calculated for the time period 1985-1989. HSCF values were normalized to values between 0 and 100, so that the values plotted are the percentages of the maximum HSCF value, rather than the actual values. This allows direct comparisons between sites, especially when the number of ozone observations and/or the time periods of analysis are different between sites. The plotted percentages range from less than 10% (white) to greater than 90%

(darkest), at increments of 20%. HCPF values are true percentages ranging from less than 20% (white) to greater than 60% (darkest).

Figure 10 shows the mid-level results and Figure 11 shows the low-level results for Mammoth Cave NP. In the mid-level case, the HSCF (Figure 10a) map shows that air most often arrived from the south and west when ozone concentrations at the park were high. The most frequently passed-over regions include western Tennessee, southeast Missouri, southwestern Kentucky, and northern Mississippi and Alabama. There is also some evidence of a transport pathway to the northeast of the park. In the low-level case (Figure 11a), two transport pathways appear to be dominant when ozone concentrations at the park are high. One is to the southwest of the park, and the other to the northeast. Most frequently passed-over regions include southern Tennessee and northern Mississippi to the southwest, and the Ohio River Valley to the northeast. This is consistent with the results of our correlation analysis which showed Mammoth Cave levels to be highly correlated with cities located SW and NE of the park. The low ozone concentrations at the park are concentration fields are also shown for Mammoth Cave in Figure 12. Low concentration fields are computed the same way as the high concentration fields, except that endpoints are counted when the below some low concentration. For the mid-level case, the LSCF (figure not shown) showed that the air most often arrived from the northwest when concentrations at the park are low. This is quite different from the high concentration results, indicating that there may be definite source areas which contribute some long-range transport component to Mammoth Cave's ozone concentrations. The low-level low concentration map (Figure 12a) is very similar to the high concentration map, indicating that meteorological conditions rather than transport from different areas are likely to be responsible for low concentrations at the park. Actual low-level trajectories were plotted for 14 days with the highest ozone daily maxima that have been measured at Mammoth Cave. Trajectories were plotted using a feature which zoomed in on the Mammoth Cave area but also included all of the surrounding non-attainment areas. Regular trajectories, which show the complete 5-day trajectory, were also plotted. These trajectories are presented in the Appendix. A review of these trajectories shows that air masses associated with the highest daily maxima often come from northeast, but in most cases air masses pass over several areas prior to arriving at the park. The highest daily maximum measured at the park in the last four years (140 ppb in 1988), was associated with a trajectory from the west-southwest (see page A-7).

Conditional probability maps are also shown in Figures 10-12 for Mammoth Cave. The HCPF map for the mid-level case (Figure 10b) shows that air arriving from the northeast and east of the park (Ohio Valley area) was associated with high ozone concentrations in up to 40% of the total time. Probabilities for air arriving from the south and west were lower, with values approaching 25% in northern Alabama and southeastern Missouri. The LCPF map for the mid-level case (figure not shown) shows that the transport pathway to the northwest of the park has some of the highest probabilities of air being associated with low concentrations. The areas north and east of the park, which showed somewhat high probabilities of being associated with high ozone concentrations, are characterized by very low probabilities of being associated with low concentrations. In the low-level case, the HCPF map (Figure 11b) shows low probabilities for all directions of air being associated with high ozone concentrations at the park. In contrast the LCPF for the low-level case (Figure 12b) shows transport from the northeast associated with low concentrations at Mammoth Cave. However, this high probability centered in southeastern Canada may be the result of a few number of trajectory endpoints in these grid squares which will result in artificially high conditional probabilities. Also it is unlikely that the use of low-level winds in the ATAD model are truly indicative of air mass transport over such large distances.

Conclusions

We have attempted to characterize ozone levels measured at Mammoth Cave NP during the period 1985-1990 and to relate these levels to those measured at nearby ozone non-attainment areas and other potential source areas. We have shown that these levels have exceeded the national ambient air quality standard for ozone on occasion. Moreover, injury surveys conducted in 1985 and 1986 indicate that these levels are causing visible injury to various tree species within the park. The implication of these

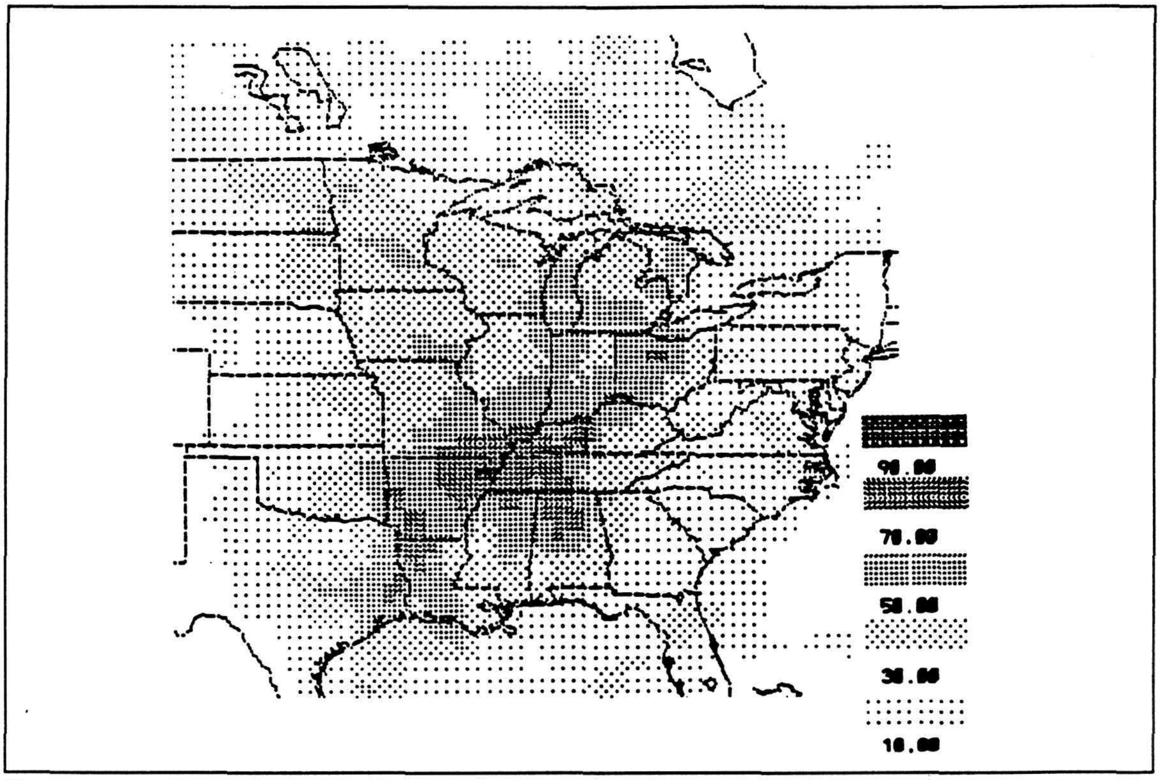


Figure 10a. Map of HSCF for Mammothe Cave NP, Mid-Level Case. The "+" indicates the park.

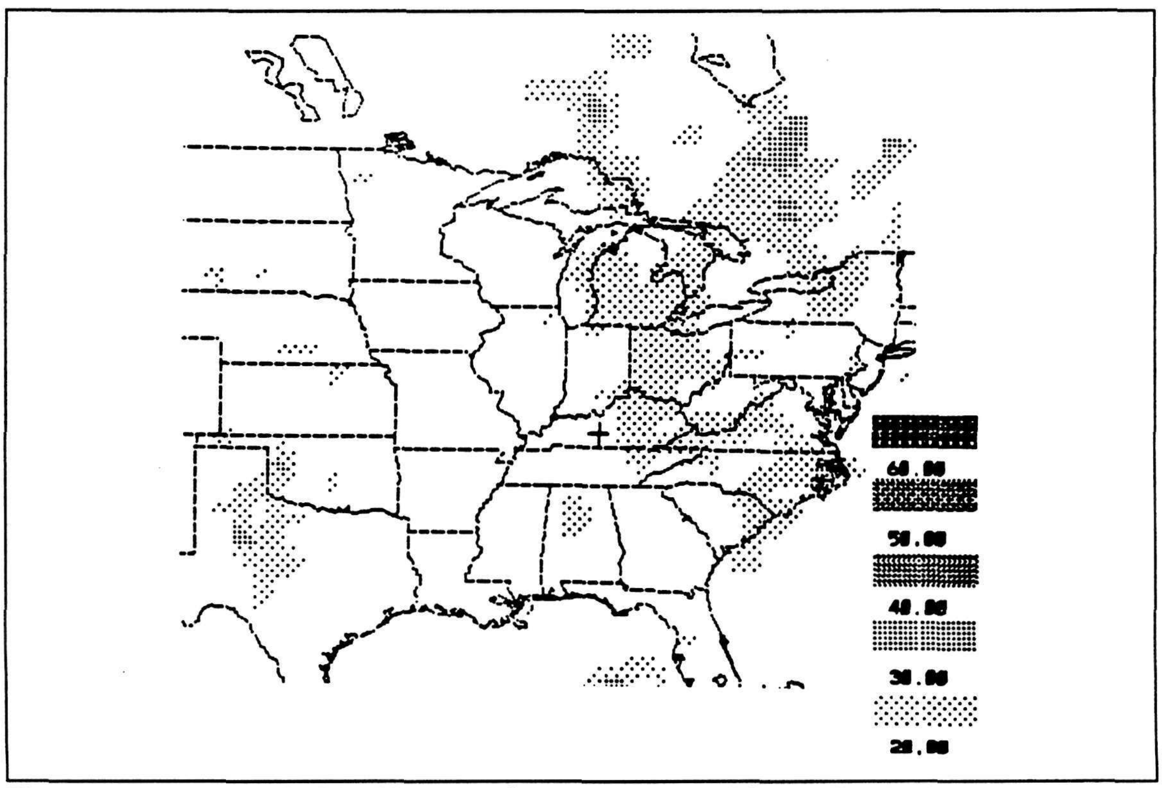


Figure 10b. Map of HCPF for Mammoth Cave NP, Mid-Level Case. The "+" indicates the park.

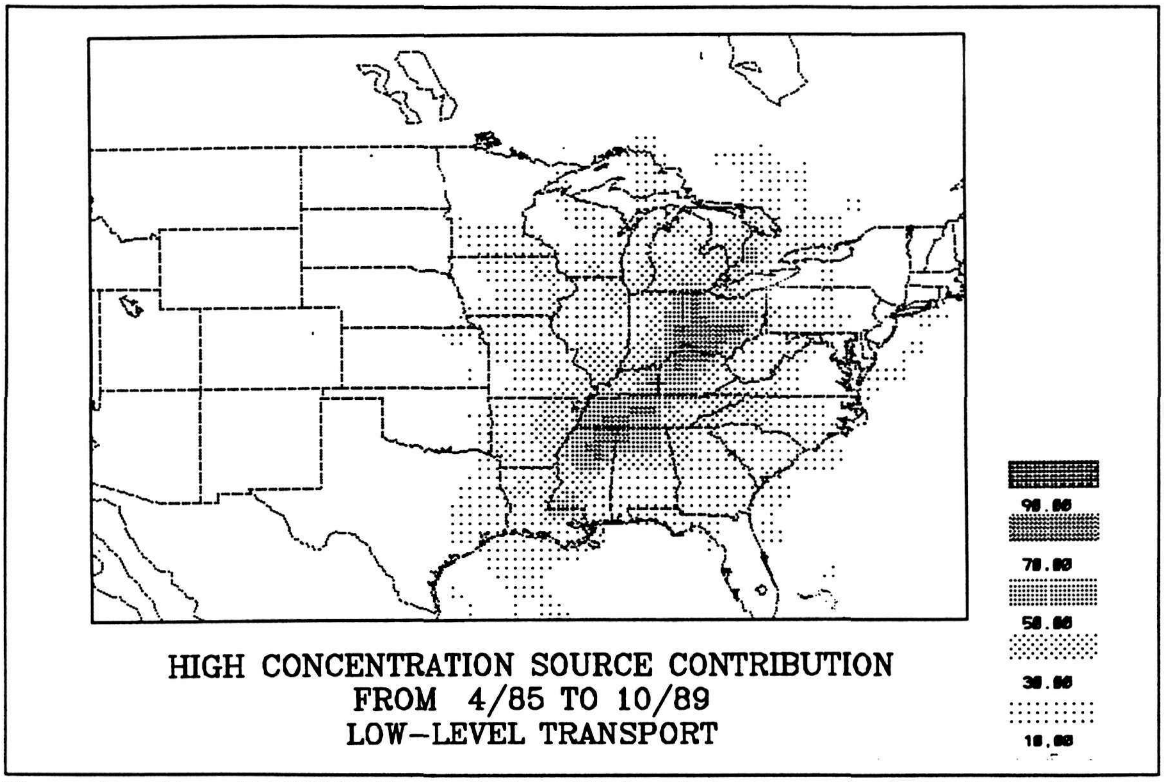


Figure 11a. Map of HSCF for Mammoth Cave NP, Low-Level Case. The "+" indicates the park.

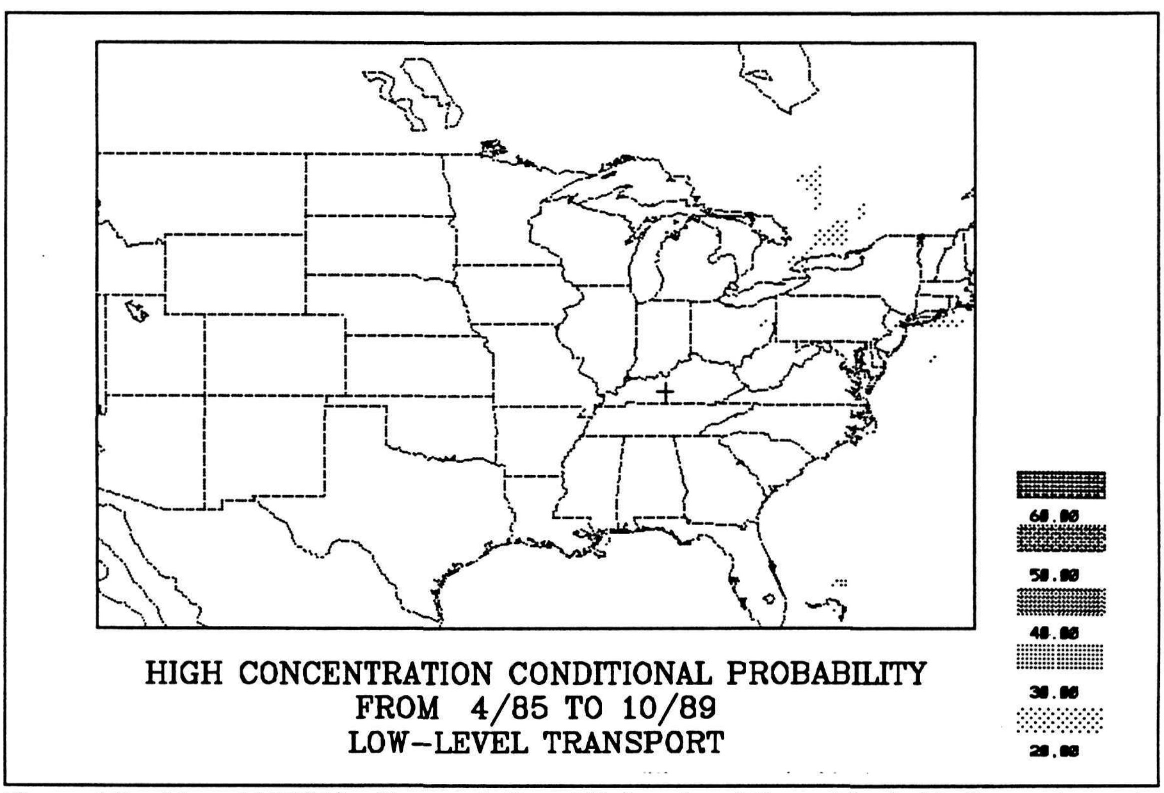


Figure 11b. Map of HCPF for Mammoth Cave NP, Low-Level Case. The "+" indicates the park.

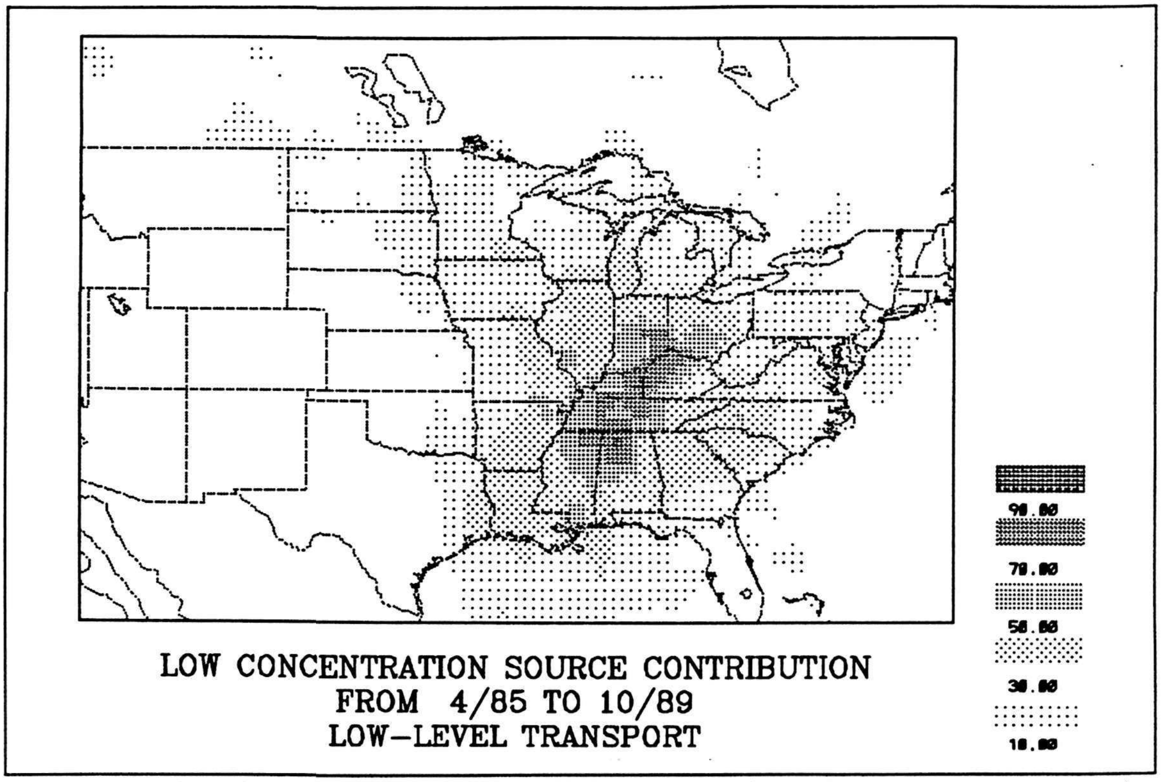


Figure 12a. Map of LSCF for Mammoth Cave NP, Low-Level Case. The "+" indicates the park.

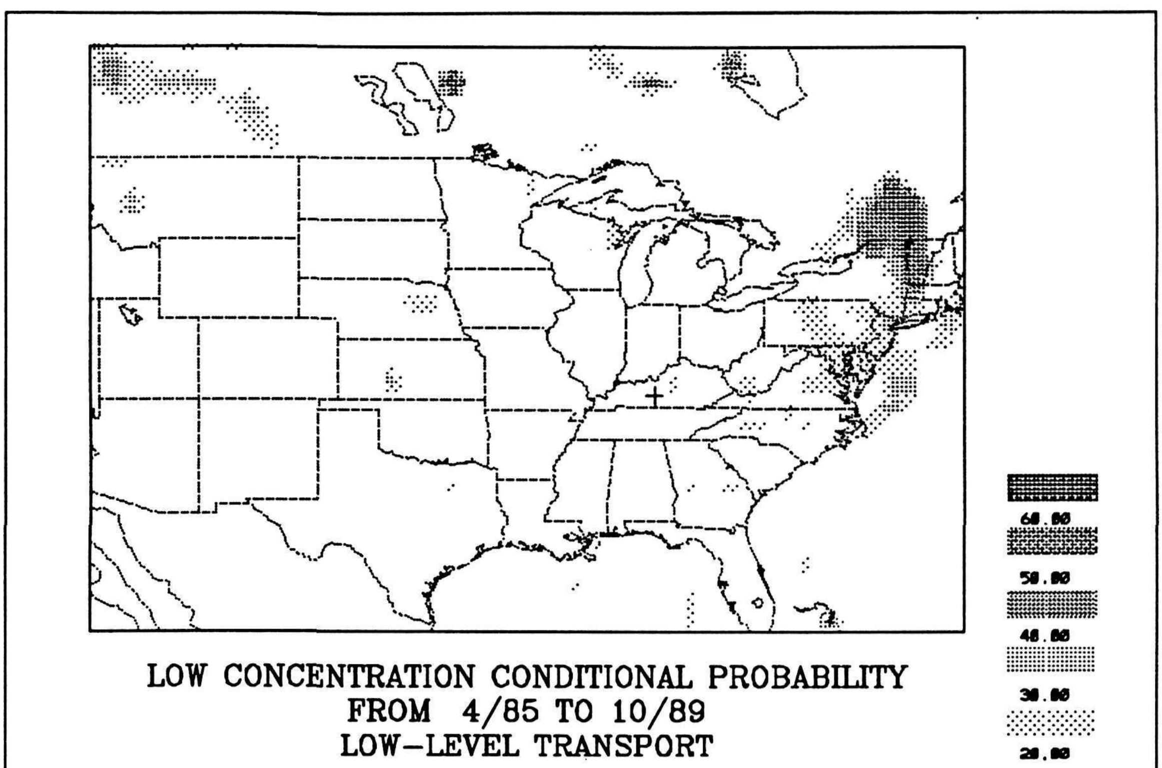


Figure 12b. Map of LCPF for Mammoth Cave NP, Low-Level Case. The "+" indicates the park.

levels on plant processes and other ecosystem effects is currently not known and can only be hypothesized as occurring.

The numerous ozone non-attainment areas which surround the park are undoubtedly influencing the levels being measured at the park. Our correlational and back-trajectory analyses indicate that although ozone levels in and around the park vary on a regional scale, several of these areas influence the ozone daily maximum (and ozone levels in general) measured at the park. Specifically, we have shown that when air masses are transported over the Paducah, Nashville, and Ohio Valley areas high concentrations are more likely to result at Mammoth Cave, with the Nashville area being implicated as having more of an influence on these high levels. Our back trajectory analysis suggests that transport from source areas farther away may also contribute to high ozone levels at the park. In general, higher daily maxima at the park are associated with persistent southwesterly and westerly flows. Northeasterly flows, on average, result in lower daily maxima at the park. Variable winds also yield higher than average daily maxima at the park.

Additional monitoring at locations between the park and these urban areas would further elucidate the cause of high ozone levels, as would the sampling and speciation of non-methane organic compounds at the park. A clearer understanding of the causes of high ozone levels at the park will allow the NPS to deal more effectively with air pollution regulatory agencies and thereby mitigate or eliminate the adverse effects of air pollution on its resources.

REFERENCES

1. National Air Quality and Emissions Trends Report, 1989, EPA-450/4-91-003, U.S. Environmental Protection Agency, Research Triangle Park, NC, February 1991.

2. P. B. Reich and R. G. Amundson, "Ambient Levels of Ozone Reduce Net Photosynthesis in Tree and Crop Species", Science 230:566-570, 1985.

3. Ibid.

4. P. B. Reich and J. P. Lassoie, "Influence of Low Concentrations of Ozone on Growth, Biomass Partitioning and Leaf Senescence in Young Hybrid Poplar Plants", Environ. Pollut. (Series A) 39:39-51, 1985.

5. L. F. Benoit, J. M. Skelly, L. D. Moore and L. S. Dochinger, "Radial Growth Reductions of Pinus Strobus L. Correlated with Foliar Ozone Sensitivity as an Indicator of Ozone-induced Losses in Eastern Forests, Can. J. For. Res. 12:673-78, 1983.

6. D. B. Houston and L. S. Dochinger, "Effects of Ambient Air Pollution on Cone, Seed and Pollen Characteristics of Eastern White and Red Pines", Environ. Pollut. 12:1-5, 1977.

7. F. W. Honing, "Impact of Air Pollution on the Forest Resource", Proc. Ann. Meet. Soil Cons. Soc. 15:1199-1201, 1973.

8. S. B. McLaughlin, R. K. McConathy, D. Duvick and L. K. Mann, "Effects of Chronic Air Pollution Stress on Photosynthesis, Carbon Allocation and Growth of White Pine Trees", For. Sci. 28:60-70, 1982.

9. G. M. Woodwell, "Effects of Pollution on the Structure and Physiology of Ecosystems", Science 168:429-433, 1970.

10. B. McCune, C. L. Cloonan and T. V. Armentano, Foliar Injury, Tree Growth and Mortality, and Lichen Studies in Mammoth Cave National Park, Final Report to the National Park Service Air Quality Division (Contract No. CX-0001-4-0058, Order No. PX-0001-5-1121), Holcomb Research Institute, Butler University, Indianapolis, IN, March 1987.

11. J. L. Heffter, Air Resources Laboratory Atmospheric Transport and Diffusion Model (ARL-ATAD), National Oceanographic and Atmospheric Administration (NOAA), NOAA Technical Memo, Boulder, CO, 1980.

12. L. L. Ashbaugh, W. C. Malm and W. Z. Sadeh, "A Methodology for Establishing the Probability of the Origin of Air Masses Containing High Pollutant Concentrations", Presented at the 76th Annual Air Pollution Control Association Meeting, Atlanta, GA, 1983.

13. L. L. Ashbaugh, W. C. Malm and W. Z. Sadeh, "A residence Time Probability Analysis of Sulfur Concentrations at the Grand Canyon National Park", Atmospheric Environment 19 (8):1263, 1985.

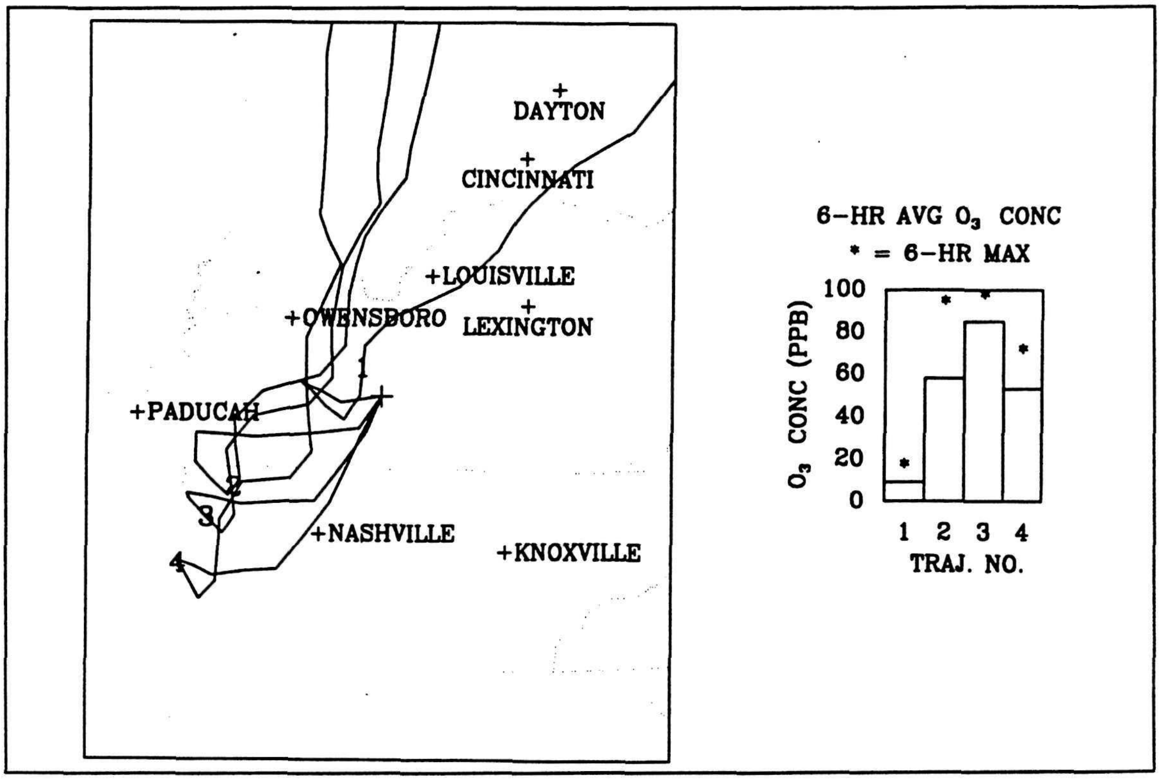
14. R. L. Poirot and P. R. Wishinski, "Visibility, Sulfate and Air Mass History Associated with the Summertime Aerosol in Northern Vermont", Atmospheric Environment 20 (7):1457, 1986.

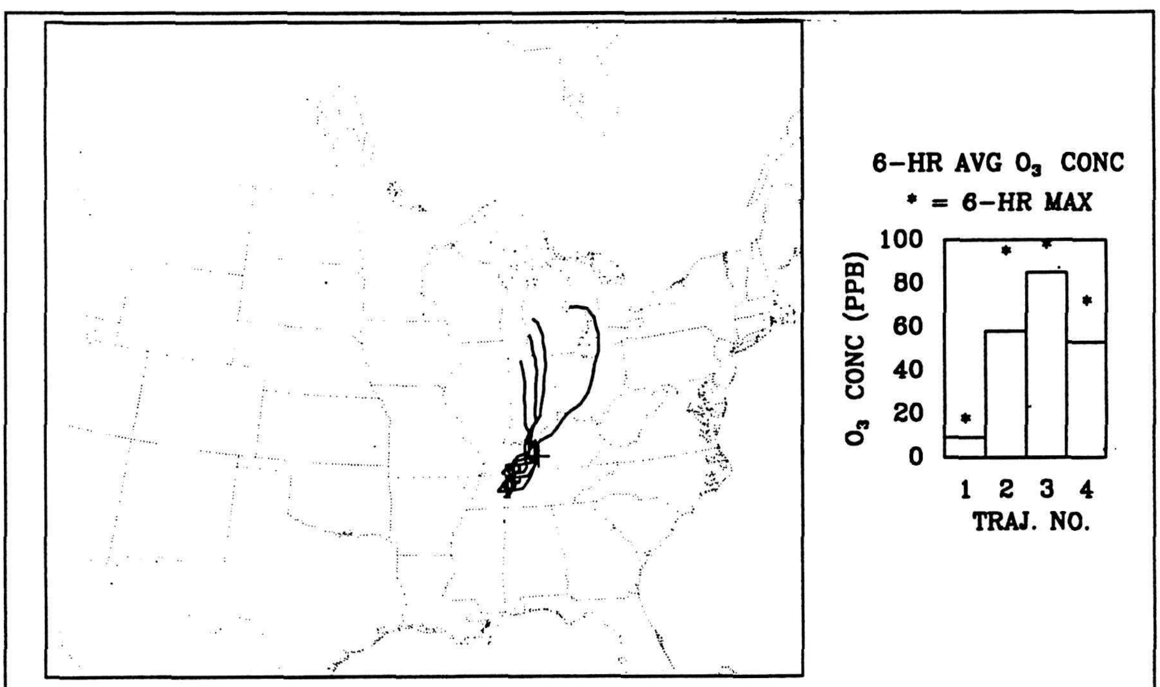
15. A. S. Lefohn, V. C. Runeckles, S. V. Krupa, D. S. Shadwick, "Important Considerations for Establishing a Secondary Ozone Standard to Protect Vegetation", J. Air & Waste Mgt Assn. 39 (8):1039-1045, 1989.

16. R. E. Dattore, K. A. Gebhardt, W. C. Malm and M. I. Flores, "Use of an Atmospheric Trajectory Model to Explore the Source Regions Affecting Ozone Concentrations at Five Eastern U. S. National Parks", Presented at the 84th Annual Meeting of the Air and Waste Management Association, Vancouver, B. C., 1991.

APPENDIX

Trajectory Plots Associated with the 14 Highest Ozone 6-hr Averages
Measured at Mammoth Cave National Park, 1986 - 1989





LOW-LEVEL TRAJECTORIES
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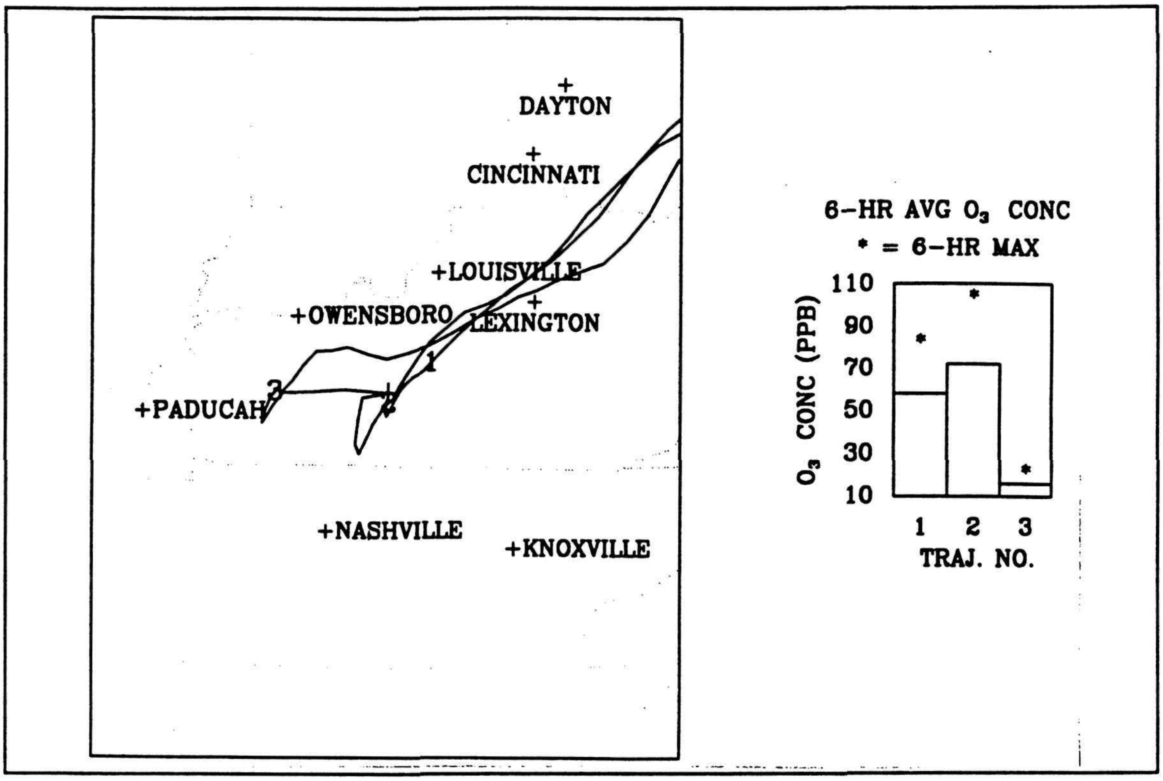

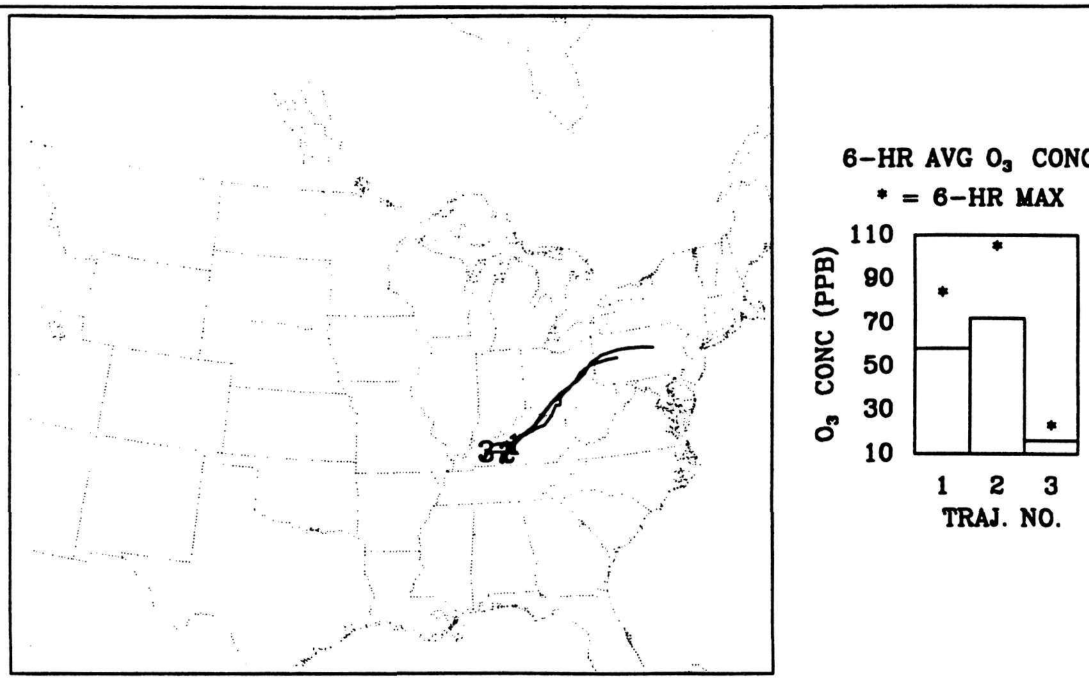

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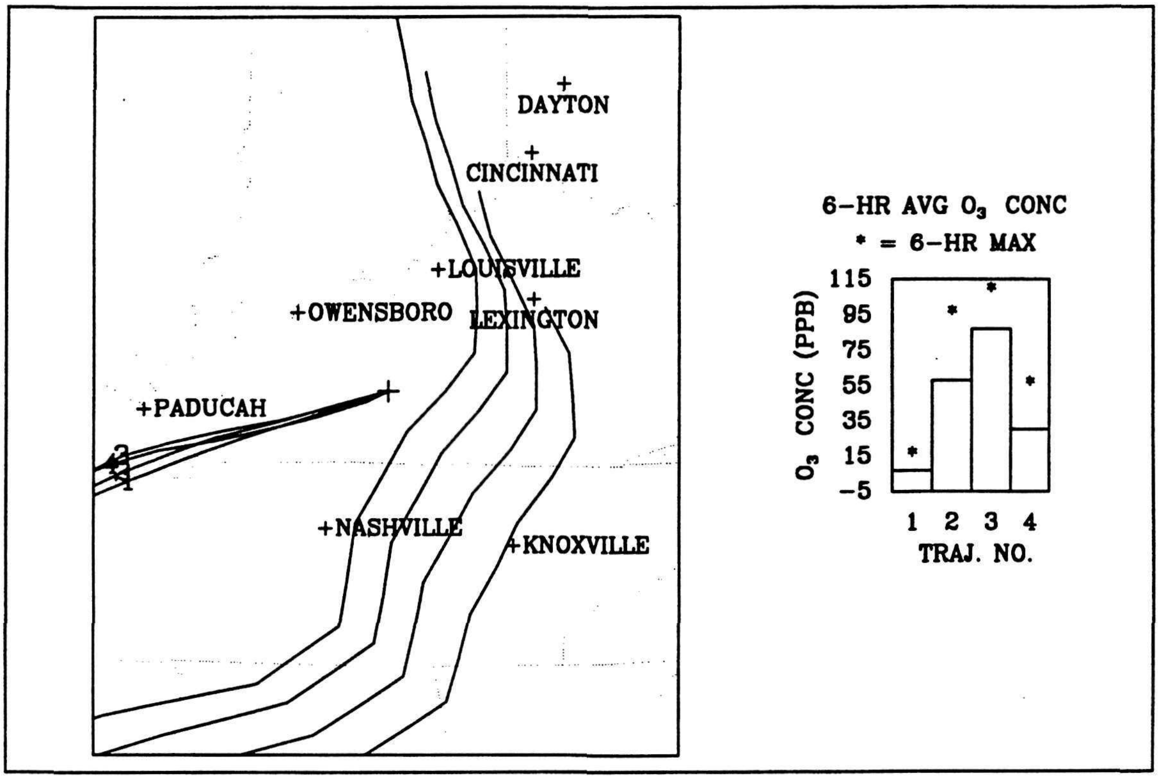

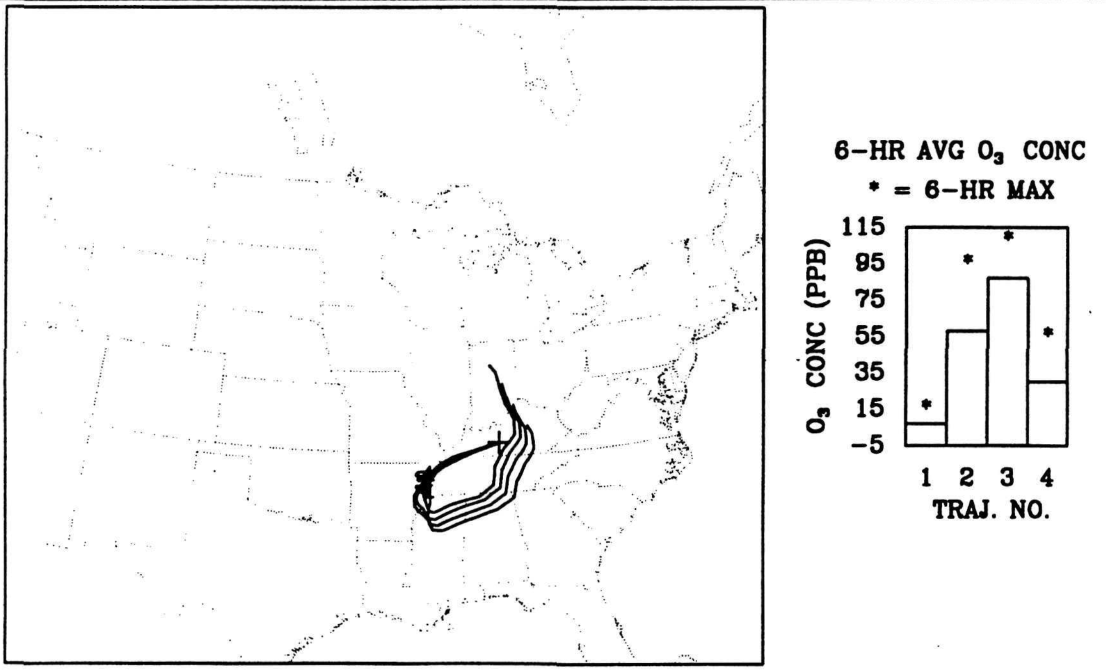

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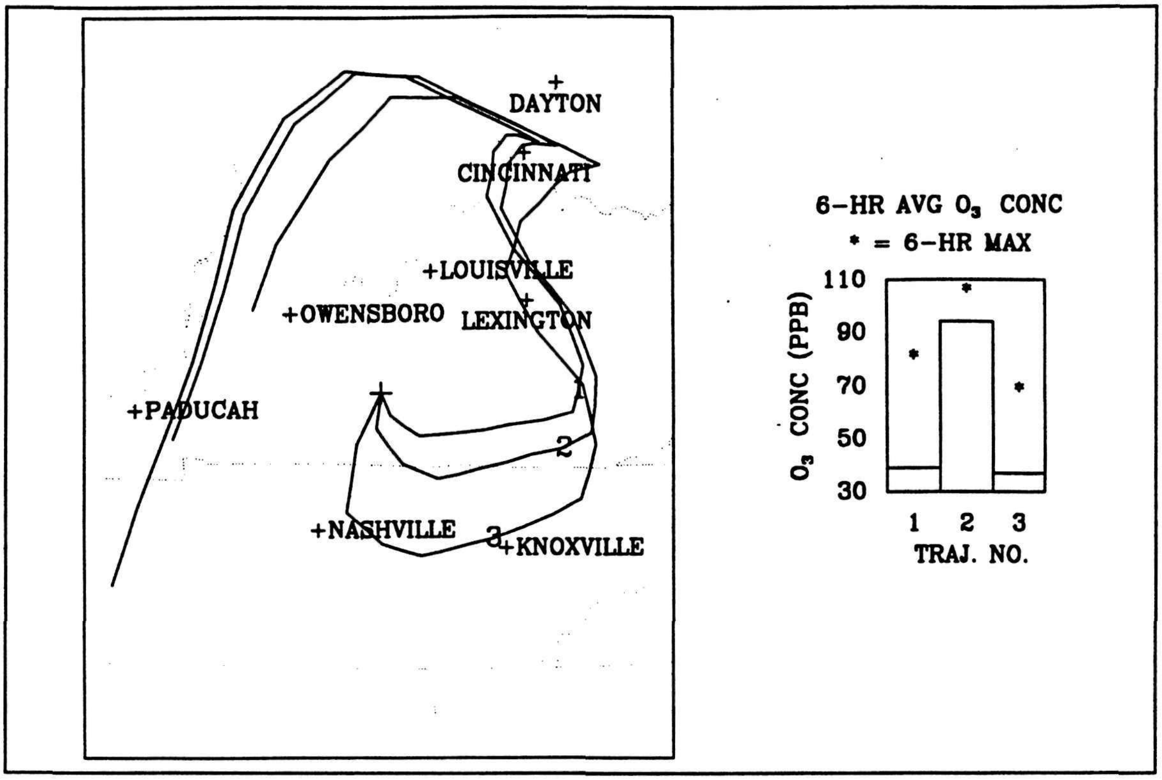

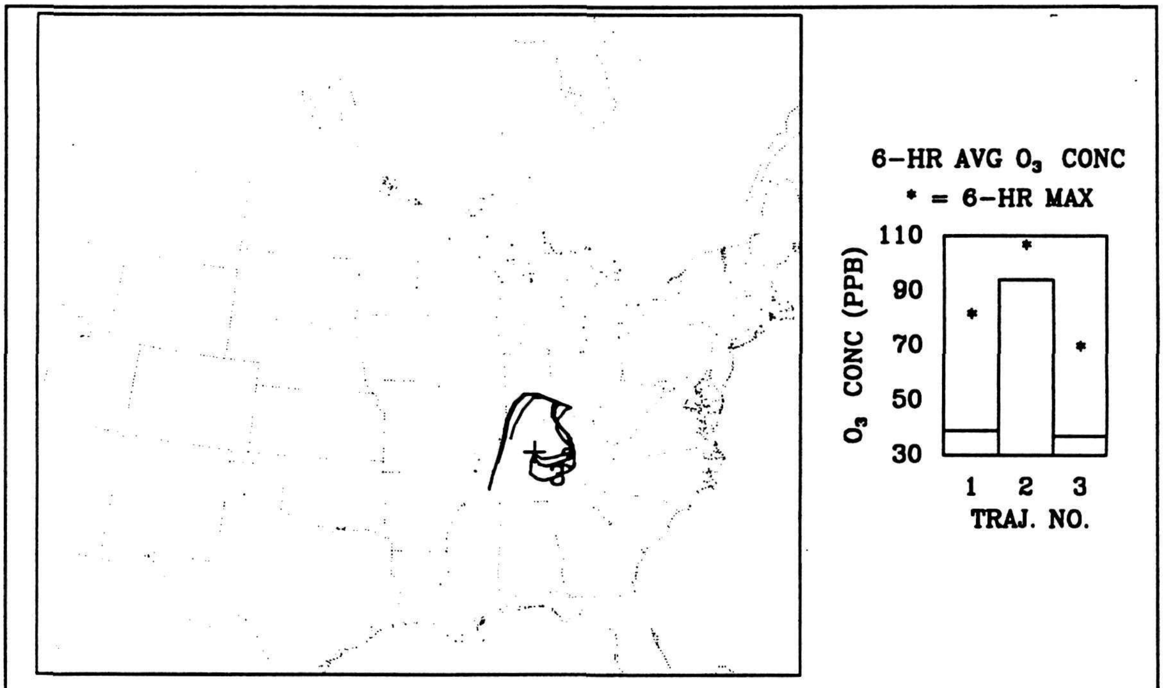

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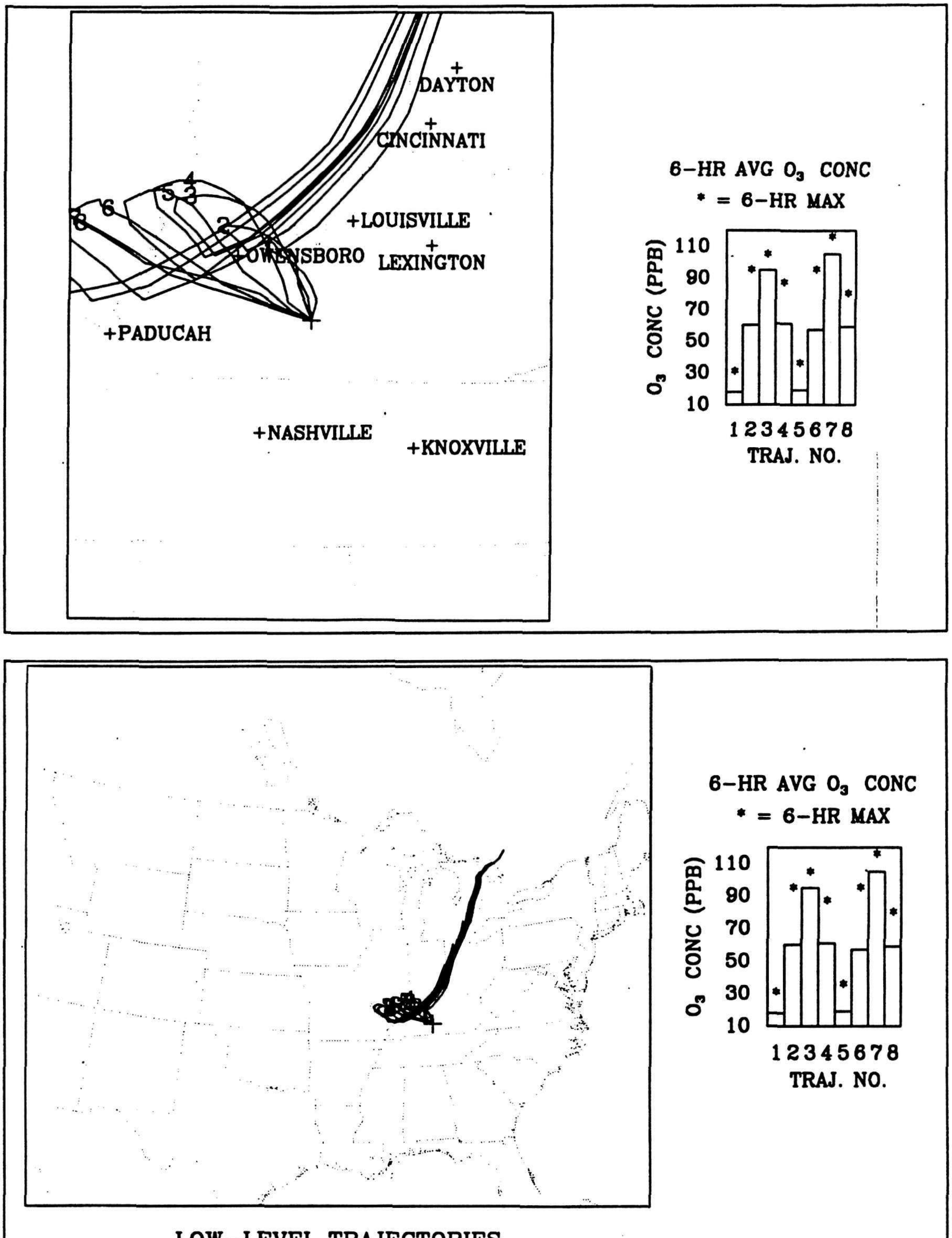

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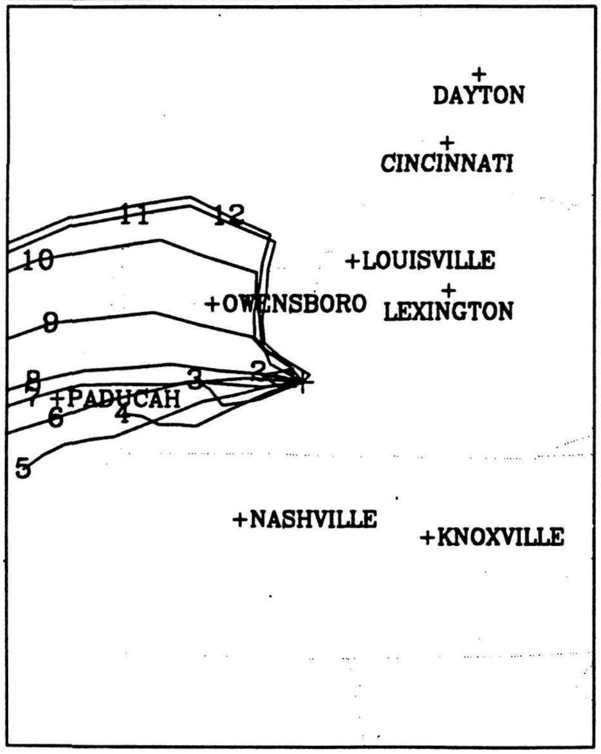

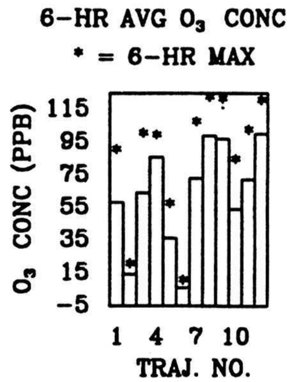

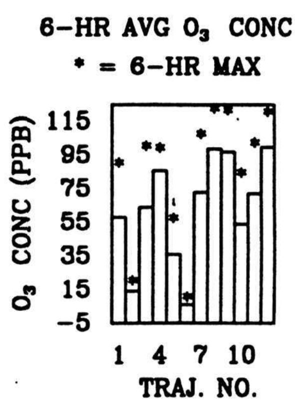

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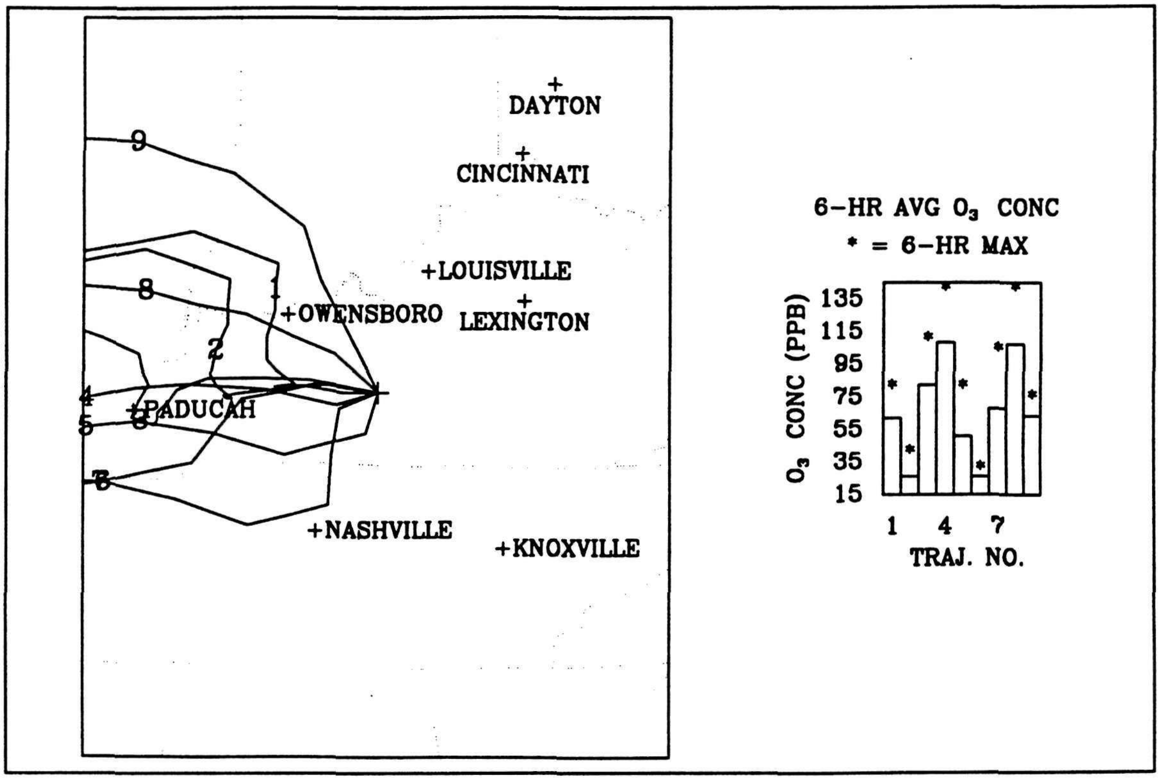

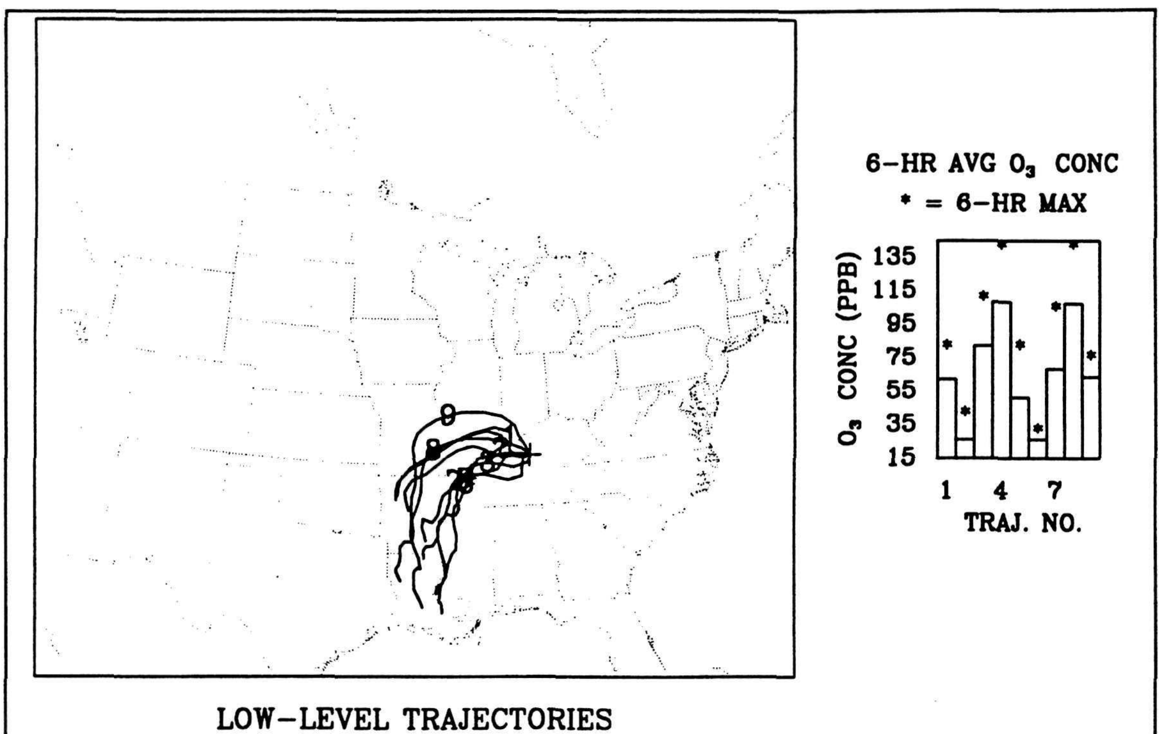

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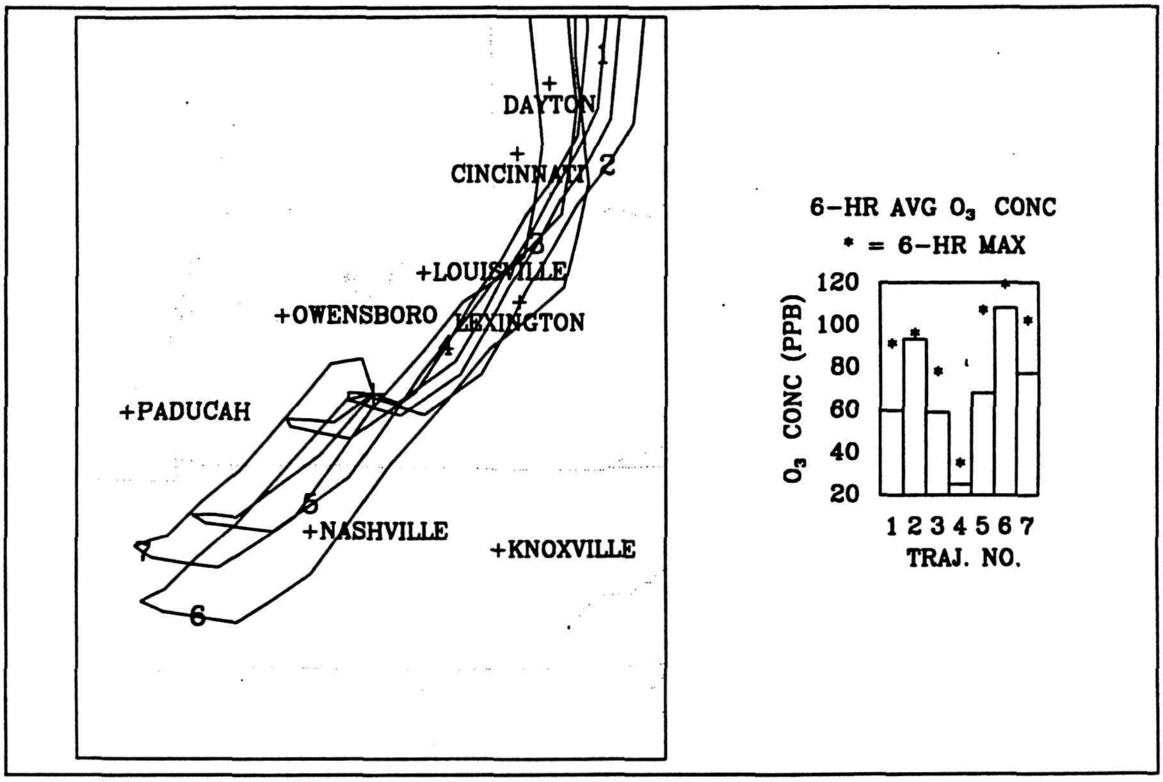

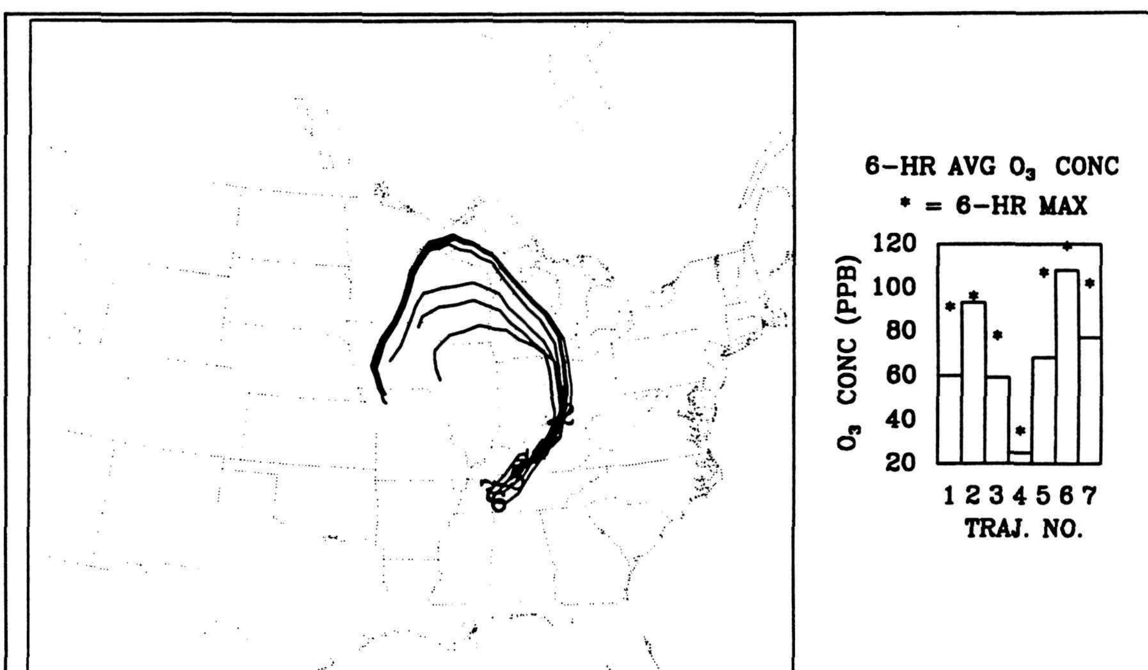

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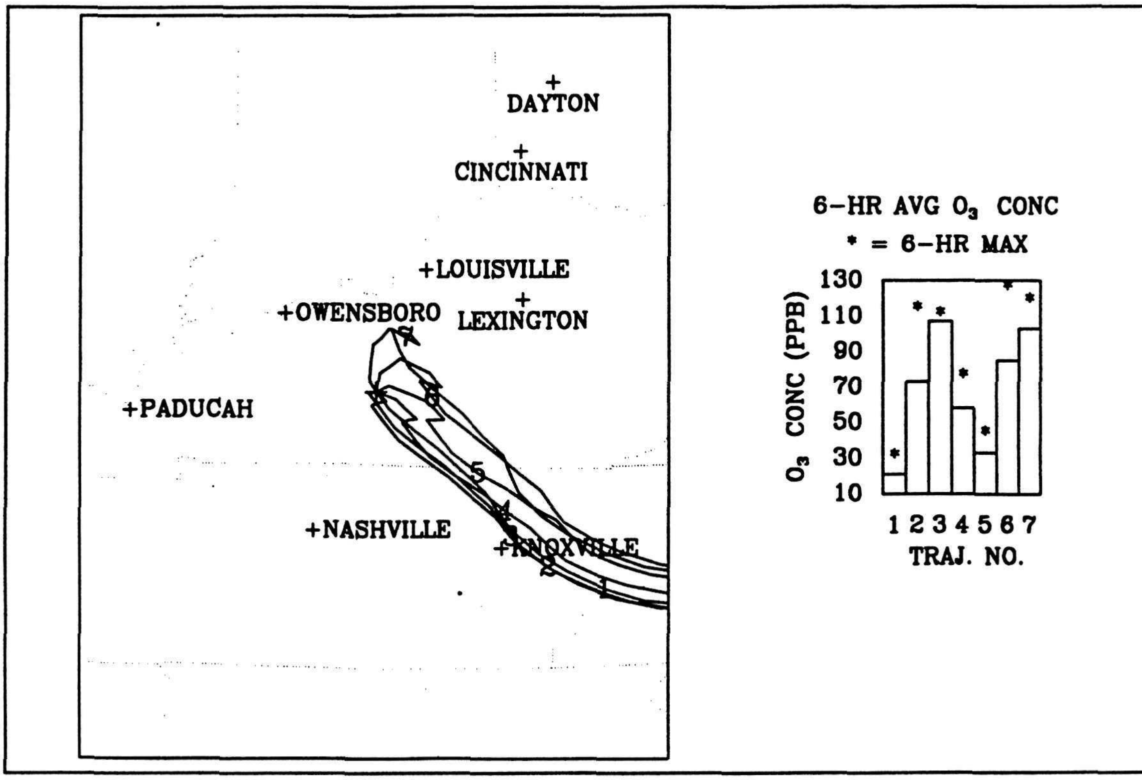

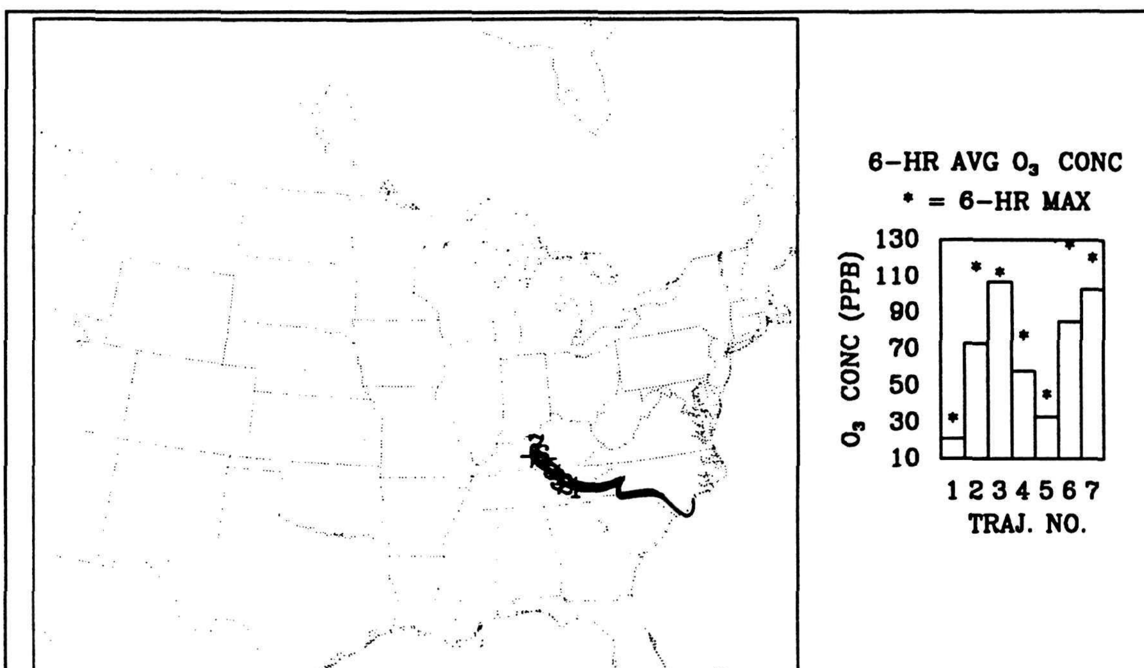

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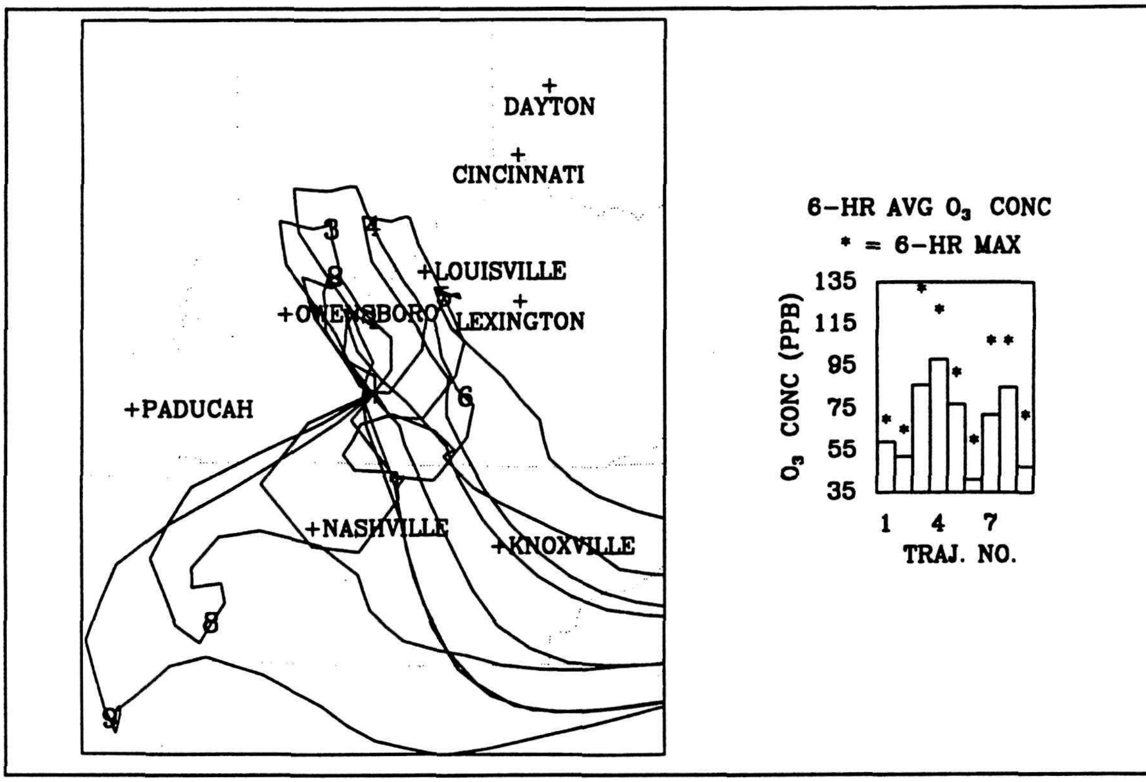

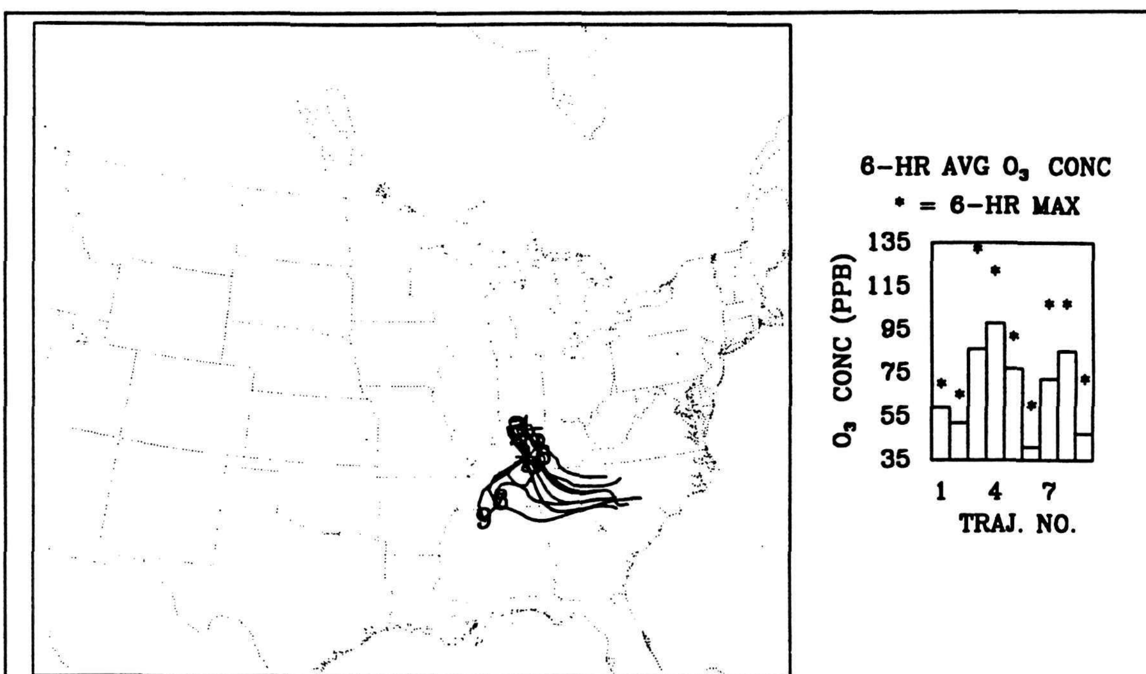

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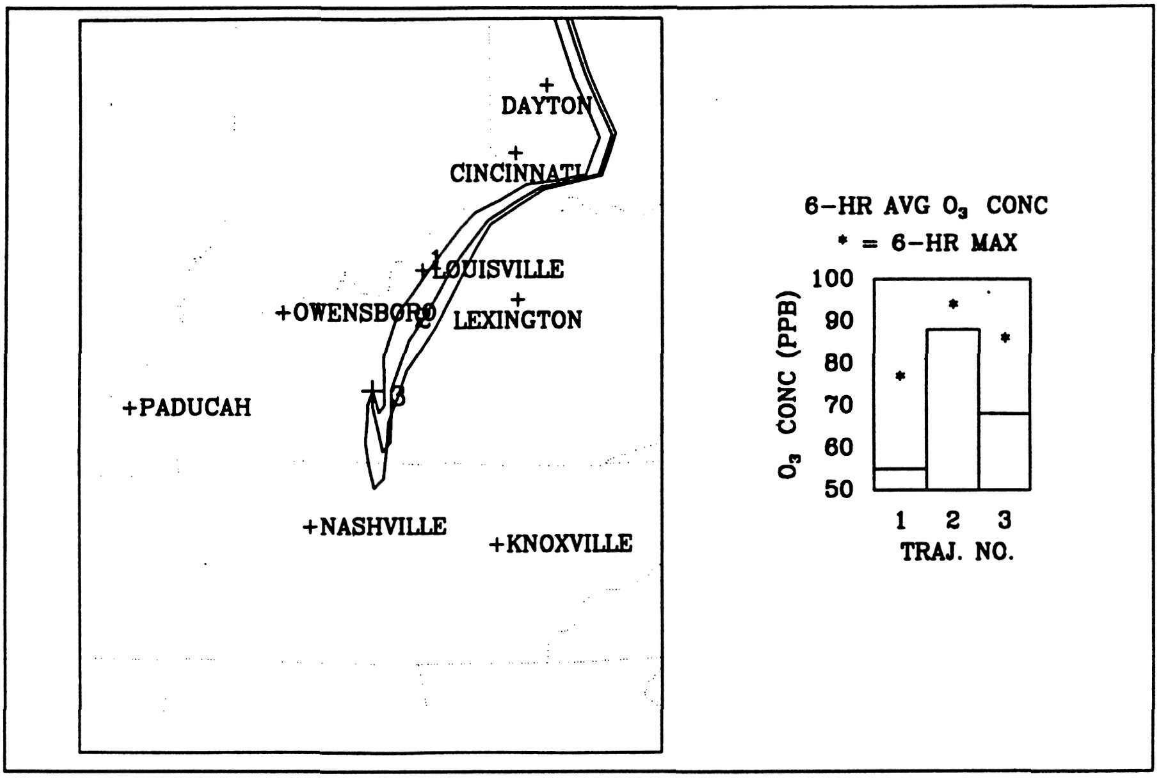

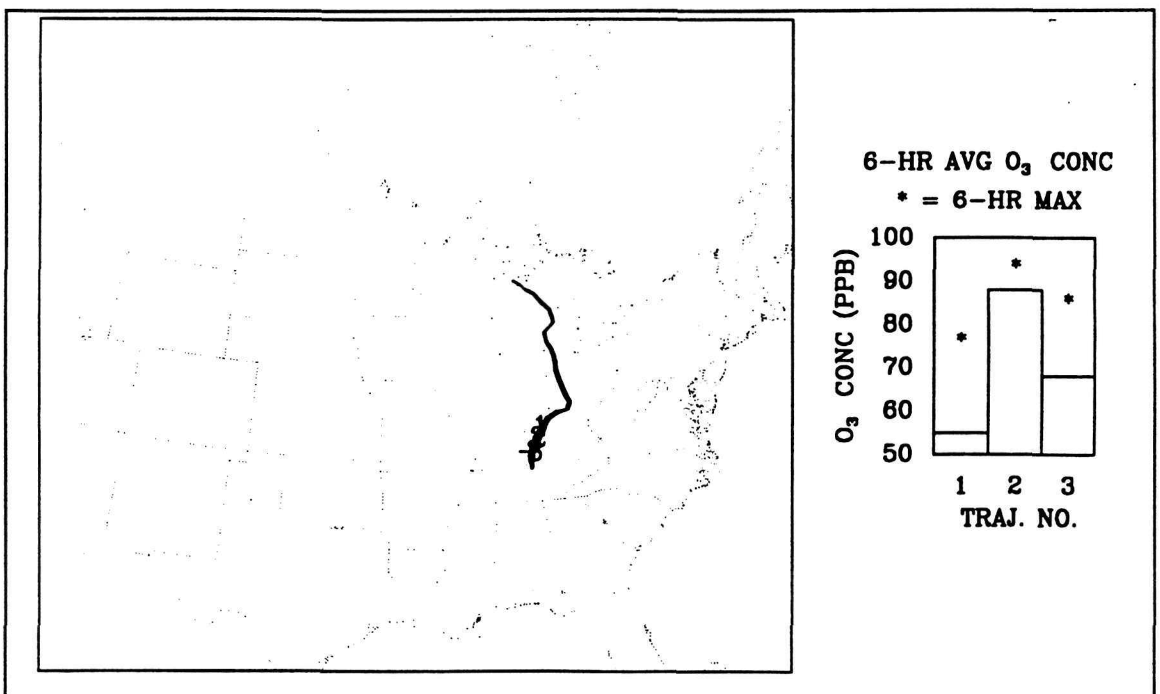

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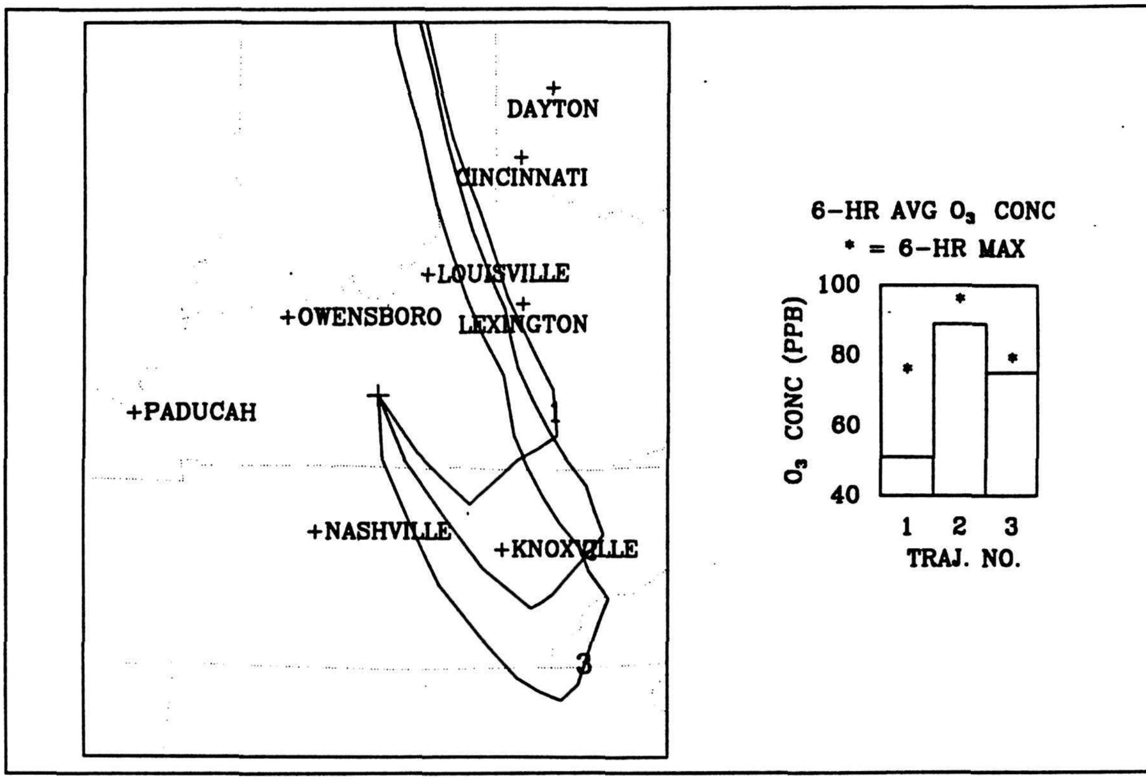

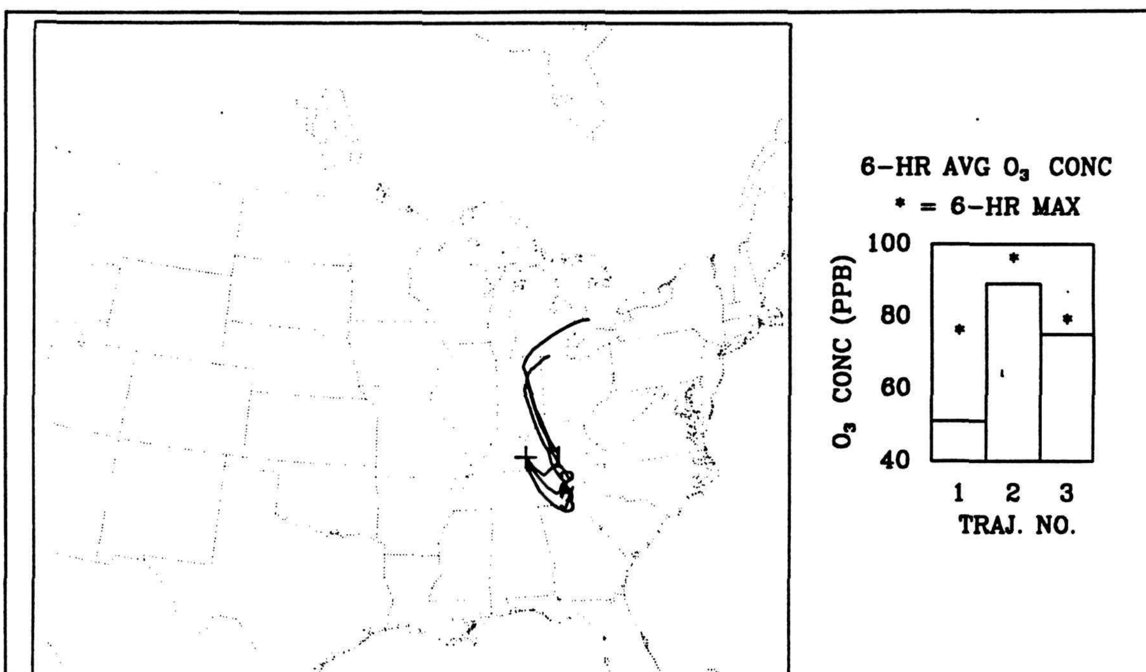

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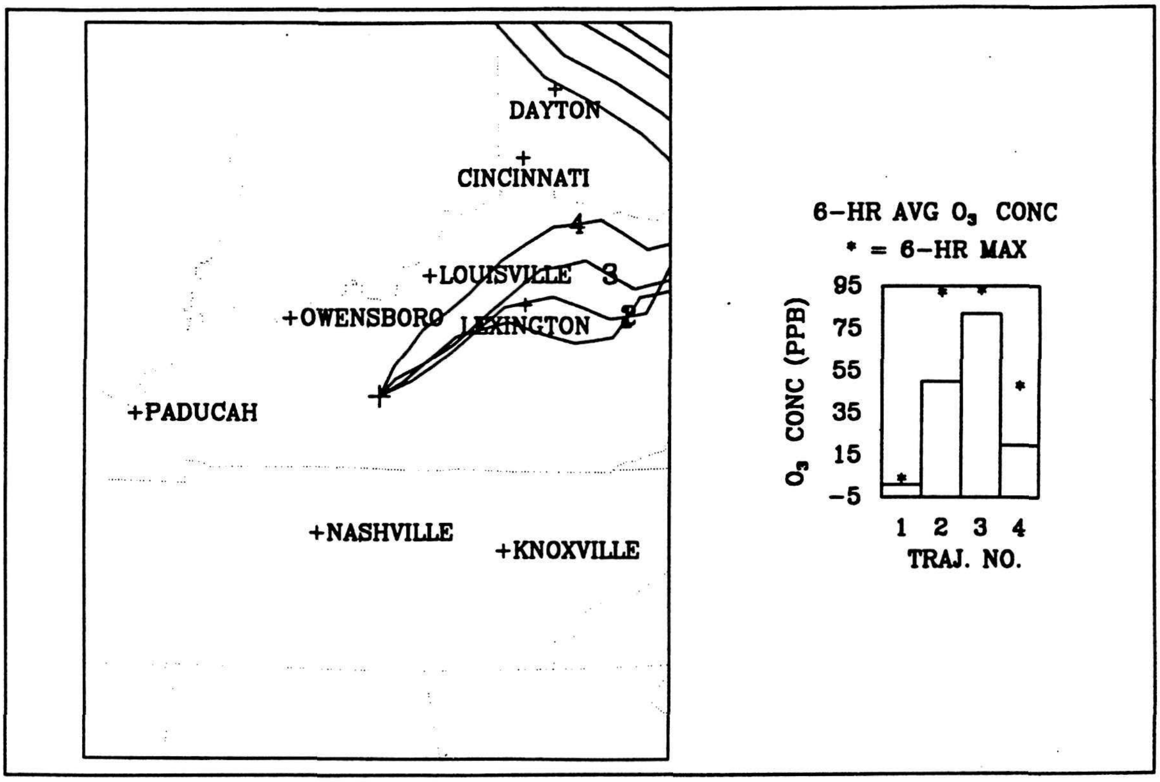

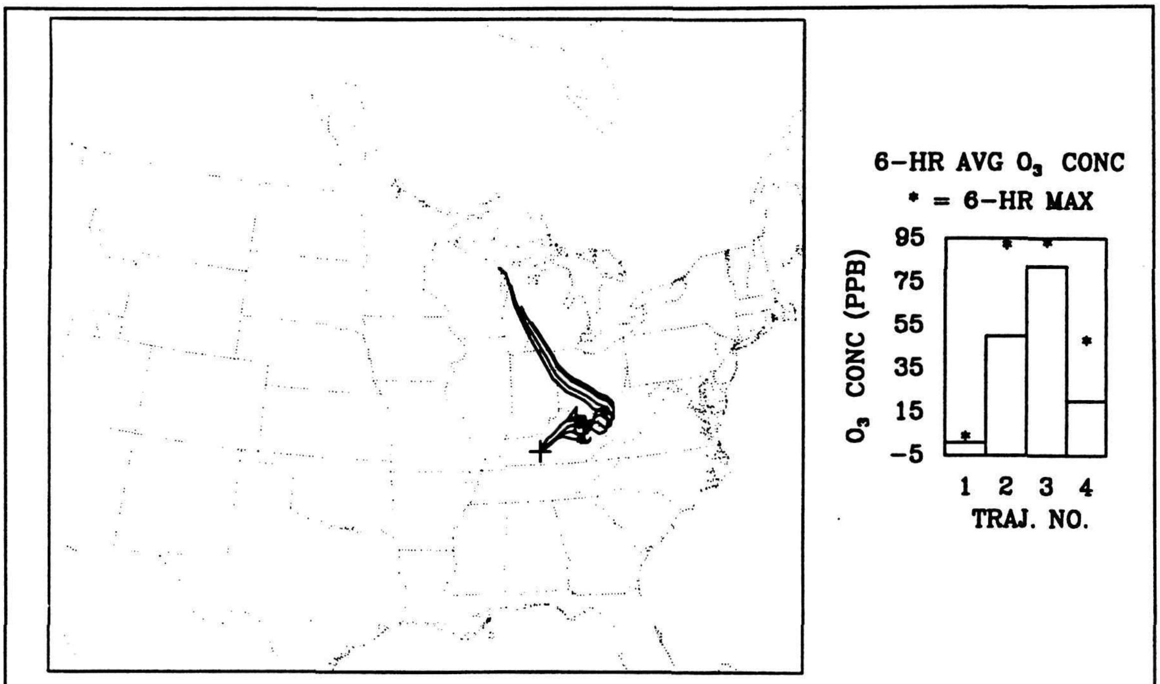

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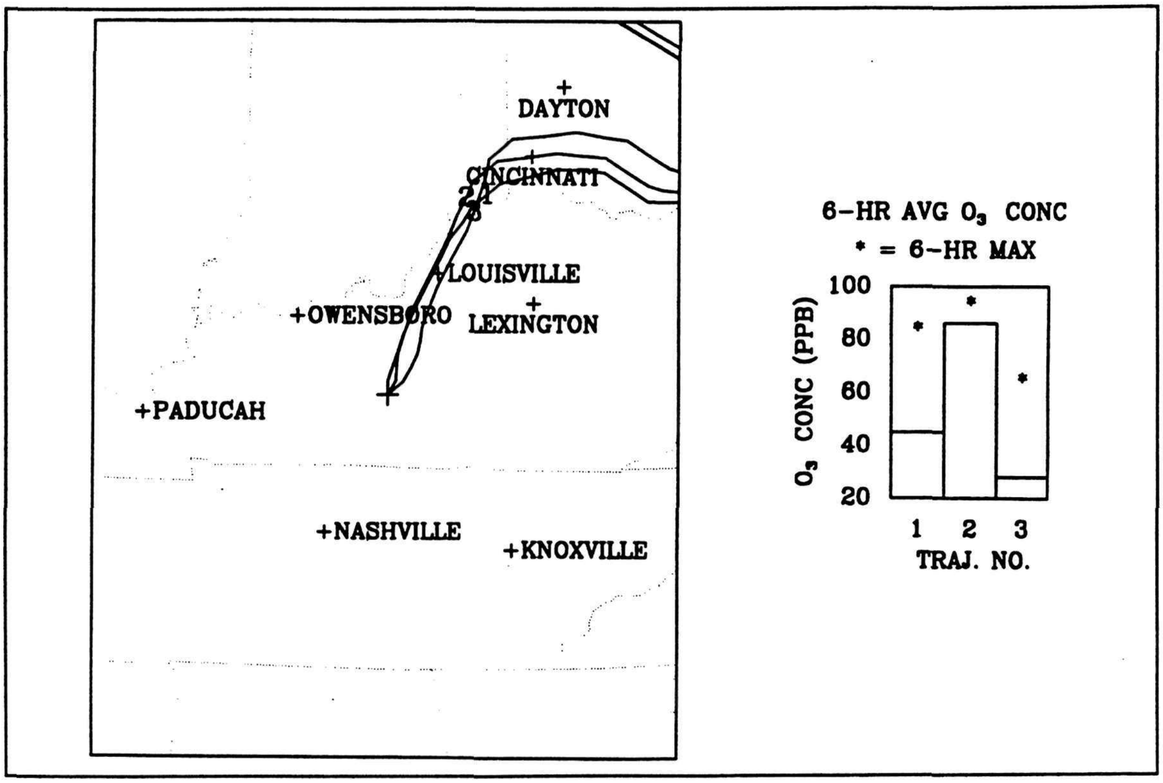

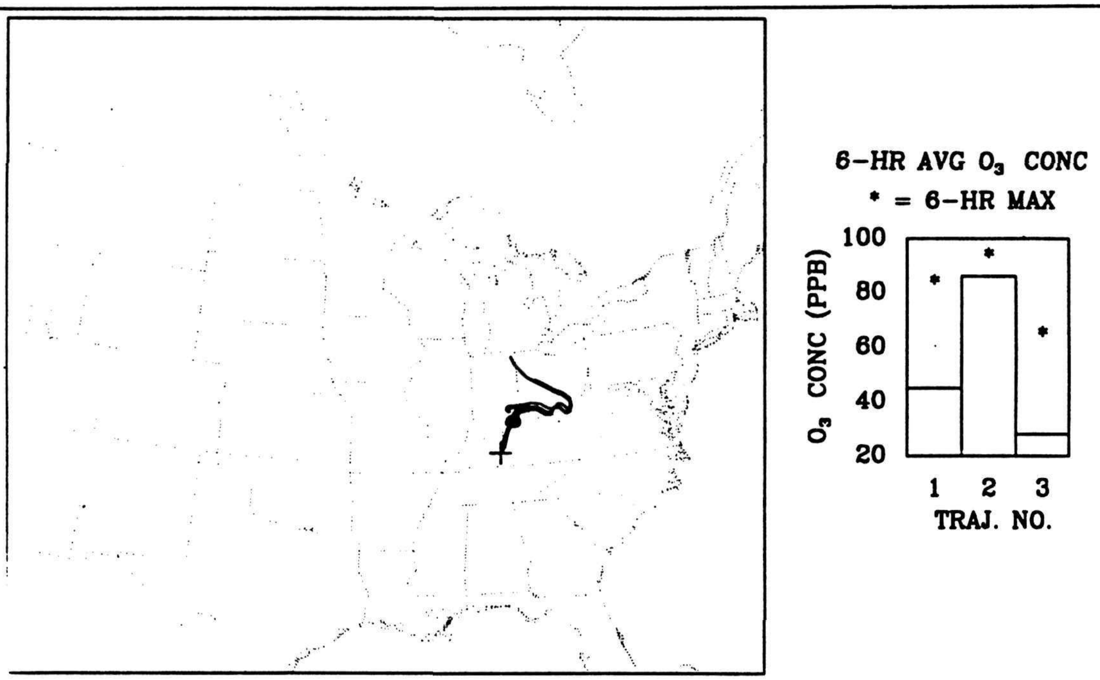

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