BNL-66382

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 103, NO. D17, PAGES 22,555–22,568, SEPTEMBER 20, 1998

Ozone production during an urban air stagnation episode over Nashville, Tennessee

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Abstract. The highest O_3 levels observed during the 1995 Southern Oxidants Study in middle Tennessee occurred during a period of air stagnation from July 11 through July 15. Extensive airborne (two fixed wing and one helicopter) and ground-based measurements of the chemistry and meteorology of this episode near Nashville, Tennessee, are presented. In situ airborne measurements include O_3, NO_y, NO, NO_2, SO_2, CO, nitrate, hydrocarbons, and aldehydes. Airborne LIDAR O_3 measurements are also utilized to map the vertical and horizontal extent of the urban plume. The use of multiple instrumented research aircraft permitted highly detailed mapping of the plume chemistry in the vertical and horizontal dimensions. Interactions between the urban Nashville plume (primarily a NO_x and hydrocarbon source) and the Gallatin coal-fired power plant plume (primarily a NO_x and SO_2 source) are also documented, and comparisons of ozone formation in the isolated and mixed urban and power plant plume are presented. The data suggest that during this episode the background air and the edges of the urban plume are NO_x sensitive and the core of the urban plume is hydrocarbon sensitive. Under these worst case meteorological conditions, ambient O_3 levels well over the level of the new National Ambient Air Quality Standard (NAAQS) for ozone (80 ppb) were observed over and just downwind of Nashville. For example, on July 12, the boundary layer air upwind of Nashville showed 60 to 70 ppb O_3, while just downwind of the city the urban plume maximum was over 140 ppb O_3. With a revised ozone standard set at 80 ppb (8 hour average) and upwind levels already within 10 or 20 ppb of the standard, only a slight increase in ozone from the urban area will cause difficulty in attaining the standard at monitors near the core of the urban plume during this type of episode. The helicopter mapping and LIDAR aircraft data clearly illustrate that high O_3 levels can occur during stagnation episodes within a few kilometers of and even within the urban area. The extremely light boundary layer winds (1-3 m s^{-1}) contributed to the creation of an ozone dome or blob which stayed very near to the city rather than an elongated plume. The small spatial scale of the zone of high O_3 concentrations is mapped in detail demonstrating that the regulatory monitoring network failed to document the maximum O_3 concentrations. Modelers using such regulatory data to test photochemical algorithms need to bear in mind that magnitude and frequency of urban ozone may be underestimated by monitoring networks, especially in medium-sized urban areas under slow transport conditions. Finally, this effort shows the value of collaborative field measurements from multiple platforms in developing a more complete picture of the chemistry and transport of photochemical O_3.

1. Introduction

Despite comprehensive local, state, and national regulatory initiatives over the past 30 years, and a long history of research in the area [*Crutzen*, 1970; *Samson and Ragland*, 1977; *Chameides et al.*, 1988; *Kelly et al.*, 1986; *Fehsenfeld et al.*, 1988; *Altshuller*, 1988; *Buhr et al.*, 1990; *Carroll et al.*, 1990; *Olszyna et al.*, 1994; *Imhoff et al.*, 1995], ambient ozone concentrations continue to be a major environmental and health concern. Early in the decade of the 1990s the National Academy of Sciences called for a rethinking of the ozone problem [*National Academy of Sciences*, 1991], and efforts were redoubled to elucidate the processes of ozone formation and transport in urban and regional settings. On a national level, for example, the North American Research Strategy for Tropospheric Ozone (NARSTO) has been formulated, a focused and coordinated program for the scientific study of tropospheric ozone concentrations, sources, formation mechanisms, and transport across the North American continent. A major emphasis of NARSTO has been the extent to which interregional transport of ozone-rich air masses have affected efforts to attain the NAAQS for ozone. The Southern Oxidant Study (SOS) has provided, in several field studies and observation-based mod-

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Paper number 98JD01641.
0148-0227/98/98JD-01641$09.00

eling efforts, a rich source of data [*Meagher et al.*, 1996] to address the details of ozone formation processes, so that the effectiveness of controls on hydrocarbon and NO_x (sum of $NO + NO_2$) emissions in reducing tropospheric ozone levels can be accurately evaluated. Part of these efforts have been focused on identifying regions and/or events where ozone levels can be reduced by restricting emissions of volatile organic compounds (VOC) ("hydrocarbon-controlled chemistry"), by reducing NO_x emission sources ("nitrogen oxide-controlled chemistry"), or when a mixture of NO_x and VOC controls is required to reduce ambient ozone. Equally important is assessing the spatial and temporal variability of the levels of ozone and its precursors, NO_x and VOC, and the rate at which emitted NO_x species are converted into oxidized products (referred to collectively as NO_z) during ozone formation. One of the goals of these studies of fundamental ozone formation processes is to evaluate the zones of influence of ozone precursor emissions and hence determine the effectiveness of controlling various types of emission sources at various distances in reducing ozone levels in areas not presently meeting the National Ambient Air Quality Standard (NAAQS) for ozone. These efforts have begun to come to fruition with recent field observational studies [*Imhoff et al.*, 1995; *Parrish et al.*, 1993; *Kleinman et al.*, 1994; *Chameides et al.*, 1992; *Trainer et al.*, 1993].

The primary goal of the SOS 1995 Nashville/Middle Tennessee Ozone Study (hereafter, SOS Nashville 95) was to develop a better understanding of the meteorological and chemical processes that lead to elevated ozone episodes in rural and urban areas in the mid south, and to provide data with which to develop and test new hypotheses regarding ozone formation and transport such as those put forth by *Sillman* [1995] and others. The quality of the acquired database would allow specific questions concerning the spatial and temporal extent of hydrocarbon-controlled and nitrogen oxide-controlled chemistry to be addressed, along with quantitative estimation of the efficiency by which ozone is formed from NO_x emissions from point sources and urban area sources [see, e.g., *Trainer et al.*, 1993].

In designing the study, an effort was made to stay in the field a sufficient length of time and with a large enough array of instrumented aircraft to successfully perform an in-depth study of an urban elevated ozone episode. Fortunately, such an episode did occur during the study in Nashville, Tennessee, lasting from July 11 through July 13, 1995, and we were able to deploy the aircraft to study the transport and chemical processing of Nashville urban emissions during a period of very stagnant high pressure. During this episode the horizontal and vertical structure of the urban plume was characterized in detail. The O_3 production efficiency and chemical transformations that occur with time were determined in the urban plume and a mixed power plant/urban plume with sufficient spatial and temporal detail so that questions such as, Do monitoring networks as currently deployed adequately document the maximum tropospheric ozone exposures that occur in urban areas?; and Does the current approach to regional modeling contain enough spatial resolution to reasonably reproduce the ozone patterns in mid-sized urban areas? could be addressed. Using data from three aircraft and several ground sites, this paper analyzes 2 days of a high-ozone episode in the Nashville, Tennessee, area during SOS Nashville 95.

2. Measurements

This paper focuses on the results from three of the aircraft participating in the collaborative study: (1) a Department of Energy Grumman G-1 operated jointly by personnel from the Pacific Northwest Laboratory and Brookhaven National Laboratory (BNL); (2) a Bell 205 helicopter operated by the Tennessee Valley Authority (TVA), and (3) a CASA-212 operated by National Oceanic and Atmospheric Administration (NOAA) Environmental Technology Laboratory. The BNL G1 measured O_3, NO_y (the sum of all the odd nitrogen compounds expressed as NO including NO, NO_2, PAN, nitric acid, particle nitrate, etc.) NO_2, NO, in situ hydrocarbons (canisters), SO_2, CO, temperature, dew point, altitude, position, UV radiation, PAN, formaldehyde and other carbonyls, hydrogen peroxide, hydroxymethyl hydroperoxide, methyl hydroperoxide, and aerosol number concentration and size distribution. Most BNL gaseous measurements were reported as 10 s averages. The TVA Bell 205 helicopter measured O_3, NO_y, NO, NO_2, nitrate, SO_2, in situ hydrocarbons (canisters) collected in canisters, altitude, position, temperature, humidity, total peroxide, and hydrogen peroxide. The TVA nitrate system uses a new dual gold tube converter system along with a nylasorb filter on one channel to provide the sum of nitric acid and particle nitrate concentration (by difference) with 5-s response time [*Tanner et al.*, this issue]. Most TVA gaseous measurements were performed with 5 s averages. The NOAA CASA 212 was equipped with a lidar system built by EPA, NOAA, and NCAR to measure the vertical distribution of ozone and aerosol backscattering. By flying above the boundary layer, the NOAA lidar was capable of measuring the ozone and aerosol properties through the boundary layer. Corrections for attenuation of the signal by particles improved the quality of the resulting data. Airborne lidar O_3 measurements were also utilized to map the vertical and horizontal extent of the urban plume. Further details on the instrumentation systems on each aircraft are available in the works of *Meagher et al.* [1996] and *Hubler et al.* [this issue]. In addition to the aircraft measurements, wind profilers were operated at three stations during the study to detail the spatial and temporal variability of the boundary layer depth and wind structure.

3. Results and Discussion

The highest O_3 levels observed at surface stations during the 1995 Nashville SOS Study occurred during a period of air stagnation from July 11 through July 15. (Plate 1 shows the highest 1 hour average which occurred between 1100 and 1800 CDT). It is evident from Plate 1 that monitoring locations within a few kilometers of each other showed significant differences in the maximum ozone levels observed on some of the days. On July 12, for example, the downtown station located atop a 300-foot office building recorded an afternoon maximum over 50 ppb higher than the suburban Youth, Inc. station.

Plate 2 illustrates that during the study period the middle Tennessee region was under the influence of a slow moving broad high-pressure system that was drifting slowly eastward and strengthening. Although the synoptic scale pattern could be described as stagnant, the wind profiler and aircraft data show that subtle changes in the boundary layer flow patterns occurred from day to day and from day to night during the episode with important ramifications for the transport and mixing of emissions from sources in the area. Therefore the discussion which follows is organized so that the flights of July

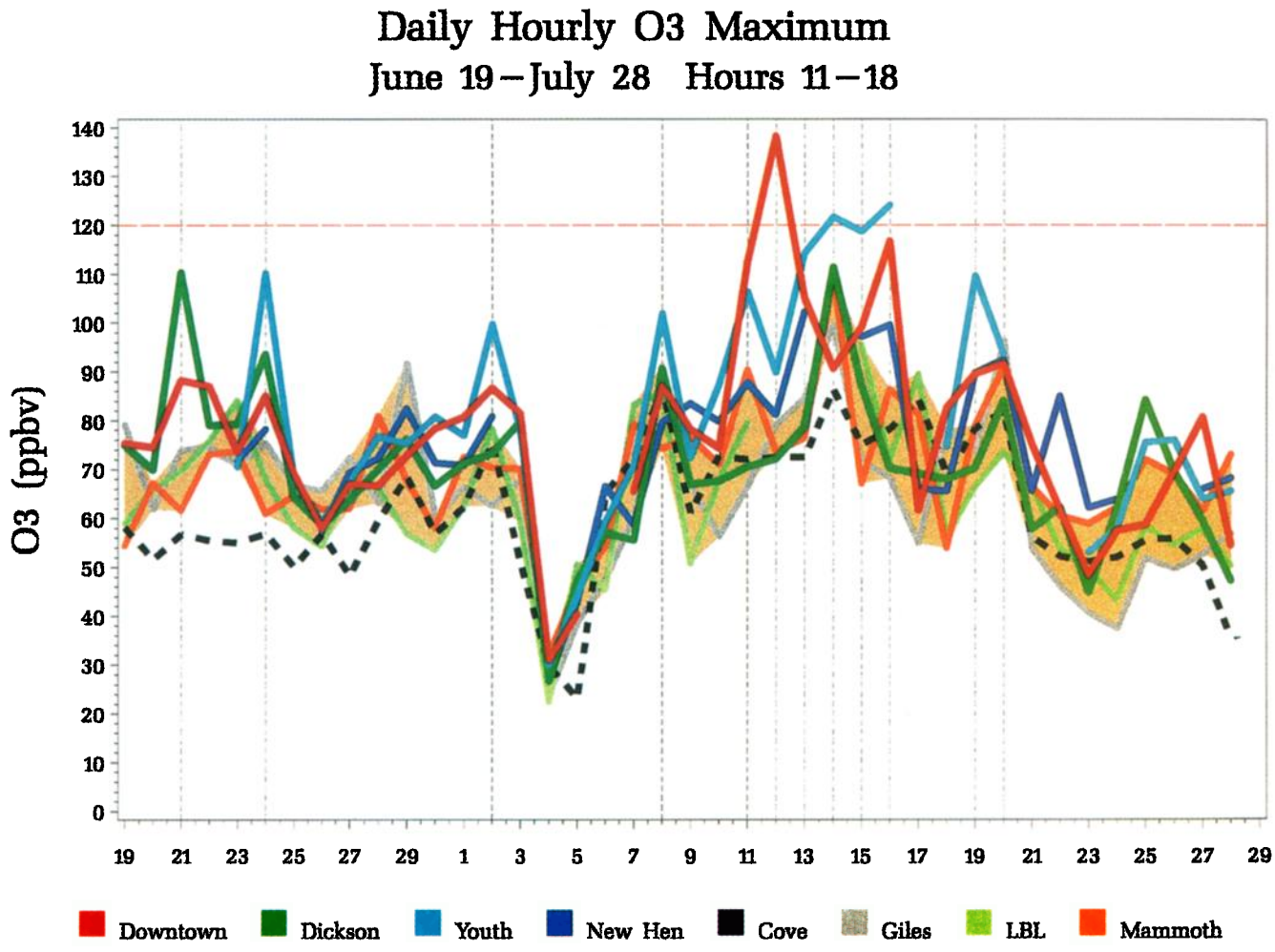

Plate 1. Highest 1 hour average ozone level occurring between 1100 and 1800 CDT for selected stations participating in the Nashville 1995 SOS study. Downtown, Dickson, Youth, and New Hendersonville are in or near Nashville, Cove, Giles, LBL, and Mammoth are regional background stations distant from Nashville. The light brown shaded area indicates the range of the regional background concentrations.

11 and 12 are analyzed as case studies of the meteorological and air quality measurements, with specific research objectives targeted to the particular situation encountered on each of these 2 days.

On July 11 the Gallatin power plant plume drifted southwestward toward the Nashville urban area, and merged with the urban plume. The intensive aircraft monitoring on this day provides information to help answer these research questions. (1) Can ozone formation in the separate plumes be determined, and if so, how does ozone formation compare between the urban and small power plant plume? (2) How does the photochemical aging process in the areal source urban plume compare with the point source power plant plume? (3) Is it possible to apportion the excess ozone observed to the different source types in the mixed urban/power plant plume? (4) How does the relative contribution of the power plant and urban area change as the plumes are transported downwind from the sources? and (5) Are photochemical processes in the plumes and background air NO_x or VOC sensitive?

In contrast to July 11, on July 12 the urban plume did not mix with the Gallatin plume due to a slight wind shift. Therefore the analysis of the urban plume for July 12 focuses on a different set of key research questions. (1) Why did such high ozone levels occur in the downtown district without being observed at any of the other ground monitoring stations? (2) How much of the observed excess ozone is due to local emissions, and how much is due to transport of ozone or precursors into the Nashville area? (3) How widespread (horizontally and vertically) is the zone of elevated ozone on this day? (4) What are the ozone/precursor/products relationships observed the urban plume? (5) How different was ozone formation on this day compared to the previous day when the Gallatin plume did mix with the urban plume? (6) What are the implications of the observations in detecting the peak ozone occurrences in cities the size of Nashville with routine monitoring networks? (7) Do model grid sizes of 10 km or larger provide sufficient resolution to represent the actual spatial variability that exists during a worst case ozone episode in Nashville, or are smaller grid sizes necessary to adequately represent the spatial variability of such a real urban plume?

4. July 11, 1995

4.1. Meteorological Discussion

On July 11 the weak center of high pressure at the surface that had been centered over Missouri the previous day moved

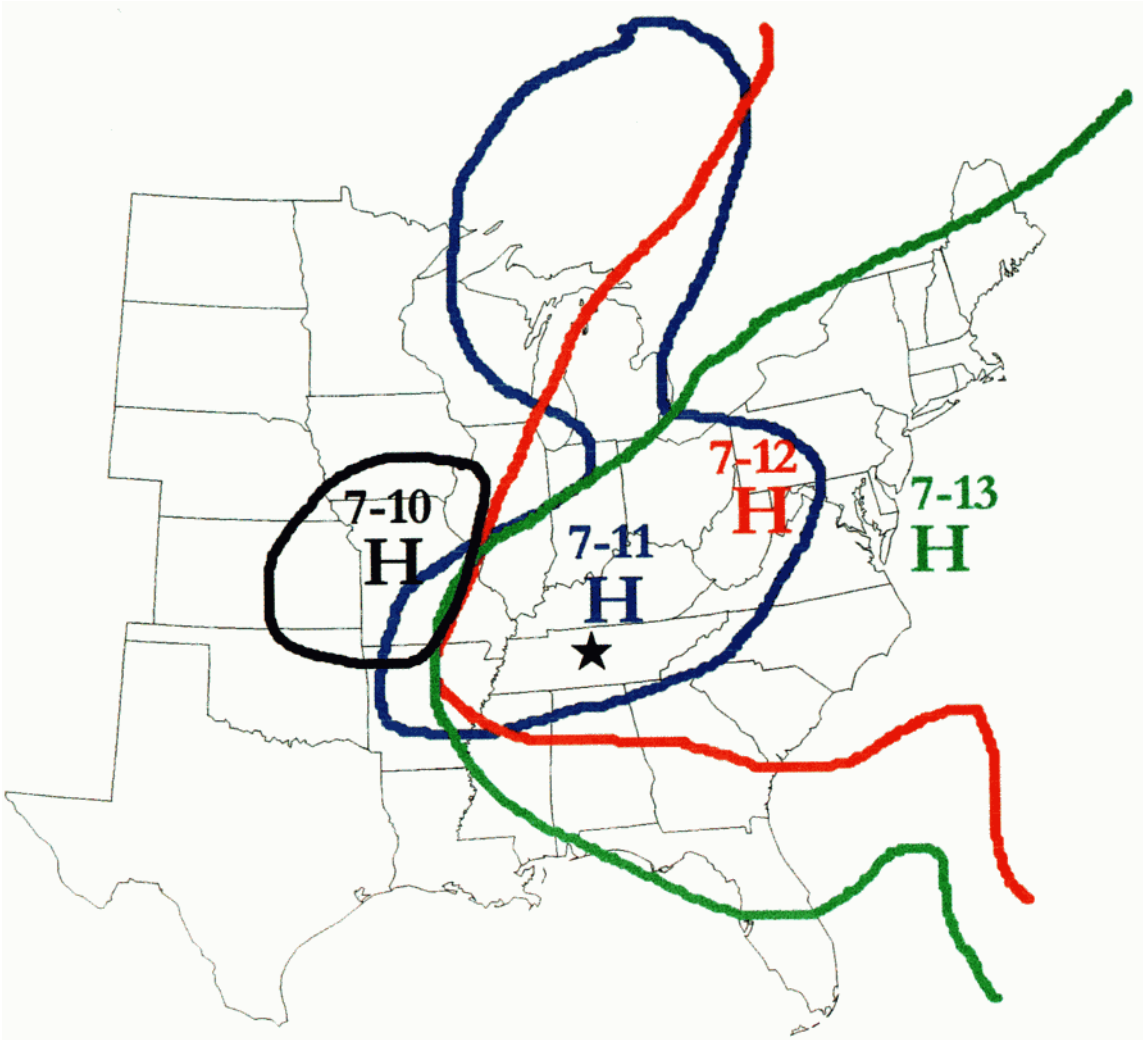

Plate 2. Development and movement of high-pressure system for July 10–13, 1995. The 1016 isobar at 1200 UTC is indicated.

eastward and was centered in central Kentucky, leaving Nashville with sunny skies, very light northeasterly flow in the boundary layer, and hot temperatures in the afternoon. A second lobe of this high was located over the Great Lakes giving a north-south orientation to the ridge pattern. The mixing height in the Nashville vicinity, measured with wind profilers at the New Hendersonville and Youth Inc. sites area, increased from about 700 m at 1000 CDT to a daily maximum near 1500 m at 1500 CDT. The BNL G-1 observed a strong temperature inversion at 1600 m on this afternoon. A profiler located west of the urban area at Dickson measured an afternoon maximum mixing height at 1200 m. Boundary layer winds from the profilers showed similar patterns at the three stations near Nashville with northeasterly flow (5 to 8 m s^{-1}) during the predawn hours throughout the layer from the ground to 2000 m but with a deepening layer of light winds (<2 m s^{-1}) corresponding to the growing boundary layer during the daylight hours. By midafternoon the zone of light and variable winds had grown to a depth of 1500 m, the approximate depth of the mixed layer. By this time, the northeasterly flow was only clearly evident from the wind profiler data at the 2000 m level. For a more detailed examination of the meteorological characteristics of this episode, see the companion paper by *Banta et al.* [this issue].

4.2. Aircraft Research Flight Results

Trace gas data from the aircraft flights over Nashville on July 11 show that the urban plume was drifting slowly southwestward from the city (Plate 3), consistent with the synoptic weather pattern and the wind profiler data. The TVA helicopter and the BNL G-1 both sampled the urban plume on this day providing good coverage and, in addition, a fortuitous opportunity for airborne comparison of plume mapping techniques by the two research groups. Considering that the two aircraft had differences in flight track, altitude, and sampling time and that the maps are interpolated from the data, the similarities in plume position and concentrations are more striking than the differences. The BNL G-1 did observe slightly higher ozone levels (by about 10 ppb at the peak) than did the TVA helicopter. The fact that the G-1 had a cruising altitude about 100 m above the helicopter may have contributed to this difference. Since the TVA Gallatin power plant is located east-northeast of the city, its plume meandered across the southern portion of the city where it merged with the urban plume (see the TVA helicopter SO_2 panel in Plate 3). On this highly reactive day the plume from the Gallatin plant had already reached stage 3 (excess ozone even in the plume core) before reaching the edge of the urban area (only 20 to 30 km

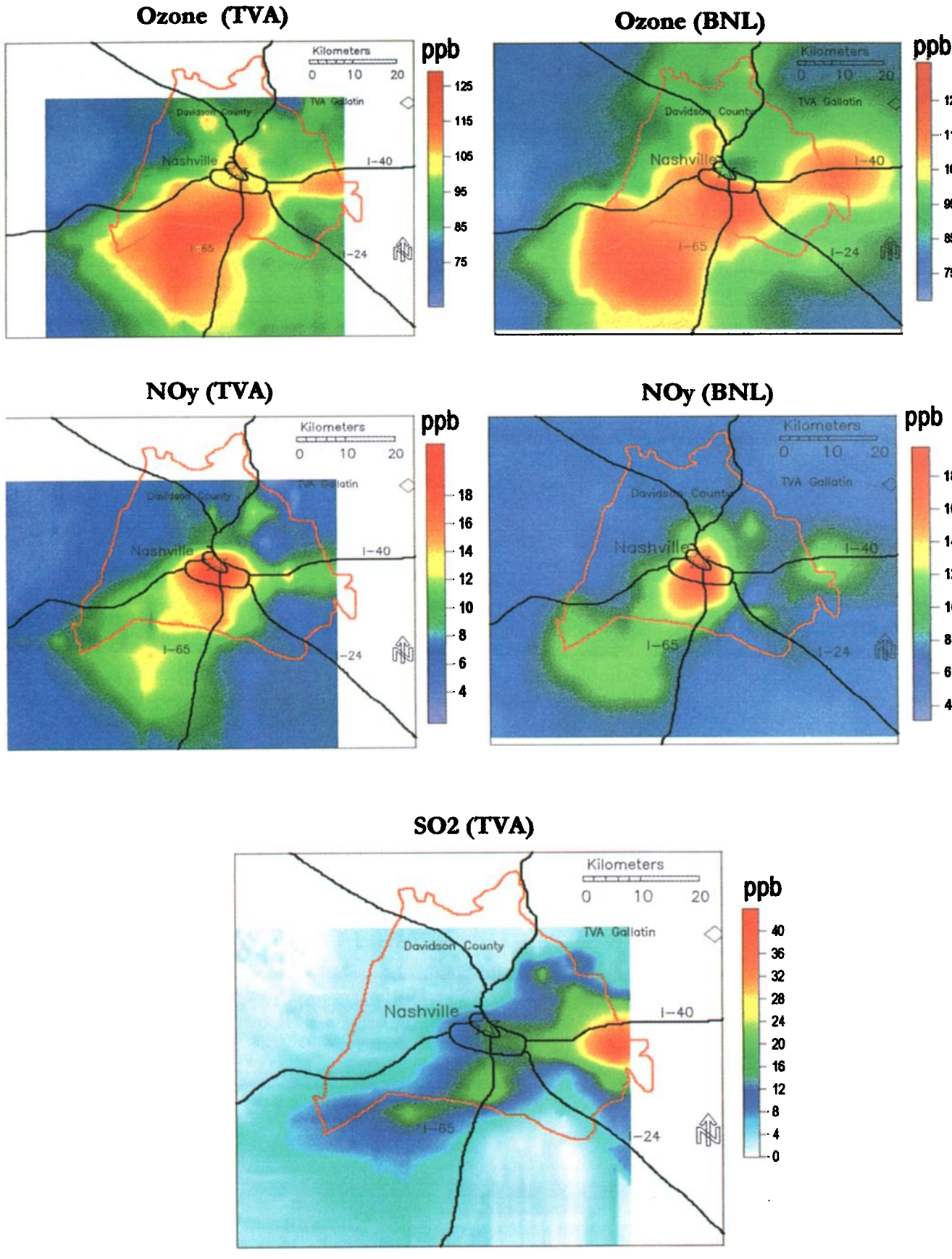

Plate 3. Maps of ozone, NO_y, and SO_2 interpolated from the flight data for July 11, 1995, from the TVA helicopter and the BNL G-1. Interstate highways (I-65, e.g.) in the region are indicated by black lines. All concentrations are in ppb.

from the plant). It is important to emphasize that although this is a very short distance, the light winds indicate that 3 to 4 hours travel time were required for the plume to reach this point. As a result, this day provides an excellent case study of interactions between the urban and power plant plumes and an opportunity to investigate the ozone formation in the two plumes under similar transport, solar radiation, and mixing height conditions.

The air in the background outside the urban and power plant plumes was characteristic of a photochemically aged air mass. In other words, the levels of primary emissions were low, and most of the NO_y was present as photochemical reaction products rather than as NO and NO_2. The term photochemical age represents the ratio NO_z/NO_y, where NO_z is $NO_y - NO_x$ Afternoon ozone concentrations ranged from 70–85 ppb with slightly higher levels north of the city, NO_y was composed mostly of NO_z giving a photochemical age near 0.90, total peroxide ranged from 5 to 7 ppb, SO_2 levels were generally less than 3 ppb, and CO concentrations ranging from 160 to 280 ppb. In the background air the ratio of total peroxide to NO_z ranged from 1.2 to 1.6 with the highest ratios coinciding with the highest ozone concentrations. The generally high values of this ratio imply that the O_3 production in the background air was limited by NO_x, which is consistent with the low observed NO_x concentrations.

The plume traverses from this afternoon may be divided into three categories to organize the analysis: (1) The Gallatin power plant plume upwind of the urban area, (2) the Nashville and Gallatin plumes mixing over the city, and (3) the Nashville and Gallatin plumes mixed downwind of the city.

4.2.1. Gallatin plume upwind of the urban area. Both the helicopter and the G-1 performed N-S traverses of the Gallatin plume 25 to 30 km southwest from the power plant near the northern end of the Percy Priest reservoir. At this location the plume had not yet reached the eastern fringe of Nashville, and the high SO_2 levels accompanied by the absence of significant excess CO above the background, suggesting little urban influence at this point, confirm that this plume is clearly dominated by the power plant at this point. Peak concentrations from the G-1 at this distance were the following: $SO_2 = 50$, $NO_y = 13$, $NO_x = 2.8$, and $O_3 = 130$ ppb. Despite the relatively short distance from the stack, the evidence indicates that plume emissions of NO_x had reached photochemical maturity, the photochemical age (NO_z/NO_y) measured by the TVA helicopter had reached 0.7 to 0.8, and the excess ozone was maximized at the plume centerline. The strong photochemical reactivity on this day, the light wind speed, and the relatively small size of the Gallatin NO_x source (30,000 T/yr) all contributed to the photochemical maturation of the plume so close to the source. The slope of the O_3 versus NO_z plot from the G-1 sampling of the Gallatin plume at 25 km was 7.6 with $r^2 = 96.5\%$. NO_z represents a portion of the reaction products of the process that forms the excess ozone. Therefore the slope gives an indication of the efficiency of ozone (more ozone molecules per NO_z observed). The slope of 7.6 is fairly typical for ozone production. Values as high as 10 or so are sometimes seen in very highly ozone productive plumes. Ten kilometers farther downwind, as the plume approached the edge of the city, the TVA helicopter found that nearly all the NO_x from Gallatin had been photochemically consumed and that centerline ozone concentrations were beginning to drop off. Clearly, the Gallatin plume had reached photochemical maturity before reaching the city. Although this occurred a relatively short distance from the plant, the travel time involved is estimated at greater than 4 hours based on the boundary layer wind profiler data at plume height.

4.2.2. Nashville and Gallatin plumes mixed over the city. The infusion of urban emissions rekindled the ozone production photochemistry as the Gallatin plume drifted southwestward across the urban area. For example, the SO_2 panel in Plate 3 clearly shows its centerline position passing just southeast of the urban center. This broader plume, now a mixture of aged Gallatin and relatively fresh Nashville emissions (see the NO_y panels in Plate 3), was sampled N-S by the TVA helicopter and on a NW/SE diagonal by the BNL G-1. Ozone levels increased again to near 135 ppb in the center of the combined plume immediately downwind of the Nashville traffic loop (Interstate-440), less than 5 km from the downtown district. Ozone remained at these levels for a distance of about 40 km to the southwest and then dropped off rather abruptly. It is clear, by reviewing the SO_2 and ozone patterns of Plate 3, that the higher ozone levels appear where the aged power plant plume extensively overlapped the urban plume. Other maximum levels observed over the city were $SO_2 = 15$, $CO = 425$, $NO_y = 22$, and $NO_x = 8$ ppbv. Over the urban area, calculated NO_z/NO_y ratios of as low as 0.4 to 0.5 were found, consistent with mixing in of fresh NO_x emissions from the city. As in the Gallatin plume, a significant depression in total peroxide was observed in the plume center. In this instance, edge concentrations averaged 7.5 ppb, and plume center total peroxide was about 2 ppb lower at 5.5 ppb.

The O_3 versus NO_z plots for the mixed plume provides useful information. The plot shows nonlinearity with the slope flattening at the urban plume center. The average slope was 5.9 with $r^2 = 92.7\%$, showing surprisingly little scatter considering the complexity of the plume. Ozone correlated fairly well with CO (slope 0.22, $r^2 = 80\%$), consistent with the increasingly urban character of the plume. As observed for the Gallatin plume alone, the mixed plume tended toward VOC limitation at the plume center and NO_x limitation at the edges.

4.2.3. Nashville and Gallatin plumes mixed downwind of the city. Both the helicopter and the G-1 observed the mixed urban and Gallatin plume, with maximum ozone concentrations of near 135 ppb (65 ppb above the regional background) extending from a few kilometers downwind of the center city to about 40 km downwind. A broad SO_2 maximum (the Gallatin plume) is clearly seen superimposed on the urban plume and coinciding with the maximum ozone levels. A very important and difficult challenge is to determine how much of this excess ozone is due to Nashville urban emissions and how much is due to emission from the Gallatin power plant. It is stressed that the analysis which follows is only an estimate and that it is difficult to provide uncertainty estimates for the calculations. If we assume that SO_2 is a conservative tracer of the Gallatin plume, then we can estimate the respective contributions of the power plant and of the urban area to the maximum excess ozone in the combined plume at various distances downwind. Two different approaches to making this estimate are presented.

The first approach is use the downwind changes in SO_2 to determine how much the power plant plume has been diluted from the point at which it stopped producing ozone (fortuitously occurring just upwind of the city on this day), thereby finding an upper limit to the power plant ozone present in the composite plume downwind of the city. Excess SO_2 concentrations of 14 ppb above background were measured by the TVA

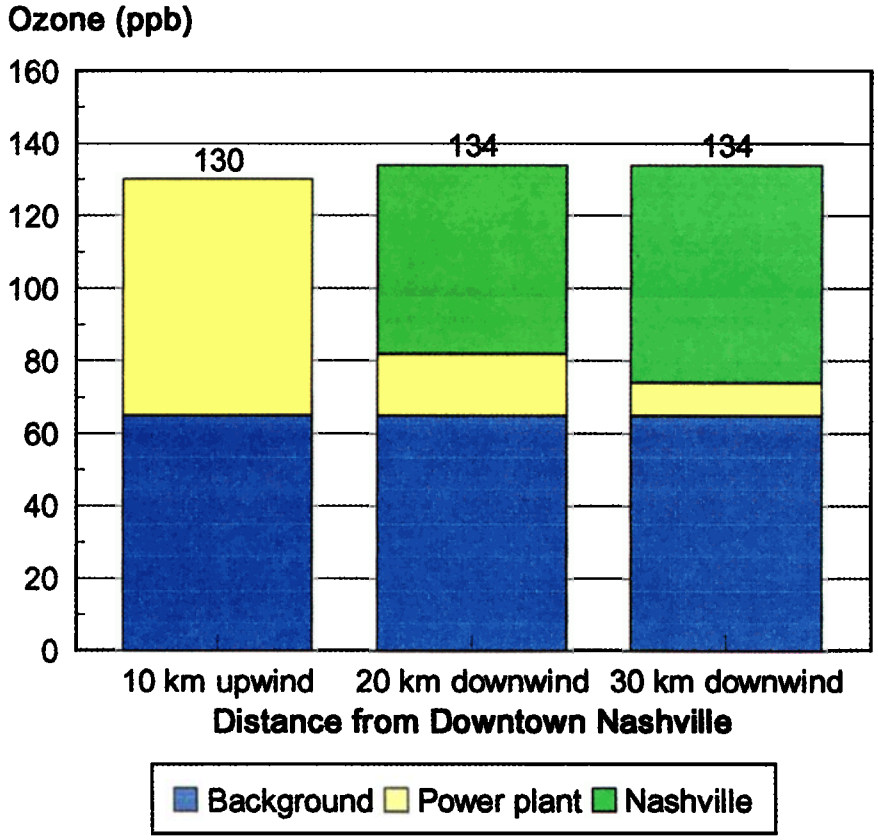

Plate 4. Apportionment of plume centerline ozone to source types for July 11, 1995.

helicopter in the composite plume centerline 20 km downwind of Nashville. This compares with an excess SO_2 of 50 ppb at the Gallatin plume centerline at the point where it had essentially exhausted its ozone forming potential upwind of the city. Therefore, assuming that the power plant ozone is simply being diluted from this point onward (i.e., ignoring deposition), the power plant's contribution to the excess ozone in the composite plume at 20 km downwind of the center city is no more than 14/50 of the excess ozone (65 ppb) found in the mature Gallatin plume centerline 25 to 30 km downwind of the power plant. This suggests that at 20 km from Nashville at the beginning of the ozone maximum in the urban plume about 17 ppb of the excess ozone is due to Gallatin, leaving about 48 ppb derived from the urban plume. The uncertainties of this analysis are admittedly difficult to quantify and stem from the facts that the ozone is probably depositing faster than the SO_2, that the flight tracks yield traverses that are not strictly Lagrangian in character, that the boundary layer is changing height as the day progresses, etc. Because of these difficulties, we also used another approach as described below to attempt to provide another estimate of the urban/power plant ozone apportionment for the mixed plume.

The second approach to addressing this same question uses the ratio of excess NO_y to excess SO_2 in traverses of the power plant plume upwind of the city. This ratio and the measured SO_2 in the composite plume are used to determine the power plant contribution to the NO_y and hence to the ozone present in the composite urban and power plant plume. A plot of excess NO_y versus excess SO_2 in the Gallatin plume alone from the G-1 data yields a slope of $dNO_y/dSO_2 = 0.121$. The peak SO_2 in the composite urban power plant plume measured by the G-1 is about 15 ppb; therefore the maximum power plant contribution to the NO_y in the composite plume is expected to be $0.121 \times 15 = 1.8$ ppb. Since the ozone to NO_y ratio was near 8.3 for this plume, the ozone due to the power plant would be expected to be near $(8.3 \times 1.8 \text{ ppb}) = 15$ ppb. This is quite similar to the 17 ppb estimated from the first approach. This approach also has uncertainties deriving from varying deposition rates for NO_y species, different O_3/NO_y relationships may exist for the background, power plant, and urban air parcels, and a possible change from NO_x control to VOC control as the plume advances from background to power plant to the urban area. Nevertheless, it is encouraging to see that two different techniques based on rather different assumptions yield similar estimates of urban/power plant ozone apportionment in the mixed plume.

Applying the above analysis technique to the helicopter plume measurements at various distances from the emission sources, we proceed to apportion the ozone observed to the power plant and the urban area. The results of this analysis (Plate 4) show that although the plume centerline concentrations were about the same (130 ppb) 10 km upwind and 30 km downwind from Nashville, the causes of observed excess ozone were decidedly different. As the diluting mature power plant plume merged with and moved through the city, there was a clear change from dominance of the observed centerline ozone by the power plant to dominance by the urban source.

4.3. NO_x Versus VOC Sensitivity

The peroxide to NO_z ratio has been proposed as an indicator of VOC versus NO_x sensitivity [*Sillman et al.*, this issue]. Plate 5 shows a map of the total peroxide to NO_z ratio in the

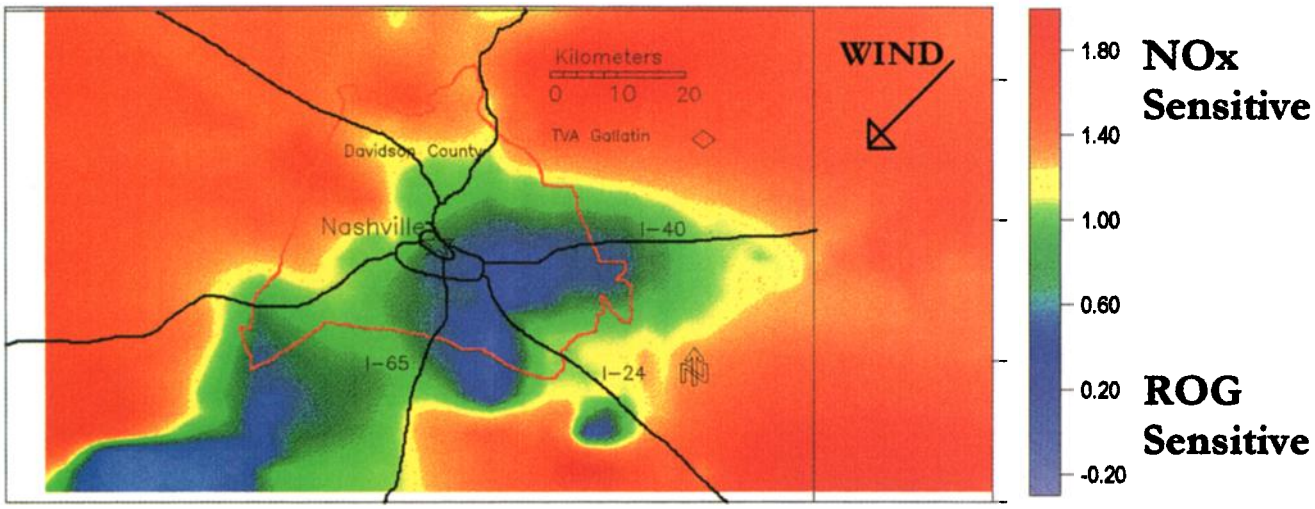

Plate 5. Total peroxide to NO_z ratio for the afternoon of July 11, 1995. Map interpolated from BNL G-1 data.

Nashville area from the BNL flight of July 11. In interpreting this information it is important to stress that this map represents a kriged field derived from the flight data and provides less than ideal information where data are sparse. For example, the gap in the deep blue section of the plume that occurs southwest of the city is an artifact due to sparse data in that area. Nevertheless, the evidence suggests that the background air and the fringes of the mixed urban/power plant plume are NO_x sensitive but that the core of the plume is VOC sensitive as well. These observations are consistent with the abundance of natural hydrocarbons in the regional background air and the abundance of NO_y in the core of the mixed plume drifting across the urban area.

5. July 12, 1995

On July 12, 1995, the ground-based ozone monitors in and around Nashville recorded some unexpected results: most of the suburban and rural stations recorded afternoon ozone maxima of less than 90 ppb; however, the downtown station recorded over 130 ppb in midafternoon, the highest ozone levels of any station during the 5 week study (Plate 1). This result is surprising for two reasons. First, with the relatively dense network of monitoring stations deployed for the Nashville SOS intensive, a 50 ppb difference in peak afternoon ozone between the highest and second highest monitoring stations in and around the urban area was not expected. In addition, it was surprising to see the highest ozone levels in the center city where titration of ozone by fresh NO emissions is typically observed throughout the day.

5.1. Meteorological Discussion

On July 12 the northern lobe of the high-pressure system drifted eastward to New York and Pennsylvania, while the southern lobe remained over the Tennessee Valley leaving the axis of the ridge oriented from southwest to northeast. The ridge was very broad, and pressure gradients were very weak over the study area. July 12 was another hot day in the Nashville area with very hazy skies and high insolation. Winds continued to be very light over the area with boundary layer wind profilers showing little air movement during the daylight hours. Profiler winds up to 1000 m were generally less than 2 m s^{-1} from midmorning through midafternoon. Mixing heights rose rapidly from around 500 m at 1000 CDT until noon then more slowly until maximum boundary layer depth was reached at about 1500 CDT: approximately 1700 m at the New Hendersonville and Youth, Inc. sites and 1100 m at the Dickson site. As on the previous day, the more rural Dickson site showed a lower mixing height than the urban/suburban sites.

5.2. Flight Results

On July 12 the TVA helicopter performed in situ transects, and the NOAA Casa 212 performed remote lidar sensing over the Nashville urban area. The urban plume showed very little transport with a slight drift toward the south southeast. The wind profiler data and the ground wind monitors confirm that winds were nearly stagnant on the afternoon of July 12 with most boundary layer observations showing less than 2 m s^{-1} wind speed. Although the boundary layer winds were extremely light, the change in wind direction from northeast the previous day to north northwest on July 12 prevented the Gallatin plume from mixing with the urban plume on this day. This presents an excellent opportunity to study the ozone formation in the isolated urban plume and to compare ozone formation to the mixed plume of July 11.

Plate 6 depicts the afternoon mixed layer observations from the helicopter, providing a detailed image of the primary and secondary photochemical pollutants and revealing several important facts. The ozone panel shows a clearly defined ozone bulge over and just downwind of the city compared to background levels. Ozone concentrations within the urban plume peaked near 140 ppb, whereas the background air concentrations upwind of the city were only 60 to 70 ppb. The dimensions of the plume were clearly identified by the aircraft and merit discussion. The ozone plume is only about 10 km wide and extends no more than 20 km from the center city where it ends quite abruptly. In fact, the gradient in ozone at the east and west sides of the plume appears similar to the gradient at the southern end of the plume. Plate 7 shows the ozone data for several heights from the NOAA Casa 212 mapping the vertical extent of the ozone bulge through the boundary layer. The NOAA lidar ozone maximum is not quite as high as the helicopter ozone maximum, but the flight tracks and times are not identical. The NOAA lidar aircraft crisscrossed directly

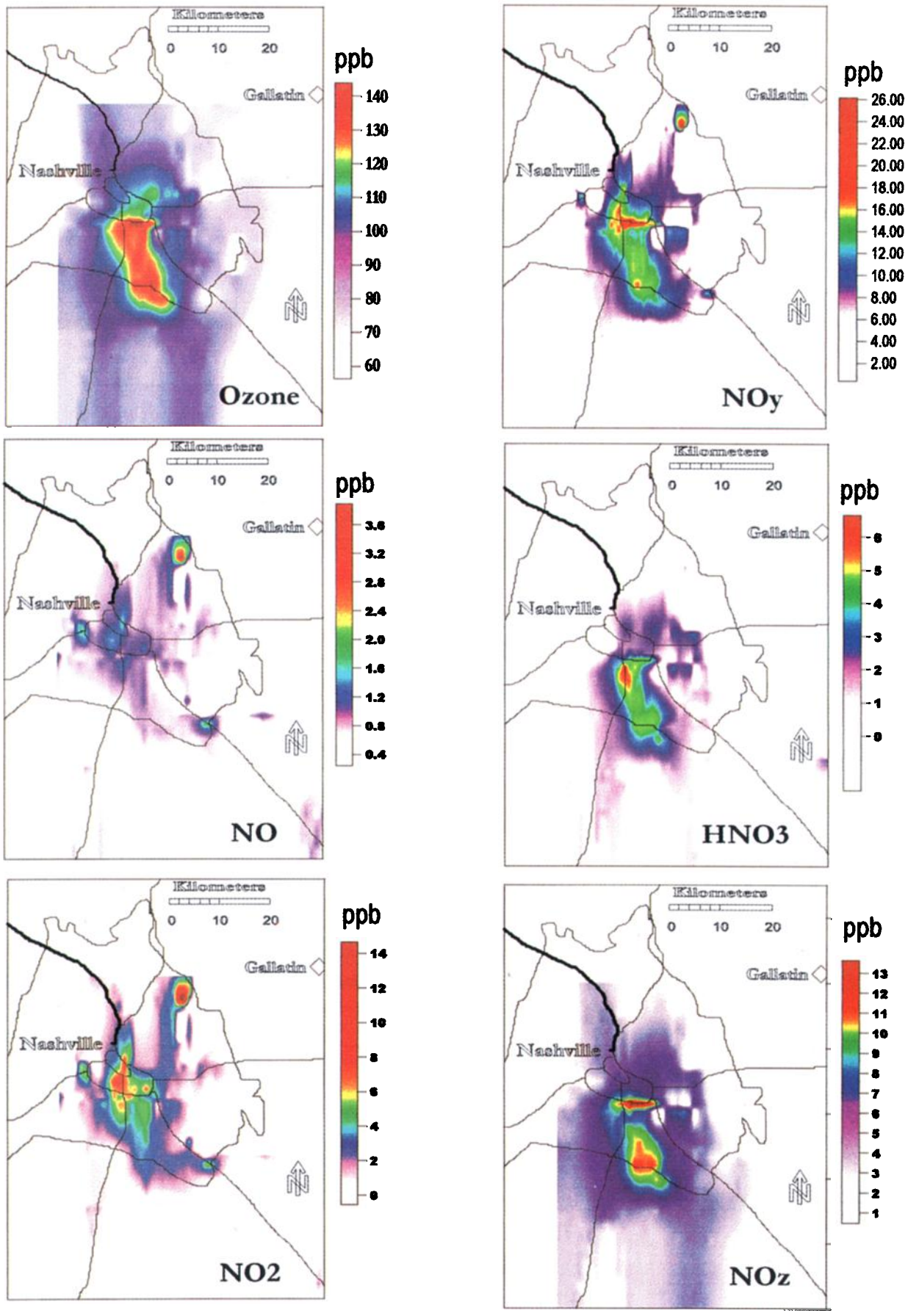

Plate 6. Ozone, precursors, and products for the afternoon of July 12, 1995. Maps interpolated from TVA helicopter data. All scales are in ppbv.

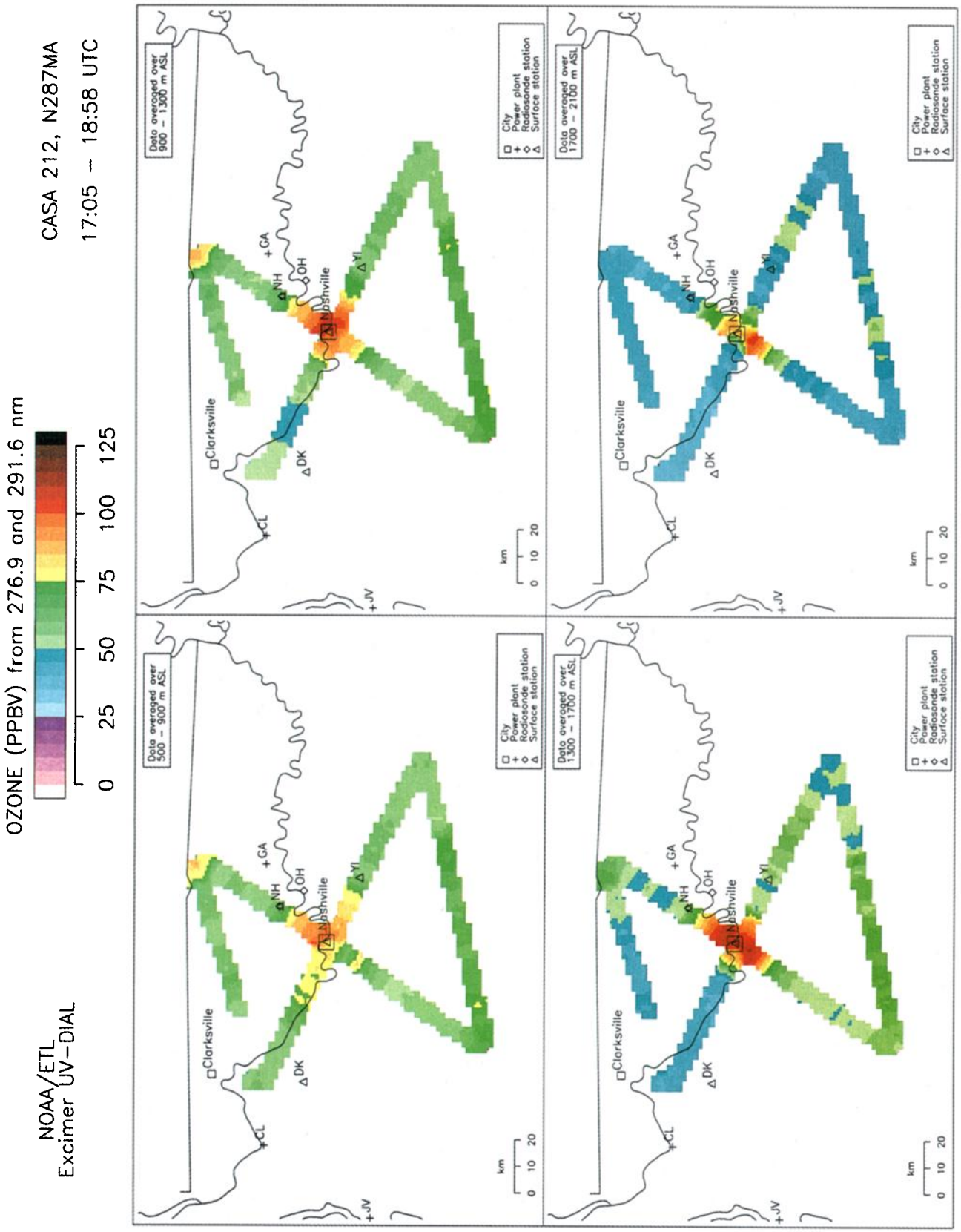

Plate 7. NOAA Casa 212 lidar ozone data averaged over four layers near noon on July 12, 1995.

over the center city, and the maximum ozone in the plume was slightly south of the city as shown by the helicopter traverses. Both the helicopter and the lidar aircraft show elevated ozone levels in the Nashville vicinity, but quantitative comparisons are not appropriate due to the different flight tracks and times of observation.

The speciated NO_y measurements reveal the chemical transformations occurring within the urban plume. The spatial correlation between ozone and NO_y is immediately apparent by comparing these two panels in Plate 6. The primary emissions from Nashville are suggested in the NO panel of Plate 6, but the NO reacts away so quickly that the NO_2 and NO_y maps give a better visualization of the primary emissions source area. Another apparent source of NO was detected northeast of the city near the Davidson county line coinciding with the location of the DuPont Rayon City plant. Background NO was quite low with upwind concentrations generally much less than 1 ppb. The NO_2 panel also reveals low background/upwind levels and elevated NO_2 appearing over and just downwind of the city. Spatial distribution of the termination products HNO_3 and NO_z is quite similar to that of ozone, and the maps for O_3, HNO_3, and NO_z clearly indicate the shape and extent of the urban plume. It is also interesting to note that concentrations of the termination products are peaking only slightly farther downwind than the NO and NO_2, a result of high photochemical reactivity and very light wind speeds. Thus the urban plume appears to end abruptly just south of the Davidson County boundary.

During this day of the ozone episode the regulatory ozone monitors missed recording the high levels that occurred. The downtown research station (not part of the routine regulatory network) was the only ground station that was impacted by the plume on July 12, causing the anomalously high ozone concentration. The small size of the plume combined with the limited number of surface monitors reduces the probability that the network will actually record the highest existing ozone concentrations. There is no simple solution for this problem because a network sufficiently dense to guarantee detection of the plume maximum ozone on this day would be prohibitively expensive. For this reason, it is also prudent for modelers comparing model output with regulatory field data to bear in mind that monitoring networks are probably underestimating the maximum ozone concentrations and frequency of elevated levels that are actually occurring in a region, sometimes by a substantial margin.

How much of the ozone and precursors present in the measured plume on July 12 came from Nashville, and how much came from sources upwind or locally generated ozone recirculated from previous days? Midboundary layer ozone concentrations within the core of the urban plume were as much as 70 ppb higher than at the same altitude outside the urban plume. With a revised ozone standard set at 80 ppb 8 hour average and background levels as high as 60 to 70 ppb during this episode, it is clear that the combination of elevated background and local ozone is likely to bring levels above the concentration limit for the new standard. The spatial distribution maps of precursor concentrations also indicate the importance of local sources in this episode. Upwind of the urban area the precursor concentrations were very low, and not until the air flowed over the source-rich urban complex did the excess, ozone-producing photochemistry occur. Elevated levels of ozone and precursors observed in Nashville on July 12, 1995, were a combination of substantial amounts of "home grown" ozone, added into an already elevated background air matrix.

The limited spatial extent of the Nashville plume elucidates grid size selection for regional modeling. Grid sizes geared toward simulating urban ozone episodes need to be carefully reevaluated in the light of these observations, especially for cities similar to Nashville. A 20-km grid cell could contain the entire urban plume on July 12, including both fringes, the core, as well as a sizable amount of background air, zones with distinctly different chemistry. Clearly, a finer grid structure (1 km, e.g.) is more appropriate to model this type of worst case ozone episode for Nashville and likely for other medium- to large-size cities as well.

6. Comparing Ozone Formation in Urban, Power Plant, and Mixed Plumes

What similarities and differences are noted between the urban plume, the power plant plume, and the mixed plumes on July 11 and July 12? In order to place these comparisons on an equal footing it is important to consider first that as a plume ages chemically, the mixture of ozone, precursors, and photochemical reaction products changes dramatically. Fresh plumes contain much NO_y (primarily as NO_x) but little and even negative ozone above background. As the plume ages and more of the NO_x is processed through the photochemical cycle, ozone increases, NO_x drops and NO_z compounds such as PAN and nitric acid increase. At some point a plume becomes "burned out" or mature, and little additional ozone is produced. The plume is then primarily diluting and depositing as it is advected by the wind. See *Gillani et al.* [this issue] for a detailed discussion of the photochemical aging process as observed in the Nashville SOS study. To further complicate the picture, deposition of all species occurs at different and varying rates depending on chemical properties of the species, turbulence, ground surface type, and whether or not the plume is in contact with the ground [e.g., *Shepson et al.*, 1992; *Wu et al.*, 1992]. The concept of photochemical age, the fraction of the nitrogen oxide species that are observed as reaction termination products, (NO_z/NO_y) or equivalently ($1 - NO_x/NO_y$), helps to clarify the analysis. By organizing data from traverses of different plumes and different days by chemical age, more meaningful comparisons may be performed.

Plate 8 shows TVA helicopter data on excess ozone formation (ozone + NO_2 above background/NO_y above background), abbreviated $\Delta O_x/\Delta NO_y$, versus chemical age, measured at the same time for the urban, power plant, and mixed plume types studied on July 11 and 12. Several important facets of the photochemical processing are revealed by this data presentation. At photochemical ages of less than about 0.4 there is little excess ozone per molecule of NO_y present for any of the plume types ($\Delta O_x/\Delta NO_y$ is about 1 or less). As the photochemical age increases from about 0.4 to about 0.7, the plumes are actively producing ozone, and the $\Delta O_x/\Delta NO_y$ is elevated. At photochemical ages from 0.7 to about 0.9 the plumes are well aged. It is at the point of chemical maturity that the most meaningful comparisons may be made among the plumes. Focusing on the points at chemical maturity ($NO_z/NO_y > 0.7$), the July 11 urban, power plant, and mixed plumes show very similar ozone-NO_y relationships with most values of $\Delta O_x/\Delta NO_y$ between 5.0 and 7.0. There is a suggestion that the centroid of the cluster of power plant data points is slightly above that of the mixed plume points, but there is substantial

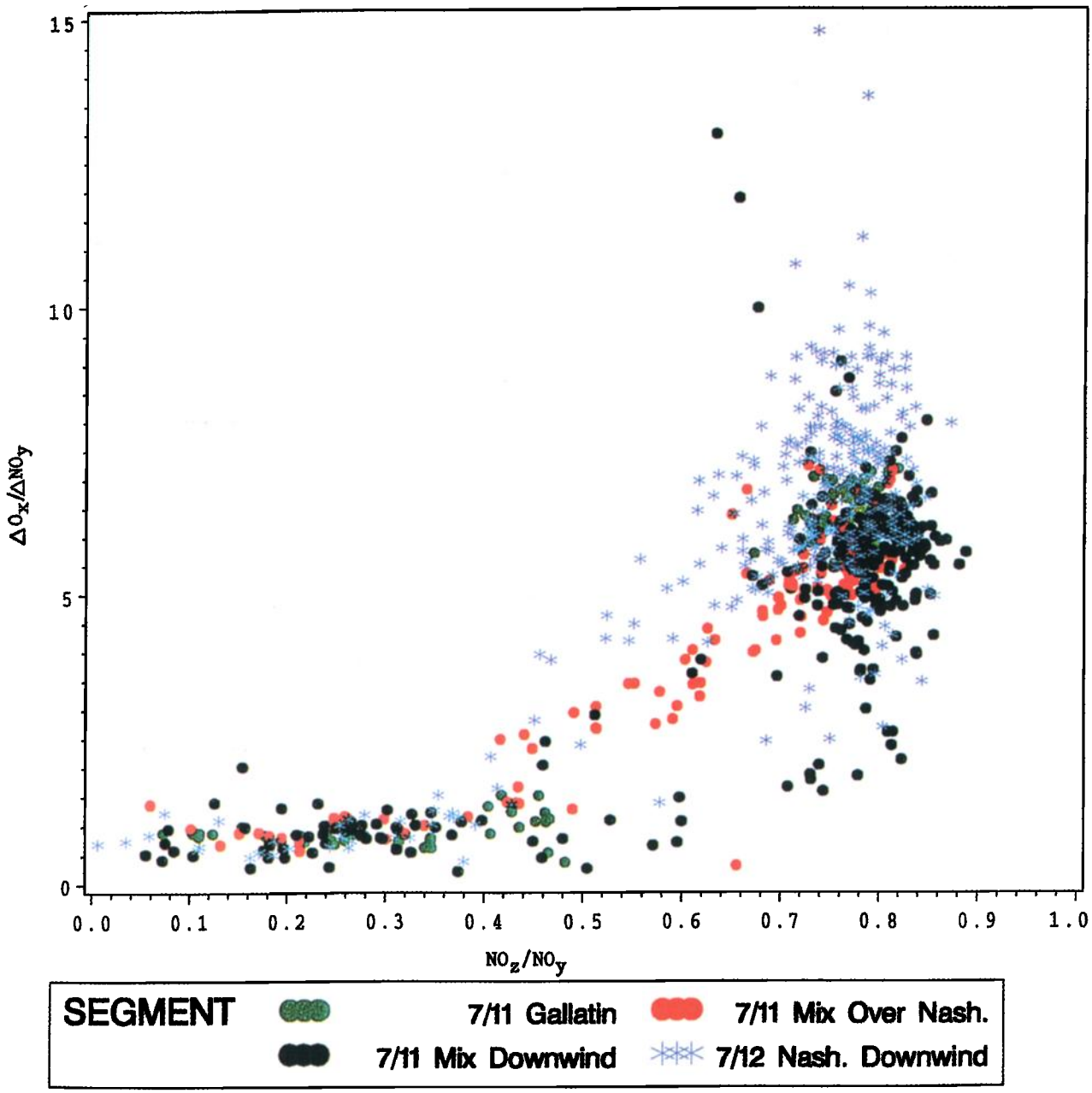

Plate 8. Ratio of excess ozone plus NO_2 to excess NO_y observed for isolated and mixed Nashville urban and Gallatin power plant plumes, plotted as a function of photochemical age for July 11 and 12, 1995 (flights 14 and 15). TVA helicopter data.

scatter of the data. The pure urban plume data from July 12 also show $\Delta O_x/\Delta NO_y$ mostly between 5.0 and 7.0 at chemical maturity, overlapping those of the mixed and separate plumes of the previous day. However, there is also a fairly large number of data points in the mature, isolated urban plume (photochemical age above 0.7) with $\Delta O_x/\Delta NO_y$ in the range from 7.0 to near 9.0, values largely absent the previous day.

7. Summary of Findings

During the 1995 Nashville SOS study the highest ozone concentrations observed occurred when very light winds and high solar radiation created an air stagnation episode highly favorable for photochemical ozone production. Extensive aircraft sampling of the plume using both in situ and remote sensing techniques permitted thorough mapping of its geographic extent. Because of the very light winds, the Nashville plume consisted of an unexpectedly small intense blob rather than an elongated plume. The entire urban plume in midafternoon measured only about 10 km wide by 20 km in length. Two important consequences of this phenomenon are that operating regulatory monitors missed peak ozone occurences and that modelers may need to use smaller grid sizes for urban plumes from cities such as Nashville, especially when modeling worst-case episodes.

The aircraft flights data permitted a quantitative comparison of the concentrations upwind and downwind of the city, and analysis of these data in the light of the new NAAQS for ozone lead to some important findings. On July 12, for example, the

data show that boundary layer air flowing into Nashville contained 60 to 70 ppb of regional background ozone and that the urban area added as much as 70 additional ppb bringing the core of the urban plume core up to 140 ppb ozone. Plate 4 shows a somewhat similar situation on the previous day with slightly lower concentrations but with interacting urban and power plant emissions. The newly promulgated NAAQS for ozone in the United States is set at the level of 80 ppb, 8 hour average. During this stagnation episode, background concentrations in the mid south were only 10 or 20 ppb less than the level of the new standard. Clearly, there is a strong likelihood that the ozone additions from the Nashville plume (or from a city similar in size and emissions mix to Nashville) during a summertime stagnation episode such as this will cause ozone levels to rise above the level of the 80 ppb standard.

In the light of these observations, abatement strategies for stagnation episodes under the new standard will need to carefully assess the relative contributions from current day local emissions, the previous day's local and subregional emissions (which contribute to the subregional background), and the longer time, longer range transport background influence. In a companion paper [*Banta et al.*, this issue] we investigate in detail the apportionment of the measured ozone levels to these source influences for several days of this same stagnation episode.

The plume from a small power plant located only 40 km from Nashville was observed to reach chemical maturity before it reached the city and mixed with the urban plume during the episode (July 11). Winds were very light, and transport time to maturity was at least 3 hours despite the short distance from the plant. Comparisons on the same day of ozone-NO_y relationships (normalized for photochemical age) between the mature small power plant plume and the mixed plume (dominated by the urban emissions) showed very similar values. Plumes from larger power plants would not necessarily be expected to show similar behavior. See *Gillani et al.* [this issue] for an in-depth comparison of large and small power plants for a variety of sampling days. On the following day the isolated urban plume was found, on average, to exhibit slightly higher ratios of excess ozone to excess NO_y. Assessment of NO_x-VOC indicator species suggests that the background air is NO_x-sensitive, whereas the core of the urban and mixed plume is likely sensitive to both VOC and NO_x levels. Analysis of the chemical composition of the urban plume shows that during this episode the plume reached photochemical maturity before traveling very far from the city and that upwind sources contributed only modestly to the elevated levels of ozone and precursors that were observed.

Profiler data showed that boundary layer winds, although very light during the daylight hours, increased substantially during the night, leading to nocturnal spreading and stretching of the previous day's plume above the nocturnal inversion. This is the reason that each day of the episode appears to begin with a relatively "clean slate." This also explains, in part, the rather abrupt end of the plume downwind of the city in the afternoon. The abrupt end of the plume in the afternoon probably represents the air that was over the city when the morning slowdown in the boundary layer winds began.

The data set collected by the SOS investigators in Nashville provides a detailed look at the geographical extent and the chemical composition and dynamics of urban and power plant plumes in the region. This work represents the beginning of a detailed analysis geared toward developing an improved understanding of photochemical ozone production. Finally, this effort shows the value of collaborative scientific field measurements from multiple airborne and surface platforms in developing a more complete picture of the chemistry and transport of photochemical O_3 in the troposphere.

Acknowledgments. The authors are deeply indebted to all the people and organizations involved in the Nashville 1994 and 1995 efforts. A few deserve special mention: Ellis Cowling and the SOS Office of the Director, Danny Duke, Larry Gautney, Richard Gillingham, Terry Hering, Jim Hill, Bob Imhoff, Larry Morris, Bill Parkhurst, Tracy Rosado, Jason Scarbrough, Esther Sparks, Stevens Aviation, and Myra Hendrix Valente. This research is part of the Southern Oxidants Study (SOS), a collaborative university, government, and private industry study to improve scientific understanding of the accumulation and effects of photochemical oxidants. Financial and in-kind support for SOS research and assessment activities is provided by the Environmental Protection Agency, National Oceanic and Atmospheric Administration, Department of Energy, Tennessee Valley Authority, Electric Power Research Institute, The Southern Company, Coordinating Research Council, and the States of Alabama, Florida, Georgia, Kentucky, Louisiana, Mississippi, North Carolina, South Carolina, Tennessee, and Texas. Although the research described in this article has been funded wholly or in part by the Environmental Protection Agency under assistance agreement CR817732 to Georgia Institute of Technology (ONA), it has not been subjected to the Agency's peer and administrative review, and therefore may not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

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(Received August 27, 1997; revised May 13, 1998; accepted May 13, 1998.)