WEEKDAY/WEEKEND DIFFERENCES IN AMBIENT OZONE AND PARTICULATE MATTER CONCENTRATIONS IN ATLANTA AND THE SOUTHEASTERN UNITED STATES

Final Report

CRC Project No. A-47

Prepared by:

Charles L. Blanchard

Shelley Tanenbaum

Envair

January 8, 2005

Coordinating Research Council, Inc.

3650 Mansell Road, Suite 140 - Alpharetta, Georgia 30022

WEEKDAY/WEEKEND DIFFERENCES IN AMBIENT OZONE AND PARTICULATE MATTER CONCENTRATIONS IN ATLANTA AND THE SOUTHEASTERN UNITED STATES

Final Report

CRC Project No. A-47

Prepared by:

Charles L. Blanchard
Shelley Tanenbaum
Envair
526 Cornell Avenue
Albany, California 94706

CONTENTS

WEEKDAY/WEEKEND DIFFERENCES IN AMBIENT OZONE AND PARTICULATE MATTER CONCENTRATIONS IN ATLANTA AND THE SOUTHEASTERN U.S.

Charles L. Blanchard
Shelley Tanenbaum
Envair

Abstract

We quantified changes between weekday and weekend ambient concentrations of ozone precursors (volatile organic compounds [VOC], carbon monoxide [CO], nitric oxide [NO], and oxides of nitrogen [NO_x]) in the Atlanta region to observe whether reduced weekend precursor emissions (as evidenced by ambient measurements of VOC, CO, NO, and NO_x) influenced ambient ozone levels. We analyzed data from air quality monitoring sites in Atlanta and surrounding areas in the Southeast, using data from 1998 through 2002 for CO, NO, and NO_x, and the period 1996 through 2003 for speciated VOC. We observed a strong weekend effect in the Atlanta region, with median daytime (6 am – 3 pm EST) decreases of 62, 57, and 31 percent for NO, NO_x, and CO, respectively, from Wednesdays to Sundays, during the ozone season (March – October). We also observed significant decreases in ambient VOC levels between Wednesdays and Sundays, with decreases of 28 percent for the sum of aromatic compounds and 19 percent for the sum of PAMS target compounds. Despite the large reductions in ozone precursors on weekends, day-of-week differences in ozone concentrations in the metropolitan Atlanta area were much smaller. Averaging over all ozone-season days, the median 1-hour and 8-hour ozone daily maxima on Sundays decreased by 4.5 and 2.3 percent, respectively, from their mean peak levels on Wednesdays, with no sites showing statistically significant Wednesday-to-Sunday differences. When restricted to high-ozone days (highest 3 peak ozone days per day of week per site per year), the median 1-hour and 8-hour ozone daily maxima on Sundays decreased by 11.3 and 9.5 percent, respectively, from their mean peak levels on Wednesdays, with 6 of 14 sites showing statistically significant Wednesday-to-Sunday differences.

Average ozone concentrations in Atlanta were about 10 to 15 ppbv higher than those measured at upwind locations in the ozone season. Regional ozone levels contributed to about 80 percent of the ambient ozone observed in Atlanta. Because of the large influence of regional, upwind ozone on Atlanta's observed ozone levels, the day-of-week differences observed in Atlanta were due in large measure to day-of-week differences in upwind transport conditions.

Because NO levels were lower on Sundays, overnight surface carryover of ozone was greater and morning titration of ozone by NO was reduced, so that local ozone accumulation began earlier on Sunday mornings than on Wednesdays. During mid-day hours, ratios of ozone/NO_x, ozone/NO_y, and ozone/nitric acid (HNO_3) were greater on Sundays than on Wednesdays, indicating that in addition to the titration effect, an increase occurred in the number of ozone molecules formed per ambient NO_x molecule on Sundays. The available data did not allow us to evaluate the effects of changing levels of NO_x on hydroxyl radical concentrations, or if ozone formation rates changed with respect to specific VOC compounds.

We also observed that aerosol black carbon (BC) and organic carbon (OC) decreased on Sundays relative to Wednesdays, with a roughly 30 percent decrease in BC in urban areas and a 10 percent decrease in OC. Nonurban areas experienced smaller Wednesday-to-Sunday differences than did urban locations. Weekend nitric acid and PM nitrate levels averaged lower than weekday levels, but the differences generally were not statistically significant. PM sulfate levels did not vary between Wednesdays and Sundays.

Our analyses of weekday/weekend differences in ozone precursor emissions show that different emission reductions of ozone precursors than normally take place each weekend will be required before significant reductions in ambient ozone can be achieved in the Atlanta area. The principal limitation of our analysis is that current weekend emission reductions are not identical to those that might occur in the future as a result of emission control programs. Regional-scale changes in ozone levels potentially could result from combined urban and nonurban reductions of ozone precursor emissions. However, it is sobering that Atlanta sites exhibited so much difference between the weekend reductions of ozone precursors compared with much smaller changes in ozone levels. Any expectation of future declines of regional ozone concentrations due to precursor reductions in the metropolitan area should be further investigated.

Introduction

The occurrence of generally comparable – or even higher - ambient concentrations of ozone on Saturdays and Sundays than on other days of the week is commonly known as the "weekend ozone effect" (Lawson, 2003). Because emissions of ozone precursors, including volatile organic compounds (VOC), oxides of nitrogen (NO_x), and carbon monoxide (CO) are lower on weekends than on weekdays, the weekend ozone effect is counterintuitive. A weekend effect has been noted for many years and in a variety of locations (Cleveland et al., 1974; Elkus and Wilson, 1977; Graedel et al., 1977; Lebron, 1975; Hoggan et al., 1989). It has been proposed that areas where ozone formation is VOC-limited tend to exhibit higher peak ozone on weekends, due to the more pronounced weekend reduction of NO_x than VOC emissions (Altshuler et al., 1995). Other explanations for higher weekend peak ozone values include possible higher precursor emissions on Friday evenings with carryover to Saturday, increased emissions of VOC in some areas on weekends (including possibly higher ratios of VOC/NO_x), changes in the times of occurrence of emissions on weekends, or increased reactivity of VOC emissions on weekends. The weekend effect in southern California has been studied by Blanchard and Tanenbaum (2003), Fujita et al. (2002, 2003a, 2003b), Larsen (1999), Motallebi et al. (2003), and Yarwood et al. (2003). Fujita et al (2003a) and Lawson (2003) conclude that several of the proposed alternative hypotheses are not supported by ambient data observations and do not explain the weekend effect in southern California, and further conclude that weekend reductions of NO_x concentrations allow ozone to accumulate earlier in the day and to reach higher concentrations compared with weekdays. In contrast, Croes et al. (2003) considered the available air quality data and photochemical models inadequate to conclusively determine the causes of the weekend ozone effect in southern California.

Pun et al. (2003) show that different day-of-week patterns for ozone concentrations occur in Chicago, Philadelphia, and Atlanta. In Atlanta, 1995-99 mean, median, and 90th percentile daily 1-hour ozone maxima generally increased from Mondays or Tuesdays to higher levels on Fridays or Saturdays (Pun et al., 2003).

This manuscript provides further analysis of the ozone weekend effect in Atlanta and its surroundings. We quantify the changes between weekday and weekend ambient concentrations of ozone precursors and ozone, and describe the effects of weekend precursor changes on ambient ozone and particulate nitrate levels in Atlanta and surrounding areas.

Methods

Data Sources. Data were obtained for the years 1998 through 2002 to provide a multi-year record with focus on near-current conditions. EPA AIRS (now AQS) data were obtained for sites in Atlanta and in Fulton County, and for sites in the neighboring counties of Douglas, Cobb, Forsyth, DeKalb, Clayton, Fayette, Coweta, Henry, Rockdale, Gwinnett, and Dawson (Figure 1). These data included measurements of ozone, NO, NO_x, and CO. Ozone data were also acquired for the nearest Clean Air Status and Trends Network (CASTNet) sites (Georgia Station, GA, Sand Mountain, AL, and Coweeta, NC). A variety of gas-phase and particle measurements were obtained from four sites in the Southeastern Aerosol Research and Characterization (SEARCH) network (Hansen et al., 2003): Jefferson Street (Atlanta), Yorkville (GA), Centreville (AL), and Birmingham (AL). Particulate matter (PM) measurements were obtained from EPA's speciated trends network (STN) for all sites in northern Georgia and Alabama. VOC data were available from Photochemical Assessment Monitoring Station (PAMS) measurements at four sites (Yorkville, South DeKalb, Tucker, and Conyers); the years 1996-2003 were included. For both gas-phase and condensed-phase species, the extension of the database to sites in northern Alabama and northern Georgia was intended to provide information on day-of-week concentration variations in areas likely to be upwind of Atlanta on many days.

Statistical Comparisons. Day-of-week averages were determined by hour of the day for hourly data (including CO, NO, and NO_x), and for 24-hour measurements (including particulate nitrate and sulfate). For ozone, day-of-week averages were determined for both peak 1-hour and peak 8-hour concentrations.

For the hourly data, statistical comparisons were made for the hours of 6 am EST (indicative of fresh emissions, typically having maximum morning concentrations) and noon EST (midday, higher photochemical activity), for three-hour intervals (6 – 9 am, 9 am – noon, noon – 3 pm EST), and for daytime (6 am – 3 pm EST) averages.

The ozone comparisons were made using both all ozone-season days and for high-ozone days, the latter facilitating a focus on conditions of greatest regulatory interest. As defined by the U.S. EPA, the ozone season in Georgia extends from March through October (U.S. EPA, 2005). Twenty-one (21) high-ozone days were selected from each year by determining the top three ozone days for each day of the week and each year. This procedure represents each day of the week and each year equally, and provides a set of about nine percent of the 245 days from March through October. Separate sets were determined for 1-hour and 8-hour high-ozone days at each monitor.

NO_x, VOC, HNO_3, and CO measurements were also restricted to the months of March through October, though in the case of VOCs, measurements were generally available only for the months of June through September. Differences in weekday and weekend concentrations of these compounds were determined using all days within the selected months to provide as large a data set as possible for quantifying the changes in precursor levels on weekends. For NO, NO_x, and NO_y, a second set of day-of-week averages was also computed for the high 8-hour ozone data subsets to determine if day-of-week differences occurred on high-ozone days as well as on average days.

PM measurements were analyzed for all days of the year because high PM days often occur during winter months and because PM samples are collected less often (typically, once every third or sixth day).

All statistical tests refer to t-tests of the differences between means. The data points constituting each mean were separated in time (e.g., Sunday noon compared with Wednesday noon) so that statistical assumptions of independence were not violated. Because a large number of statistical tests were carried out, a stringent significance probability ($p<0.01$) was used to evaluate statistical significance. Using $p<0.01$, approximately one statistical test in one hundred is expected to yield an apparently significant result when no statistical difference actually exists.

To facilitate comparisons, for each monitoring site and each specified pollutant and time of day, the differences between mean Wednesday and mean Sunday concentrations were determined and expressed as the percent decrease from the Wednesday mean:

Difference = 100% x (Wednesday mean – Sunday mean)/(Wednesday mean)

Statistical Characterization of Weekday/Weekend Differences in Pollutant Levels

Primary pollutants. As determined from all ozone-season days, the median daytime (6 am – 3 pm) declines of NO, and NO_x , and CO from Wednesday to Sunday were 62 percent, 57 percent, and 31 percent, respectively (Figure 2). The median decreases at 6 am and noon bracketed the median daytime (6 am – 3 pm) average decreases, and were similar to the decreases for the 3-hour averaging times of 6 am – 9 am and 12 noon – 3 pm. Declines exceeding approximately 30-40 percent were statistically significant, and all urban monitors exhibited statistically significant weekend decreases of NO, NO_x, and CO during one or more time periods (Appendix A). Declining ambient concentrations of NO and NO_x also occurred on high-ozone days (Appendix A).

According to EPA's 2001 national emission inventory, CO emissions derive predominantly from gasoline vehicles (79.4 percent), while gasoline and diesel motor vehicles contributed 18.3 percent and 24.6 percent of U.S. NO_x emissions, respectively, or 42.9 percent combined (www.epa.gov/ttn/chief/net/index.html) (including both on-road and non-road vehicles). Within Atlanta, motor vehicles are the single largest emissions source category: in Fulton County (metropolitan Atlanta), on-road and non-road motor vehicles accounted for 78.7 percent of NO_x emissions and 93.3 percent of CO emissions in 1999 (www.epa.gov/air/data). Consequently, the 31 percent median reduction in ambient CO concentrations on Sundays could not have occurred unless gasoline vehicle emissions were lower in Atlanta on Sundays than on Wednesdays. However, gasoline vehicles could not have been not the only contributor to weekend NO_x reductions, because the ambient NO_x reductions (~60 percent) on Sundays exceeded the gasoline-vehicle portion of NO_x emissions in Fulton County; ambient NO_x decreases did not exceed the combined contributions of gasoline and diesel motor vehicles (79 percent) to total NO_x emissions in Fulton County.

Sulfur dioxide (SO_2) measurements made at the SEARCH site in Atlanta showed lower mean levels during morning and early afternoon hours on Sundays compared with Wednesdays (Figure 3), consistent with the occurrence of weekend decreases in operations of some commercial or industrial facilities. As noted, stationary sources in Fulton County accounted for 21 percent of countywide NO_x emissions, which limits the potential contribution of weekend reductions of stationary source NO_x emissions to the total observed decline in ambient NO_x concentrations on Sundays (but does not imply that no contribution occurred).

Diesel exhaust emissions are typically thought to be the principal source of ambient black carbon (BC) concentrations, though recent experimental studies demonstrate that gasoline vehicles also emit BC, especially at near-freezing temperatures (Zielinska et al., 2004). Depending upon temperature, age, and engine condition, diesel vehicles may emit BC at ~3 to over 30 times the rate (g per mile basis) as gasoline vehicles (Zielinska et al., 2004). In the Denver area, mean BC emission rates from diesel vehicles ranged from 12 to 490 times the rates from high- and low-emitting gasoline vehicles, respectively (Fujita et al., 2003b); in Los Angeles, BC was not a unique source marker for diesel exhaust but was found to be a reasonable approximation through comparison with vehicle activity data and highway sampling (Fujita et al., 2003b). In Atlanta, the median Wednesday-Sunday decline in 24-hour BC concentrations at urban sites was 33 percent, with statistically significant differences at three of the five urban sites (Appendix A), all of which showed 24-hour declines in the range of 31 to 37 percent. The 24-hour BC declines on Sundays were smaller at the two nonurban sites of Centreville (16 percent) and Yorkville (13 percent). Hourly measurements of BC at SEARCH sites indicate that the reductions of BC on Sundays occurred at both urban and rural sites and were larger during some time periods than others. The median reductions of BC concentrations were 44 percent during the mid-day hours (6 am – 3 pm) and 47 percent during the period 9 am to noon (Appendix A).

Since CO and BC may be transported over substantial distances, the urban CO and BC concentrations likely include background levels; therefore, the urban CO and BC emission decreases on Sundays could have exceeded the ambient CO and BC concentration decreases reported above. As a first approximation, the Wednesday and Sunday mean CO and BC concentrations at the SEARCH sites of Birmingham and Atlanta were recomputed with subtraction of the corresponding Wednesday and Sunday mean CO and BC levels at Centreville and Yorkville (representing nonurban background). This calculation yielded mean Wednesday-Sunday 6 am CO decreases of 45 percent at Birmingham and 47 percent at Jefferson Street, compared with 33 and 36 percent, respectively, when background correction was not employed. For noon, the mean Wednesday-Sunday background-corrected CO decreases were 69 percent at Birmingham and 63 percent at Jefferson Street, compared with 37 and 35 percent, respectively, when background correction was not employed. For BC, background correction yielded mean Wednesday-Sunday BC decreases of 43 percent at Birmingham and 42 percent at Jefferson Street (24-hour samples) and 44 percent at Birmingham and 65 percent at Jefferson Street (6 am – 3 pm data). If CO and BC are taken as reasonable approximations of the source contributions of gasoline and diesel exhaust, respectively, then these simple comparisons suggest that urban-scale diesel and gasoline motor vehicle emissions on Sundays were each approximately 40 to 60 percent lower than on Wednesdays. Although we have not attempted a precise quantification, both diesel and gasoline vehicle emission reductions appear to contribute to the observed Sunday reductions of ambient NO and NO_x levels.

The ambient hydrocarbon measurements were more limited than the NO_x and CO data, but indicated that VOC declines occurred on Sundays, especially at urban locations. For the four Atlanta-area PAMS sites, the median mid-day (6 am to 3 pm) Wednesday to Sunday decreases in ambient hydrocarbon concentrations computed from all ozone-season days were 16 percent for alkanes, 13 percent for alkenes, 28 percent for aromatics, 21 percent for benzene, 5 percent for isoprene, and 19 percent for the sum of PAMS target compounds (Appendix A). The largest declines were observed for aromatics, including benzene, for which gasoline and gasoline vehicles are a major source. Declines were greater during morning than afternoon (Figure 4). In addition, the declines were greater at the urban locations (Tucker and South DeKalb) than at the non-urban sites (Yorkville and Conyers): mid-day aromatic levels, for example, declined by 32 percent and 58 percent, respectively, at South DeKalb and Tucker, by 25 percent at Conyers, and by zero (0) percent at Yorkville (Figure 4). The Wednesday-to-Sunday declines of alkanes, aromatics, and the sum of PAMS target compounds were statistically significant ($p<0.01$) at Tucker and South DeKalb; the benzene decrease was also statistically significant at Tucker.

Excluding Yorkville (which is designated by EPA as PAMS Type 1, or upwind), the median Wednesday-to-Sunday decline in the mid-day sum of PAMS target compounds was 25 percent and the median decline in aromatics levels was 32 percent. These declines are of comparable magnitude to the previously discussed median CO decline of 31 percent. If Yorkville concentrations are used to represent background, and background correction is applied to the data from South DeKalb and Tucker, then mid-day Wednesday-to-Sunday declines of aromatics were 40 percent at South DeKalb and 69 percent at Tucker; mid-day declines of benzene were 36 percent at South DeKalb and 62 percent at Tucker. These declines are consistent with the previously-discussed background-corrected declines of CO (69 and 63 percent at Birmingham and Jefferson Street, respectively, at noon).

<u>VOC/NOx ratios</u>. An important, though coarse, indicator of ozone sensitivity to precursors is the ratio of VOC/NO_x, with higher ratios indicating greater sensitivity to changes in NO_x. The differential changes in ambient NO_x and VOC levels in Atlanta imply that weekend ratios of VOC/NO_x differ from weekday ratios (Table 1). Considering the two urban locations, the mean VOC/NO_x ratios increased from 1.3:1 to 2.3:1 at South DeKalb and from 2.7:1 to 4.4:1 at Tucker when computed from all ozone-season days (Table 1).

<u>Nitric acid, nitrate, and sulfate</u>. The median Wednesday-to-Sunday daytime (6 am – 3 pm) HNO_3 concentration decline at the four SEARCH sites was 21 percent, while the median 24-hour nitrate decrease at the same four SEARCH sites plus two STN sites was 19 percent (Appendix A). Although the 6 am, 12 noon, 6- 9am, 9 am-12 noon, 12 noon-3 pm and 6 am-3 pm nitric acid levels declined on Sundays at all four SEARCH sites, only the 9 am-12 noon decrease at Yorkville was statistically significant ($p<0.01$). None of the 24-hour Wednesday/Sunday PM nitrate concentration differences was statistically significant, though the differences were within the range of 15 to 25 percent at five of the six sites. Mean Wednesday/Sunday sulfate concentration differences were not statistically significant; three sites showed Sunday increases and three showed decreases, with the median change being a 1.4 percent decline on Sunday.

Thus, nitric acid and PM nitrate exhibited declines on Sundays; with one exception, the declines were not statistically significant, but they were consistent in magnitude among sites. The results indicate that nitric acid and PM nitrate levels decreased in response to lower NO_x levels on Sundays, but not in proportion to the magnitude of the NO_x decline.

Ozone. Both peak 1-hour and peak 8-hour ozone concentrations were lower on high-ozone Sundays than on high-ozone Wednesdays, with one exception; these decreases were statistically significant at 6 of the 14 sites that were studied (Table 2). For the high-ozone days, the mean Sunday 8-hour concentrations averaged 9.6 percent lower than the mean Wednesday 8-hour concentrations; the mean Sunday 1-hour concentrations averaged 10.9 percent lower than the mean Wednesday 1-hour concentrations (Table 2). In contrast, the differences between average Wednesday and Sunday ozone levels nearly disappeared when all days (March-October) were included in the averages. For the all-days averages, the mean Sunday 8-hour concentrations averaged 1.9 percent lower than the mean Wednesday 8-hour concentrations; the mean Sunday 1-hour concentrations averaged 5 percent lower than the mean Wednesday 1-hour concentrations (Table 2). None of these differences was statistically significant. The modest changes in peak ozone levels on Sundays compared with Wednesdays contrast with the much larger reductions in ozone precursor concentrations occurring on Sundays.

Ozone Formation, Loss, and Accumulation

Ambient ozone concentrations are the net result of numerous atmospheric processes, any or all of which could exhibit important changes on weekends compared with weekdays. Different processes predominate during different periods of the day.

Overnight surface carryover. Because the nocturnal inversion retains pollutants within a shallow surface layer, concentrations from midnight through 4 am typically reflect surface carryover of previous-day pollutants; fresh emissions tend to be lower than at other times of day. All sites showed lower concentrations of CO and NO and higher ozone concentrations on Sundays than on Wednesdays from midnight through 4 am (Figure 3). Thus, during this time period, surface carryover of ozone precursors was lower on Sundays than on Wednesdays, while surface carryover of ozone was greater. Since the higher levels of surface ozone on Sundays were associated with lower levels of NO during the same hours, reduced titration of ozone by NO caused the higher Sunday ozone surface carryover. Note that ozone carryover aloft need not have been affected in the same way due to the nocturnal isolation of air aloft from surface-level NO_x emissions.

Fresh emissions. Diurnal profiles indicate that fresh emissions of CO and NO were greater from 6 am through 8 am on Wednesdays than on Sundays (Figure 3; Appendix C). Because ozone reacts with NO, ozone cannot accumulate until NO levels fall below ozone concentrations. As a result of lower levels of NO on Sunday mornings, less ozone was lost to NO titration on Sundays. Ozone accumulation began earlier on Sundays than on Wednesdays, as indicated by the times when morning ozone concentrations first exceeded the ambient NO levels (Figure 5). These times were shifted about one hour earlier on Sundays at two sites; at two other sites, NO levels were always lower than ozone concentrations on Sundays but not on Wednesdays. Ozone concentrations exceeded NO levels on all days at Yorkville, but even there, NO levels during the hours of 6 am to 8 am were lower on Sundays than on Wednesdays.

Carryover aloft. Ozone concentrations increased most rapidly during the hours from 9 am through 12 noon (Figures 3, 5). On Sundays, the mean temporal rate of ozone concentration increase from 9 am through 12 noon was marginally lower than on Wednesdays, so that by noon the mean Sunday and Wednesday ozone concentrations were nearly identical at most sites even though ozone levels at 9 am Sundays exceeded those at 9 am Wednesdays (Figure 3; Appendix C). Potentially, concentration increases during morning hours could reflect either or both increased rates of ozone formation or increases in mixing depth and incorporation of higher ozone concentrations from aloft; as noted previously, because aloft air masses are isolated from surface emissions of NO overnight, higher ozone levels can persist above the nocturnal inversion. Separation of the effects of mixing from ozone formation is difficult. We did not have vertical soundings, but we observed that average surface wind speeds increased most rapidly between the hours of 7 am and 10 am, which suggests that mixing effects need to be considered especially during this time period.

The most direct empirical test of upper-air carryover requires early morning measurements from aloft. Such data are not available routinely. For our purposes, determining if differences in the magnitudes of ozone carryover aloft occurred as a function of the day of the week was of interest. Even though data were lacking for quantifying the ozone concentrations aloft, the surface ozone data provided some insight into the possible existence of day-of-week differences in carryover of ozone aloft. Using surface data from Los Angeles sites, Fujita et al. (2002) showed that weekend-weekday differences in ozone concentrations were established early in the day in Los Angeles and the weekend-weekday differences remained constant during daylight hours (the ozone profiles were parallel during the morning concentration increase, from which it was concluded that the dominant driver of higher weekend ozone concentrations was the earlier onset of ozone formation on weekends rather than a mid-day effect). As in Los Angeles, weekday/weekend ozone differences in Atlanta were established early in the day, but unlike in Los Angeles, these differences diminished during the morning (Figure 6). For example, at the 8-hour ozone design-value site (Confederate Avenue), the mean Monday 8-hour ozone maxima were indistinguishable from the Wednesday means at all hours; in contrast, the differences between Sunday and Wednesday ozone concentrations were greatest from 4 am to 11 am and diminished by noon, so that mean midday ozone concentrations on Sundays were approximately equal to mean midday Wednesday levels (Figure 6). Potentially, the diminution of these differences from about 9 am to noon could have occurred because: (1) ozone carryover aloft was lower on Sundays than during the week, (2) late morning ozone production rates were lower on Sundays than during the week, (3) both carryover and formation were reduced on Sundays, (4) reduced ozone carryover aloft predominated over equal or increased morning ozone formation rates on Sundays, or (5) reduced ozone formation rates predominated over equal or increased ozone carryover aloft on Sundays. Additional analyses discussed next suggest that ozone transport aloft was marginally greater on Wednesdays than on Sundays.

Regional transport. We evaluated weekend changes in ozone transport into the Atlanta area by comparing weekend to weekday peak 8-hour ozone levels at upwind and downwind sites (Appendix D). The specific question to be addressed was: are day-of-week differences in ozone concentrations within or downwind of Atlanta attributable to day-of-week differences in ozone production within the metropolitan area or to day-of-week differences in ozone transport from upwind areas? Peak 8-hour ozone concentrations typically occurred between the hours of 10 am and 7 pm, an interval during most of which substantial vertical mixing is typical. We used surface wind directions to select subsets of days when it was reasonable to characterize one group of sites as upwind from Atlanta and another as downwind, and confirmed the characterizations using HYSPLIT back-trajectories (www.arl.noaa.gov/ready). The transport analyses were carried out for high-ozone days (top three peak 8-hour daily maximum days per day of week per year for each site). For each high-ozone day, hourly surface wind speed and direction were obtained for three SEARCH sites (Jefferson Street, Yorkville, and Centreville) and three CASTNet sites (Georgia Station, Sand Mountain, and Coweeta). The surface meteorological data from these six sites were also used for ozone sites lacking meteorological measurements based on distance (Yorkville for Douglasville, Georgia Station for Fayetteville, and Jefferson Street for Confederate Avenue, Tucker, DeKalb, Conyers, and Gwinnett – Figure 1). We computed 24-hour vector average wind speed and direction for each site's high-ozone days (from the hourly averages with start times of 7 pm on a previous day to 6 pm on each high-ozone day). For each monitoring site, we then classified the 24-hour surface wind direction according to quadrant of origin (NE, SE, SW, NW). The HYSPLIT model was run using three trajectory levels (100, 500, and 1000 m) for ten dates with vector-average surface winds from the northwest quadrant and ten with surface winds from the southwest quadrant, randomly chosen from high ozone days (top 3 8-hour days per day of week) during June-August, 1999-2002. Trajectories were carried back from DeKalb County airport for 48 hours at 6-hour time intervals. The three trajectory heights remained reasonably coherent (within the classification of transport quadrants) and supported the classifications into quadrants using surface winds (Appendix D).

The urban/downwind sites exhibited mean concentrations of about 80 to 100 ppbv, whereas the far upwind sites showed mean concentrations of about 60 to 80 ppbv, thus indicating that transported ozone made a large contribution to peak ozone levels in and near Atlanta (Figure 7). Note that the Atlanta urban plume could itself have contributed to the regional background depending upon circulation patterns, as is suggested by the partially elevated mean ozone levels at the nominally upwind sites of Yorkville, Douglasville, and Fayetteville. All back trajectories for the cases with winds from the northwest quadrant extended at least 48 hours back into areas to the northwest without recirculation; 30 percent of the back trajectories arriving from the southwest exhibited a trajectory rotation extending to the southeast of Atlanta and suggestive of recirculation around a high-pressure system. Besides Atlanta, nearby urban areas, including, for example, Chatanooga, could have contributed to the observed regional background when winds were from the northwest quadrant. Previous studies have shown that transported ozone contributes substantially to the magnitude of peak ozone concentrations in the major metropolitan areas of the southeastern U.S. (Trainer et al., 1995).

The differences between the mean 8-hour peak ozone concentrations at the urban/downwind sites and the far upwind sites are interpreted here as indicating the magnitude of the mean contribution of the Atlanta urban plume to the regional background on high-ozone days. For all days of the week, the differences between the peak 8-hour ozone means at the urban/downwind sites and at the far upwind sites were about 15 to 20 ppbv.

Under both northwesterly and southwesterly transport patterns, the mean day-of-week concentrations at far upwind, upwind, and urban/downwind sites followed approximately parallel lines (Figure 7). For clarity, we grouped sites into far upwind, near upwind, and urban/downwind locations; the results for individual sites were also approximately parallel within each group (Appendix D). The parallelism was within the standard errors of the means and implies that the day-of-week differences in mean ozone concentrations at Atlanta sites were partially or wholly driven by day-of-week differences in upwind transport concentrations. The transport contribution was lower on Sundays than on Wednesdays, Thursdays, or Fridays (Figure 7), implying that regional carryover of ozone was lower on Sundays (the day-of-week concentration differences at the upwind locations were not statistically significant, however).

If, as noted above, the differences between upwind and downwind ozone concentrations are taken as a measure of the influence of the Atlanta urban plume, then these analyses provide no statistical evidence indicating that the amount of local ozone production in Atlanta varied by day of the week. Although the differences between the far upwind and urban/downwind ozone concentrations varied somewhat among the days of the week, none of the differences was statistically significant (Appendix D). However, other comparisons of day-of-week differences in ratios of reactive species, discussed next, indicate that day-of-week differences in the rates of ozone formation occurred at sites in Atlanta.

Local ozone formation. The SEARCH sites provide measurements of one of the most important NO_x reaction products, namely, HNO_3, as well as NO_y. Thus, for these sites, it is possible to compare ozone levels to concentrations of NO_x reaction products, and to compare product levels to total oxidized nitrogen species concentrations. A key reaction product is HNO_3, which is produced by reaction of HO radical with NO_2. This reaction removes a radical and an NO_2 molecule. Since each conversion of NO_2 to NO produces an ozone molecule, with some loss processes, removal of an NO_2 molecule ends that molecule's contribution to ozone production (some reaction products, e.g., PAN, can serve as a reservoir of NO_2, however, because a reverse reaction may occur). The ratio of ozone to HNO_3 concentrations provides a relative measure of the mean number of ozone molecules produced per NO_x molecule. The ratio of HNO_3 to NO_y provides one measure of the relative amount of NO_x reaction product (the ratio of NO_x to NO_y is more indicative of the amount of reactant to the sum of reactants and products, but the available NO_2 record was much shorter than the HNO_3 record).

The mean Sunday HNO_3 levels were lower than Wednesday concentrations (Appendix A). During morning, the time rate at which NO_2 was converted to HNO_3 was similar on Sundays and Wednesdays, as demonstrated by mean HNO_3 concentrations that were approximately the same from 8 am through 12 noon on Wednesdays and Sundays (Appendix C). However, both central city and rural SEARCH sites exhibited higher ratios of HNO_3 to NO_y on Sundays compared with Wednesdays (Appendix C). Because the atmospheric lifetime of HNO_3 is of the order of hours to a day, these day-of-week differences imply that a greater fraction of the NO and NO_2 was converted to HNO_3 by a specified hour on Sundays compared with the same hour on Wednesdays. This result is consistent with the observed increase in ambient VOC/NO_x on Sundays (Table 1), which suggests the occurrence of a more reactive mix on weekends.

For brevity, we refer to the mean number of ozone molecules produced per NO_x molecule as ozone production efficiency (Trainer et al., 1993). An increase in the ratios of ozone to HNO_3 concentrations indicates that the efficiency of ozone production was greater on Sundays than on

Wednesdays (Figure 8). At Jefferson Street, the O_3/HNO_3 ratios increased from ~18:1 on Wednesdays to ~24:1 on Sundays during the afternoon (sample start hours noon through 4 pm), indicating an approximate 35 percent increase in the number of ozone molecules produced per NO_x. The increase in ozone production efficiency per NO_x acts in opposition to the decreases of NO emissions on Sundays. Modeling studies confirm the importance of the increase in ozone production efficiency per NO_x as NO_x emissions decline (Reynolds et al., 2004).

The ratios of ozone/NO_y or ozone/NO_x were also higher on weekends than on Wednesdays at other monitoring sites (Appendix C). Ratios of ozone/CO were greater on Sundays compared with Wednesdays at three locations having CO data (Jefferson Street, Yorkville, and DeKalb), and on Saturdays relative to Wednesdays at Jefferson Street and DeKalb.

Ozone Response to Emission Controls

The future response of ozone concentrations in Atlanta to emission controls depends upon the response of both transported and locally-formed ozone. Because transported ozone may have formed over a period of many days, including both weekdays and weekends, the differences between weekday and weekend concentrations of ozone sites such as Yorkville do not necessarily represent the changes in transported ozone that might occur in response to regional-scale emission reductions. However, the weekend changes in local ozone formation in Atlanta provide one possible indicator of the response of locally-formed ozone to future local emission controls. This indicator is imperfect, because the emission changes occurring from weekdays to weekends are not reflective of the emission reductions characteristic of control plans. Nonetheless, the ambient measurements do provide a direct empirical indicator of the response of local ozone formation to reductions of VOC and NO_x emissions of the type typical of the transition from weekdays to weekends.

The analyses discussed previously indicate that local emission reductions on the order of ~30 to 60 percent (Figures 2, 4) did not change the amount of ozone formed locally (Table 2; Figure 7); ozone began forming ~ 1 hour earlier (Figure 3) and more ozone formed per unit NO_x (Figure 8). The average peak ozone hour was 2 or 3 pm at all sites, and the peak hours did not shift to an earlier mean time on weekends as might be expected if lower weekend NO_x levels were limiting ozone production (Figure 3; Appendix C). Together, these results support the conclusion that local ozone formation was not typically limited by the availability of NO_x.

Since both NO_x and VOC levels were lower on Sundays than on Wednesdays, local ozone formation might be expected to decline in response to one of the reductions, regardless of which precursor was limiting. However, the magnitudes of local ozone formation on weekends represent the net effects of the combined reductions of VOC and NO_x emissions, which in the present case appear to act in opposition: an earlier start of ozone accumulation and increasing ozone formation per unit conversion of NO_2 to HNO_3 may have opposed the expected decreasing rate of ozone formation in response to lower VOC levels.

The mean 6 am – 3 pm VOC/NO_x ratios were low (1.3:1 to 5.8:1) at all PAMS monitoring sites on both Wednesdays and Sundays (Table 1) (the 6 am – 9 am ratios ranged from 1.0:1 to 5.1:1). These ratios underrepresent VOC as they are based upon the sum of PAMS target compounds; the mean ratio of the target compounds to the measured total VOC is our data set was 0.85. Historical EPA guidance has indicated that 6 am – 9 am ratios of ambient VOC/NO_x less than about 8:1 are indicative of VOC-limited conditions (U.S. EPA 1977; 1989). However, photochemical aging is as important as VOC/NO_x ratios in determining the sensitivity of ozone to changes in VOC or NO_x emissions (Sillman, 1999), so that variations in ozone response to emission reductions should be expected depending upon the hour of the day, downwind distance, meteorological conditions and their relation to photochemical aging, and the influence of highly reactive VOCs (e.g., isoprene).

One indicator of where and when VOC or NO_x limits local ozone formation is the extent of reaction estimation from a smog production algorithm (Appendix E). We calculated this indicator on an hourly basis using all available data and observed important differences among hours, days of the week, and types of days (high ozone or not). On high-ozone Wednesdays, the mean hourly extent of reaction remained below 60 percent (VOC-limited conditions) prior to 10 am at all sites (Figure 9). By 12 noon and until 6 pm, mean extent exceeded 80 percent (NO_x limited) at the nonurban sites of Yorkville and Conyers. At the suburban sites of DeKalb and Tucker, extent varied from 60 to 80 percent (transitional) from noon through 6 pm, whereas at

Jefferson Street the extent remained below 60 percent during most hours (Figure 9). In contrast to these high-ozone days, the mean extent of reaction averaged approximately 40 percent (VOC limited) from noon through 6 pm at all sites when the averages were determined from all ozone-season days. According to this calculation, therefore, high-ozone days exhibited a different sensitivity to ozone precursor than did other days, and the sensitivity of the peak hour was different than the mean sensitivity of the eight hours comprising the peak 8-hour ozone levels. In addition, the mean extent of reaction estimates between noon and 6 pm on high-ozone Sundays were higher than during corresponding hours on high-ozone Wednesdays by 10 to 20 percentage points at Tucker and DeKalb, a result that is directionally consistent with the observed increase in VOC/NO_x ratios at those sites on Sundays compared with Wednesdays (Table 1). Increases in the mean extent of reaction from Wednesdays to Sundays occurred at all sites when the means were determined from all ozone season days.

The estimated precursor sensitivities of ozone formation on different days and at different times varied in a way that was related to the observed changes in ozone concentrations on Sundays, as follows. The greatest ozone reductions observed were for peak one-hour ozone concentrations on high ozone days (averaging 9.6 percent); the lowest ozone reductions were for peak 8-hour ozone concentrations averaged over all ozone-season days (1.2 percent) (Table 2). As noted in the preceding discussion, the former were characterized by the highest mean extent of reaction, while the latter exhibited the lowest mean extent. Both the mean Wednesday-to-Sunday peak ozone decrease and the mean extent of reaction during peak ozone hours declined as functions of the number of hours included in the averages (Figure 10). For each site, the peak ozone decreases therefore increased as a function of the mean extent of reaction. These results have important implications for the potential effectiveness of emission control programs in reducing both average peak ozone levels and peak ozone concentrations on high-ozone days. As previously noted, the mean ozone decreases were the net result of weekend changes in both transported and locally-produced ozone.

PM Nitrate Response to Emission Controls

As demonstrated above, nitric acid and PM nitrate levels decreased in response to lower NO_x levels on Sundays, but not in proportion to the magnitude of the NO_x decline (~20 percent compared with ~60 percent). Future changes in PM nitrate levels depend on changes in SO_2 emissions and sulfate concentrations, as well as on changes in NO_x emissions and HNO_3 concentrations. In addition, changes in ammonia levels may affect PM nitrate concentrations. Blanchard and Hidy (2003; 2005) used measurements from sites of the SEARCH program along with a thermodynamic equilibrium model to investigate the responses of fine particulate nitrate and $PM_{2.5}$ mass concentrations to projected changes in concentrations of nitric acid and sulfate (Appendix F). Present cool-season concentrations of PM nitrate tend to be limited by the availability of ammonia (Blanchard and Hidy, 2003), but with declining sulfate concentrations more ammonia would become available and PM nitrate levels are predicted to increase unless HNO_3 concentrations decrease (Blanchard and Hidy, 2005). Future PM nitrate levels would become more responsive to changes in ambient HNO_3, because PM nitrate formation would then be less ammonia-limited (Appendix F). The actual changes in PM nitrate levels will depend upon the responses of HNO_3 to NO_x reductions.

Conclusion

We observed a strong weekend effect in the ambient concentrations of ozone precursors in the Atlanta region, with median daytime (6 am – 3 pm EST) decreases of 62, 57, and 31 percent for NO, NO_x, and CO, respectively, from Wednesdays to Sundays, during the ozone season (March – October). We also observed significant decreases in ambient VOC levels between Wednesdays and Sundays, with decreases of 28 percent for the sum of aromatic compounds and 19 percent for the sum of PAMS target compounds. Despite the large reductions in ozone precursors on weekends, day-of-week differences in ozone concentrations in the metropolitan Atlanta area were much smaller. Averaging over all ozone-season days, the median 1-hour and 8-hour ozone daily maxima on Sundays decreased by 4.5 and 2.3 percent, respectively, from their mean peak levels on Wednesdays, with no sites showing statistically significant Wednesday-to-Sunday differences. When restricted to high-ozone days (highest 3 days per day of week per site per year), the median 1-hour and 8-hour ozone daily maxima on Sundays decreased by 11.3 and 9.5 percent, respectively, from their mean peak levels on Wednesdays, with 6 of 14 sites showing statistically significant Wednesday-to-Sunday differences.

Average ozone concentrations in Atlanta were about 10 to 15 ppbv higher than those measured at upwind locations in the ozone season. Regional ozone levels contributed to about 80 percent of the ambient ozone observed in Atlanta. Because of the large influence of regional, upwind ozone on Atlanta's observed ozone levels, the day-of-week differences observed in Atlanta were due in large measure to day-of-week differences in upwind transport conditions.

Because NO levels were lower on Sundays, overnight surface carryover of ozone was greater and morning titration of ozone by NO was reduced, so that local ozone accumulation began earlier on Sunday mornings than on Wednesdays. During mid-day hours, ratios of ozone/NO_x, ozone/NO_y, and ozone/nitric acid (HNO_3) were greater on Sundays than on Wednesdays, indicating that in addition to the titration effect, an increase occurred in the number of ozone molecules formed per ambient NO_x molecule on Sundays. The available data did not allow us to evaluate the effects of changing levels of NO_x on hydroxyl radical concentrations, or if ozone formation rates changed with respect to specific VOC compounds.

Our analyses of weekday/weekend differences in ozone precursor emissions show that different emission reductions of ozone precursors than normally take place each weekend will be required before significant reductions in ambient ozone can be achieved in the Atlanta area. The principal limitation of our analysis is that current weekend emission reductions are not identical to those that might occur in the future as a result of emission control programs. Regional-scale changes in ozone levels potentially could result from combined urban and nonurban reductions of ozone precursor emissions. However, it is sobering that Atlanta sites exhibited so much difference between the weekend reductions of ozone precursors compared with much smaller changes in ozone levels. Any expectation of future declines of regional ozone concentrations due to precursor reductions in the metropolitan area should be further investigated.

Acknowledgments

We thank the Coordinating Research Council for funding this study and the CRC reviewers who read an earlier draft and provided suggestions that significantly improved this report.

References

Altshuler SL, Arcado TD, and Lawson DR. 1995. Weekday vs. weekend ambient ozone concentrations: discussion and hypotheses with focus on northern California. J. Air & Waste Manage. Assoc. 45: 967-972.

Blanchard, C.L.; Lurmann, F.W.; Roth, P.M.; Jeffries, H.E.; Korc, M. 1999. The use of ambient data to corroborate analyses of ozone control strategies. Atmos. Environ. 33, 369-381.

Blanchard, C.L. 2000. Ozone process insights from field experiments- Part III: Extent of reaction and ozone formation. Atmos. Environ. 34, 2035-2043.

Blanchard, C.L.; Stoeckenius, T. 2001. Ozone response to precursor controls: comparison of data analysis methods with the predictions of photochemical air quality simulation models. Atmos. Environ. 35, 1203-1215.

Blanchard CL and Tanenbaum SJ. 2003. Differences between weekday and weekend air pollutant levels in southern California. J. Air Waste Manage. Assoc. 53: 816-828.

Blanchard CL and Hidy GM. 2003. Effects of changes in sulfate, ammonia, and nitric acid on particulate nitrate concentrations in the southeastern United States. J. Air Waste Manage. Assoc. 53: 283-290.

Blanchard CL and Hidy GM. 2005. Effects of SO_2 and NO_x emission reductions on $PM_{2.5}$ mass concentrations in the southeastern United States. J. Air Waste Manage. Assoc. In press.

Cleveland WS, Graedel TE, Kleiner B, and Warner JL. 1974. Sunday and workday variations in photochemical air pollutants in New Jersey and New York. Science 186: 1037-1038.

Croes BE, Dolislager LJ, Larsen L, and Pitts JN. 2003. Forum – the O_3 "weekend effect" and NO_x control strategies – scientific and public health findings and their regulatory implications. EM (July 2003): 27-35.

Elkus B and Wilson KR. 1977. Photochemical air pollution: weekend-weekday differences. Atmos. Environ. 11: 509-515.

Fujita EM, Stockwell WR, Campbell DE, Chinkin LR. Main HH, and Roberts PT. 2002. Weekend/Weekday Ozone Observations in the South Coast Air Basin: Volume I – Executive Summary, Final Report. Prepared for National Renewable Energy Laboratory, NREL Subcontracts ACI-0-29086-01 and ACI-0-29086-02, and the Coordinating Research Council Contract No. E-53. http://www.arb.ca.gov/aqd/weekendeffect.

Fujita EM, Stockwell WR, Campbell DE, Keislar RE, and Lawson DR. 2003a. Evolution of the magnitude and spatial extent of the weekend ozone effect in California's South Coast Air Basin. J. Air Waste Manage. Assoc. 53: 802-815.

Fujita EM, Campbell DE, Zielinska B, Sagebiel JC, Bowen JL, Goliff W, Stockwell WR and Lawson DR. 2003b. Diurnal and weekday variations in the source contributions of ozone precursors in California's South Coast Air Basin. J. Air Waste Manage. Assoc. 53: 844-863.

Graedel TE, Farrow LA, and Weber TA. 1977. Photochemistry of the "Sunday Effect." Environ. Sci. Tech. 11: 690-694.

Hansen DA, Edgerton ES, Hartsell BE, Jansen JJ, Hidy GM, Kandasamy K, and Blanchard CL. 2003. The Southeastern Aerosol Research and Characterization Study (SEARCH): 1. Overview. J. Air Waste Manage. Assoc. 53: 1460-1471.

Hoggan M, Hsu M, Kahn M, and Call T. 1989. Weekday/weekend differences in diurnal variation in carbon monoxide, nitrogen dioxide, and ozone - implications for control strategies. 82nd Annual Meeting & Exhibition, Air & Waste Management Association, Anaheim California, June 25-30, 1989.

Johnson G.M. 1984. A simple model for predicting the ozone concentration of ambient air. Proceedings of the Eighth International clean Air Conference. Melbourne, Australia. pp. 715-731.

Larsen L. 1999. Day of Week Patterns of Heavy-Duty and Non-Heavy Duty Vehicle Activity at Weigh-in-Motion (WIM) Stations Relevant to the South Coast Air Basin During the Summer of 1997. California Air Resources Board Sacramento, CA. http://www.arb.ca.gov/aqd/weekendeffect.

Lawson DR. 2003. Forum – the weekend ozone effect – the weekly ambient emissions control experiment. EM (July 2003): 17-25.

Lebron F. 1975. A comparison of weekend-weekday ozone and hydrocarbon concentrations in the Baltimore-Washington metropolitan area. Atmos. Environ. 9: 861-863.

Motallebi N, Tran H, Croes BE, and Larsen LC. 2003. Day-of-week patterns of particulate matter and its chemical components at selected sites in California. J. Air & Waste Manage. Assoc. 53: 889-896.

Pun BK, Seigneur C, and White W. 2003. Day-of-week behavior of atmospheric ozone in three US cities. J. Air Waste Manage. Assoc. 53: 789-801.

Reynolds SD, Blanchard CL, and Ziman SD. 2004. Understanding the effectiveness of precursor reductions in lowering 8-hr ozone concentrations – Part II. The eastern United States. J. Air Waste Manage. Assoc. 54: 1452-1470.

Sillman S. 1999. The relationship between ozone, NO_x, and hydrocarbons in urban and polluted rural environments. Atmos. Environ. 33: 1821-1845.

Trainer M, Parrish DD, Buhr MP, Norton RB, Fehsenfeld FC, Anlauf KG, Bottenheim JW, Tang YZ, Wiebe HA, Roberts JM, et al. 1993. Correlation of ozone with NO_y in photochemically aged air. J. Geophys. Res. 98: (D2) 2917-2925.

Trainer M, Ridley BA, Buhr MP, Kok G, Walega J, Hubler G, Parrish DD, and Fehsenfeld FC. 1995. Regional ozone and urban plumes in the southeastern United States: Birmingham, a case study. J. Geophys. Res. 100 (D9) 18823-18834.

U.S. EPA. 1979. Uses, Limitations, and Technical Basis of Procedures for Quanitfying Relationships Between Photochemical Oxidants and Precursors. EPA-450/2-77-021a. US EPA, Research Triangle Park NC.

U.S. EPA 1989. Procedures for Applying City-Specific EKMA. EPA-450/4-89-012. US EPA, Research Triangle Park NC.

U.S. EPA. 2005. www.epa.gov/oar/oaqps/greenbk/o3season.html (accessed January 7, 2005).

Yarwood G, Stoeckenius TE, Heiken JG, and Dunker AM. 2003. Modeling weekday/weekend ozone differences in the Los Angeles region for 1997. J. Air Waste Manage. Assoc. 53: 864-875.

Winer AW, Peters JW, Smith JP, and Pitts, Jr JN. 1974. Response of commercial chemiluminescent NO-NO2 analyzers to other nitrogen-containing compounds. Environ. Sci. Technol. 8: 1118-1121.

Zielinska B, Sagebiel J, McDonald JD, Whitney K, and Lawson D. 2004. Emission rates and comparative composition from in-use diesel and gasoline-fueld vehicles. J. Air Waste Manage. Assoc. 54: 1138-1150.

Table 1. Mean daytime (6 am – 3 pm EST) concentrations of the sum of PAMS target compounds, NO_x or NO_y, and the ratios of VOC/NO_x or VOC/NO_y at three locations, determined from all ozone-season days having both VOC and NO_x data. The uncertainty limits are one standard error of the mean. The number of observations for Wednesday and Sunday means are listed in that order after the site name.

Site	**Wednesday**			**Sunday**		
	VOC (ppbC)	**NO_x (ppbv)**	**VOC/ NO_x**	**VOC (ppbC)**	**NO_x (ppbv)**	**VOC/ NO_x**
S. DeKalb (144,143)	62.3 $\pm$ 4.3	48.9 $\pm$ 4.0	1.3	47.0 $\pm$ 3.4	20.3 $\pm$ 2.2	2.3
Tucker (161,158)	65.3 $\pm$ 3.9	24.4 $\pm$ 1.3	2.7	39.4 $\pm$ 2.4	9.0 $\pm$ 0.6	4.4
Conyers (168,167)	17.8 $\pm$ 1.0	8.0 $\pm$ 0.4	2.2	20.4 $\pm$ 1.4	5.0 $\pm$ 0.2	4.1
Yorkville* (134,132)	36.3 $\pm$ 3.1	11.4 $\pm$ 0.7	3.2	32.7 $\pm$ 2.5	5.6 $\pm$ 0.7	5.8

* NO_y and VOC/NO_y

Table 2. Differences between mean Wednesday and Sunday peak 1-hour and 8-hour concentrations (percent declines relative to mean Wednesday levels). Positive numbers represent higher Wednesday concentrations. Statistically significant (p<0.01) differences are shown in bold. The averages were determined from both all days and high-ozone days during 1998-2002. The number of observations for Wednesday 8-hour means are listed after the city name.

AIRS/ SEARCH/ CASTNET	CITY	**Wednesday – Sunday Decrease (percent)**			
		Top 3 per Day of Week		All Days	
		8-hour Ozone	1-hour Ozone	8-hour Ozone	1-hour Ozone
130890002	So. DeKalb/Decatur (157)	5.3	9.0	-1.4	4.0
130893001	Tucker (162)	7.5	8.0	2.4	7.2
130970004	Douglasville (166)	**11.3**	**18.7**	-0.3	4.1
131130001	Fayetteville (166)	**15.3**	**17.5**	2.9	6.8
131210055	Confederate/Atlanta (166)	7.5	9.5	-0.1	4.3
131270006	Brunswick (164)	6.8	7.8	0.2	2.3
131350002	Lawrenceville (153)	7.6	8.1	0.9	6.2
132470001	Conyers (165)	**15.0**	**16.7**	6.2	8.6
CTR	Centreville* (137)	**15.0**	15.1	5.0	4.6
JST	Jefferson St/Atlanta* (137)	11.4	11.7	-4.4	1.1
YRK	Yorkville* (138)	**11.4**	**11.8**	3.6	6.6
COW137	Coweeta (137)	0.1	-13.7	2.2	1.6
GAS153	Georgia Station (136)	**16.5**	10.9	5.8	4.5
SND152	Sand Mountain (140)	3.0	21.3	3.2	7.8
	Mean	9.6	10.9	1.9	5.0
	Median	9.5	11.3	2.3	4.5

*1999-2002

Figure Captions

Figure 1. Locations of monitoring sites.

Figure 2. Median percent decreases in NO, NO_x, and CO from Wednesdays to Sundays for three 3-hour periods (6 am - 9 am, 9 am - 12 noon and 12 noon - 3pm), hourly (at 6 am, 9 am, and 12 noon), and averaged over the period 6 am to 3 pm. The data are from March-October, 1998-2002. The medians were determined from all Atlanta-area AIRS monitoring sites with available data (Confederate Avenue, Conyers, South DeKalb, and Tucker for NO and NO_x; DeKalb Technical and Roswell for CO). The SEARCH site at Jefferson Street, Atlanta, was not included in the computation of the medians, but during the period 1999-2002 it exhibited Wednesday-Sunday declines comparable to those shown here (at noon, the NO, NO_y, and CO declines were 64 percent, 51 percent, and 35 percent, respectively).

Figure 3. Diurnally-averaged concentrations of ozone, CO, SO_2, and NO at Jefferson Street (Atlanta). All hourly measurements from the years 1999-2002 during the months March-October were used in determining the averages. Each point represents approximately 130 samples.

Figure 4. Diurnal profiles of mean ambient benzene levels at Yorkville, South DeKalb, Tucker and Conyers during the period 1996-2003, shown for each day of the week.

Figure 5. Diurnally-averaged concentrations of the O_3 and NO on Wednedays and Sundays.

Figure 6. Mean Monday (top) and Sunday (bottom) hourly ozone concentrations versus mean Wednesday ozone concentrations at the Atlanta 8-hour ozone design-value monitoring site.

Figure 7. Mean daily 8-hour ozone maxima by day of week for high-ozone days at downwind sites (Conyers and Gwinnett), 1998-2002. The data have been averaged across monitoring locations representing far upwind (blue, circles), near upwind (red, x's), and urban/downwind (green, +'s) locations. The top and bottom panels shows days when 24-hour vector-average

wind directions were from the northwest and wouthwest quadrants, respectively, based upon surface meteorological observations from Jefferson Street.

Figure 8. Hourly ratios of the mean concentrations of ozone and HNO_3 on Wednesdays and Sundays. Hourly averages were determined from measurements made at the SEARCH sites at Jefferson Street (Atlanta) (99-02), Yorkville (GA) (98-02), Birmingham (AL) (00-02) and Centreville (AL) (98-02) during the months of March through October, with each point representing approximately 30 hourly measurements per year.

Figure 9. Hourly mean extent of reaction, ozone, NO, NO_x, and NO_y concentrations on high-ozone Wednesdays (top 3 peak 8-hour ozone-concentration Wednesdays per year), 1998-2002. For Yorkville and Jefferson Street, two alternative formulations of the extent of reaction were calculated using the measurements of NO_y and NO_x; the NO_x data were available only for 2001 and 2002 at Jefferson Street and 2002 at Yorkville. For the remaining three sites, upper and lower bounds of the extent of reaction were calculated using the available NO_x measurements and a best estimate is presented as the mean of the bounds.

Figure 10. Mean Wednesday-to-Sunday decrease in peak ozone concentrations (top) and mean extent of reaction during peak ozone hours (bottom) versus the number of hours per day of week per year included in each average. From left to right, the number of hours correspond to peak 1-hour ozone averages on high-ozone days (top 3 days per day of week per year), peak 8-hour ozone on high-ozone days, peak 1-hour ozone on all ozone season days, and peak 8-hour ozone on all ozone season days.

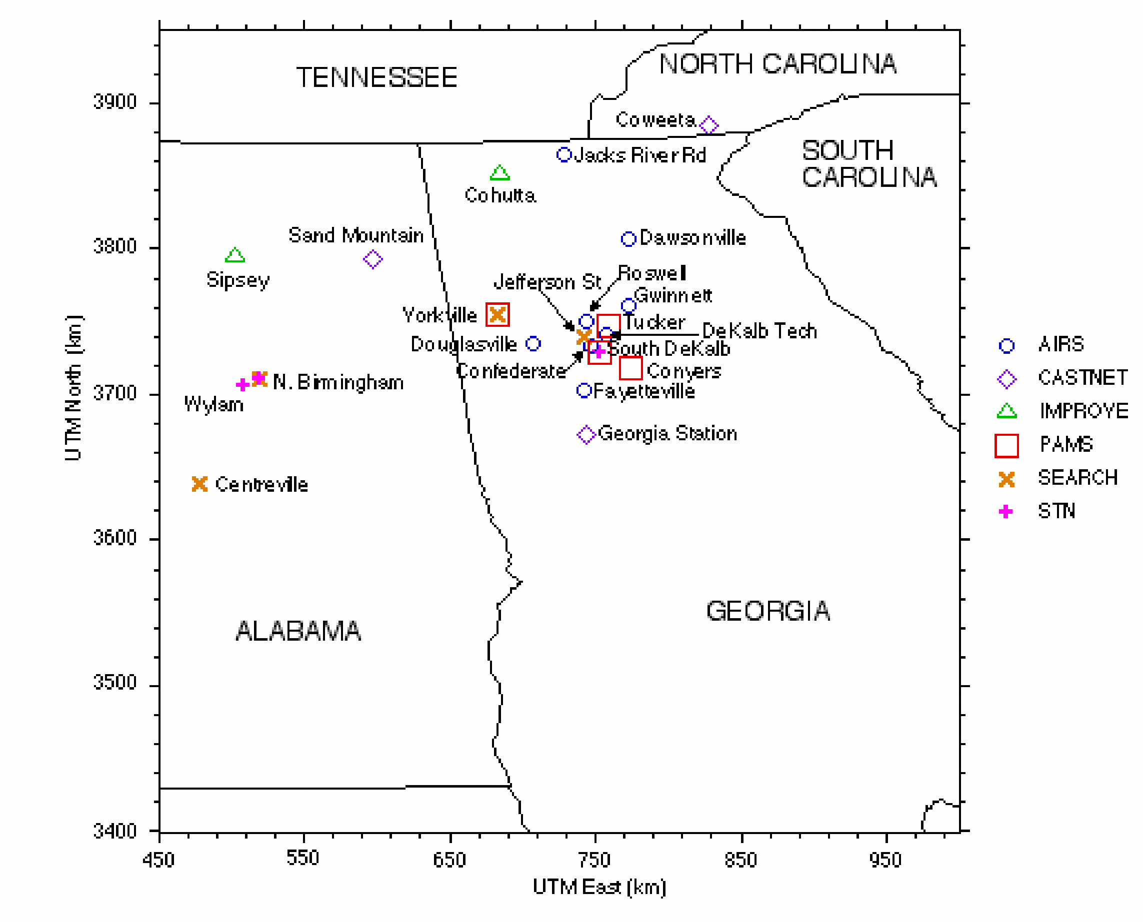


Figure 1. Locations of monitoring sites.

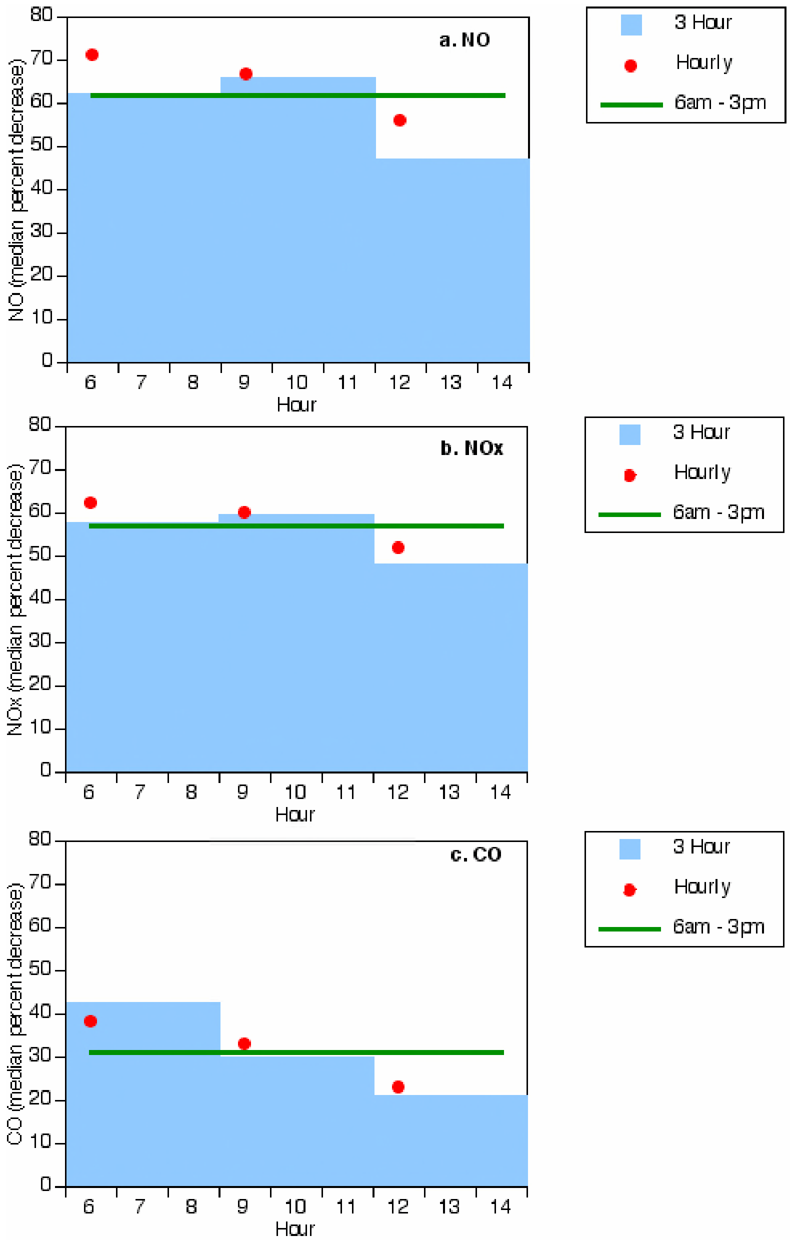


Figure 2. Median percent decreases in NO, NO_x, and CO from Wednesdays to Sundays for three 3-hour periods (6 am - 9 am, 9 am - 12 noon and 12 noon - 3pm), hourly (at 6 am, 9 am, and 12 noon), and averaged over the period 6 am to 3 pm. The data are from March-October, 1998-2002. The medians were determined from all Atlanta-area AIRS monitoring sites with available data (Confederate Avenue, Conyers, South DeKalb, and Tucker for NO and NO_x; DeKalb Technical and Roswell for CO). The SEARCH site at Jefferson Street, Atlanta, was not included in the computation of the medians, but during the period 1999-2002 it exhibited Wednesday-Sunday declines comparable to those shown here (at noon, the NO, NO_y, and CO declines were 64 percent, 51 percent, and 35 percent, respectively).

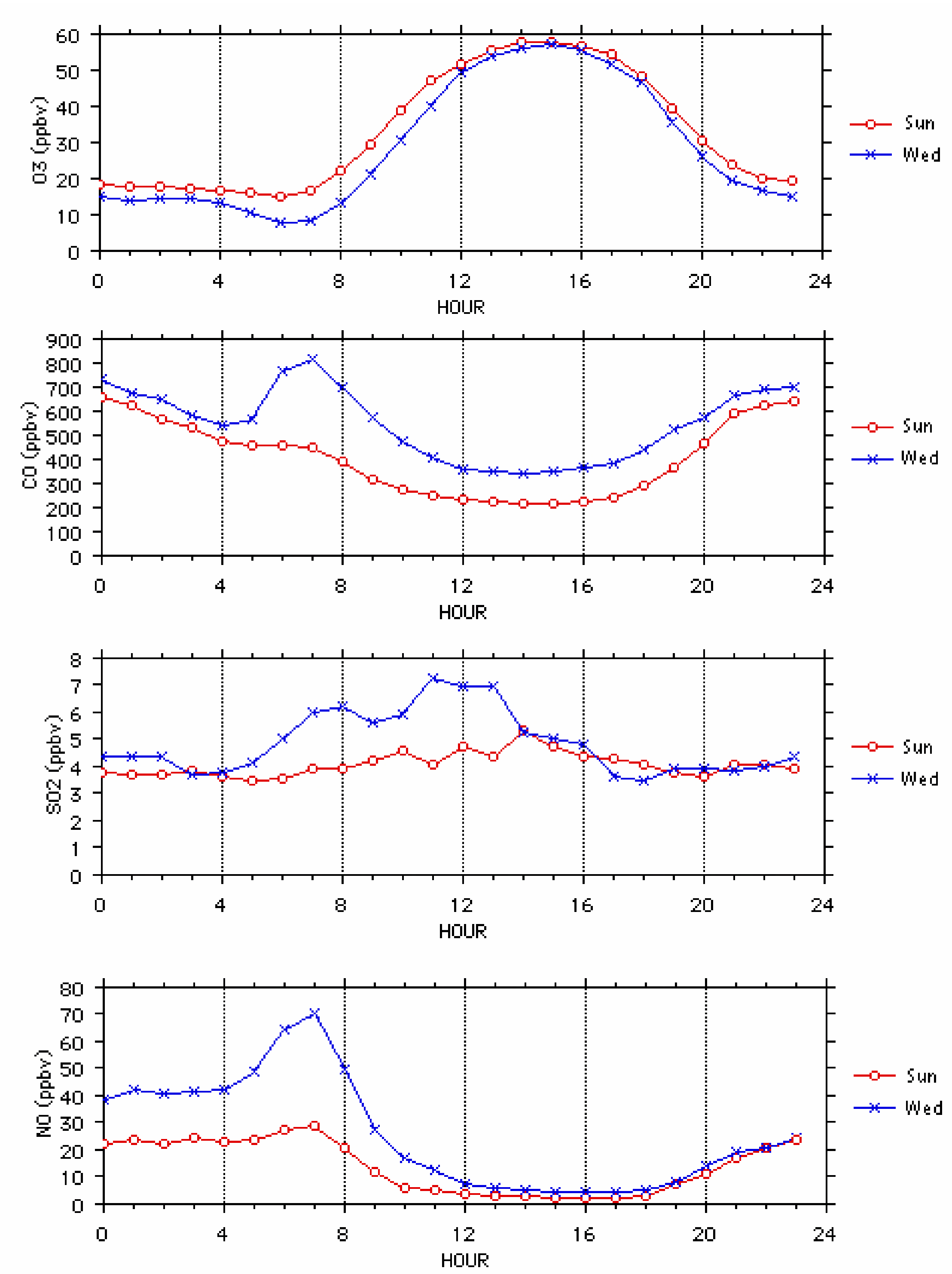


Figure 3. Diurnally-averaged concentrations of ozone, CO, SO_2, and NO at Jefferson Street (Atlanta). All hourly measurements from the years 1999-2002 during the months March-October were used in determining the averages. Each point represents approximately 130 samples.

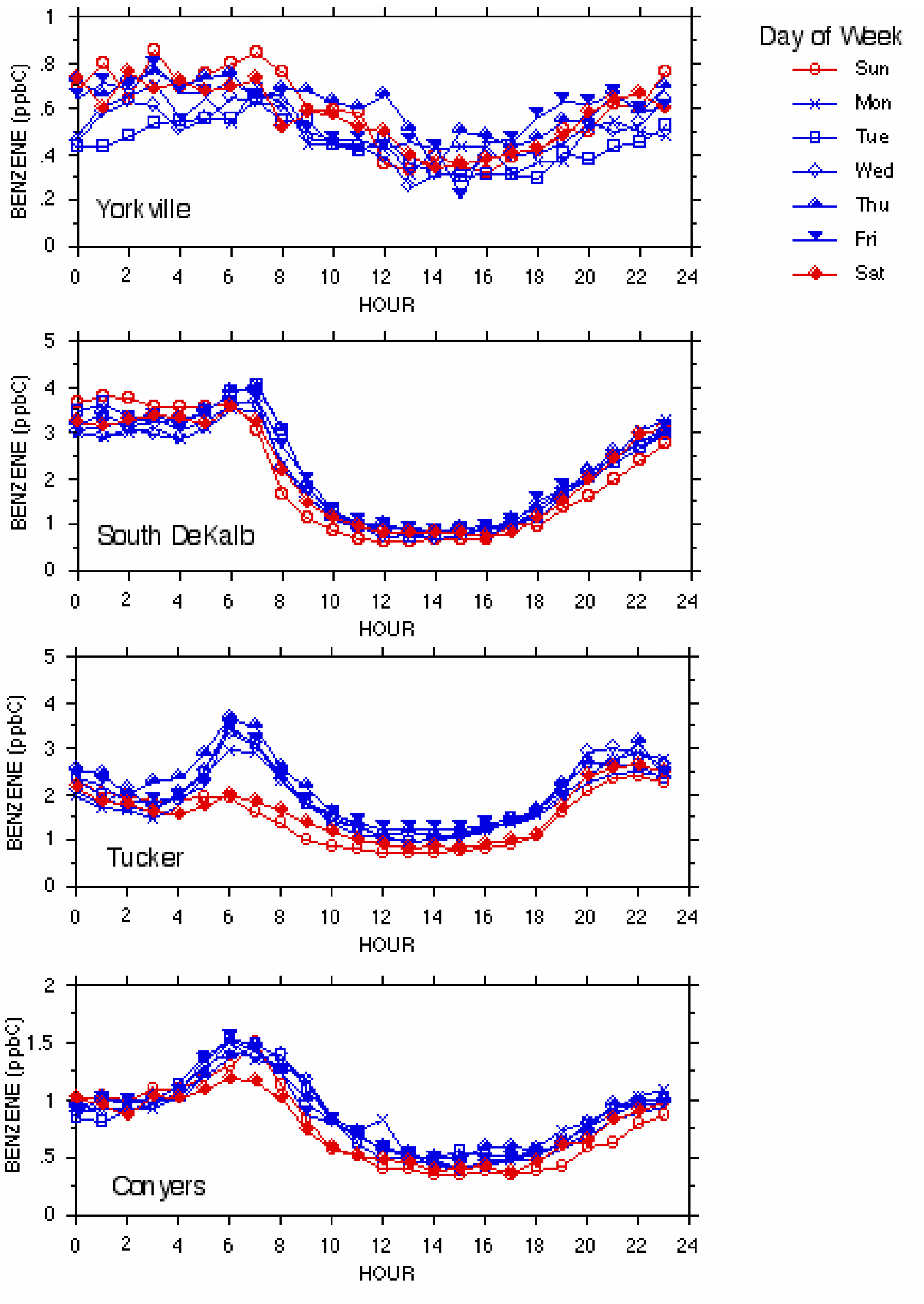


Figure 4. Diurnal profiles of mean ambient benzene levels at Yorkville, South DeKalb, Tucker and Conyers during the period 1996-2003, shown for each day of the week. The number of observations per day of week are as follows: Yorkville (22-37), So. DeKalb (67-93), Tucker (41-65) and Conyers (32-52).

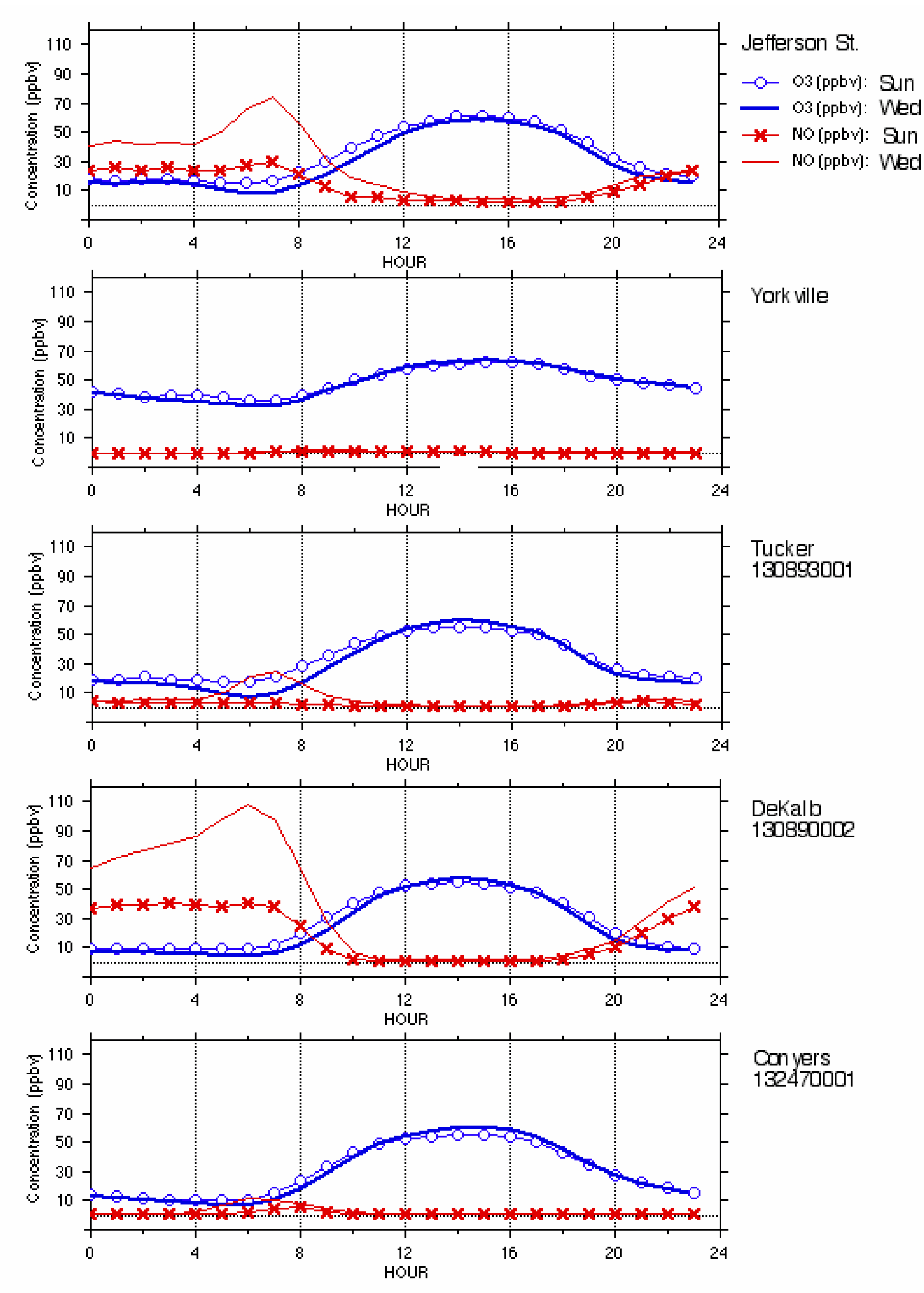


Figure 5. Diurnally-averaged concentrations of O_3 and NO on Sundays and Wednesdays.

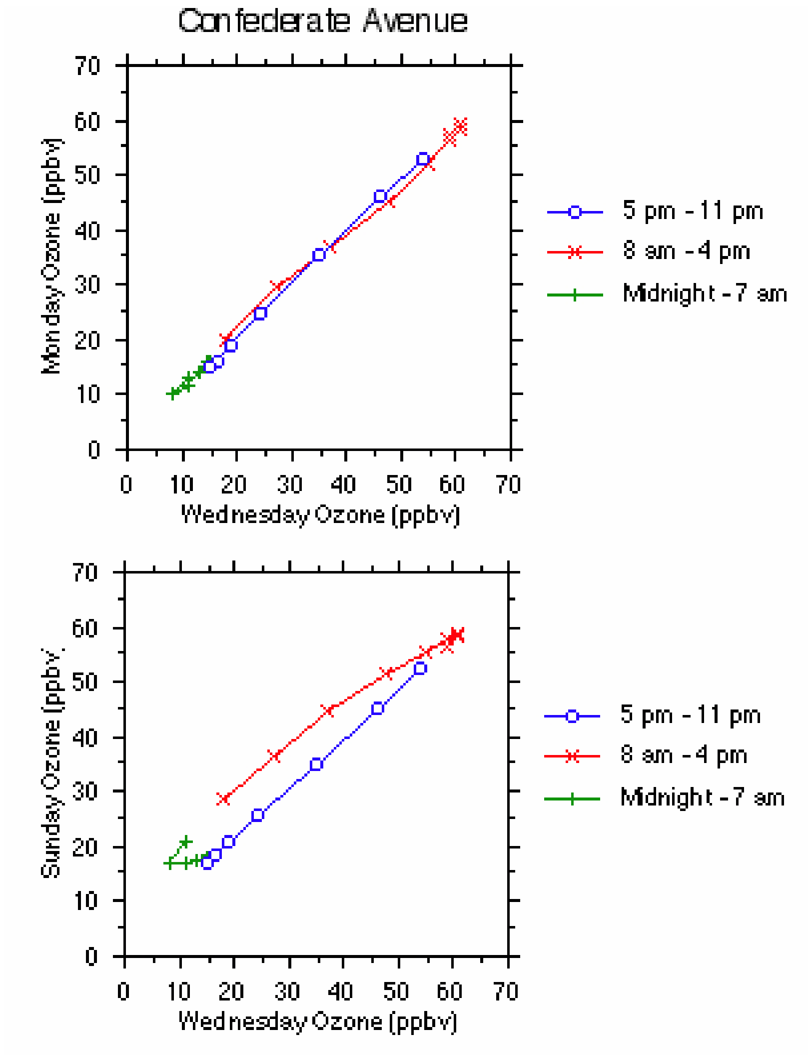


Figure 6. Mean Monday (top) and Sunday (bottom) hourly ozone concentrations versus mean Wednesday ozone concentrations at the Atlanta 8-hour ozone design-value monitoring site (Confederate Ave).

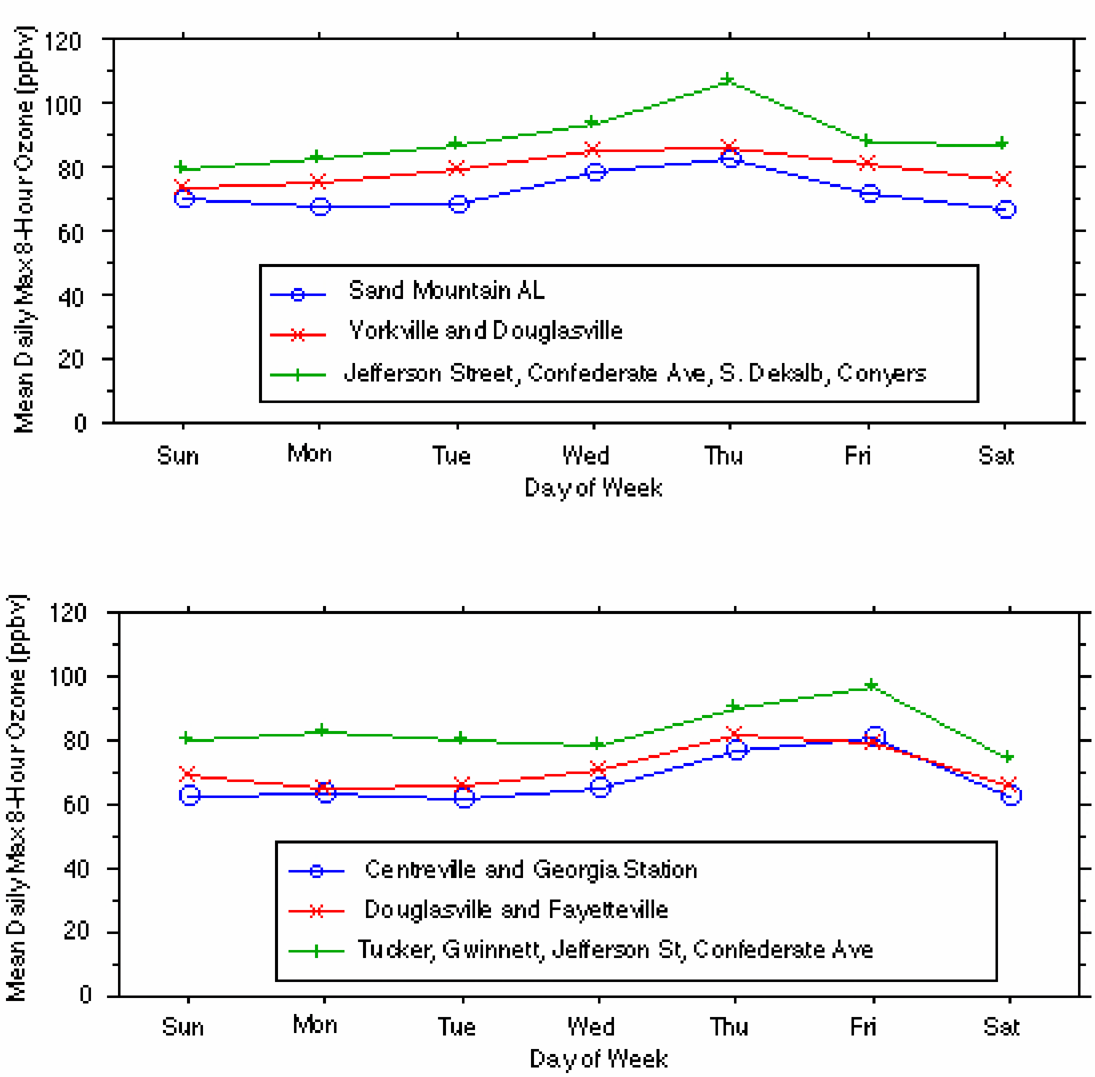


Figure 7. Mean daily 8-hour ozone maxima by day of week for high-ozone days at downwind sites (Conyers and Gwinnett), 1998-2002. The data have been averaged across monitoring locations representing far upwind (blue, circles), near upwind (red, x's), and urban/downwind (green, +'s) locations. The top and bottom panels shows days when 24-hour vector-average wind directions were from the northwest and wouthwest quadrants, respectively, based upon surface meteorological observations from Jefferson Street.

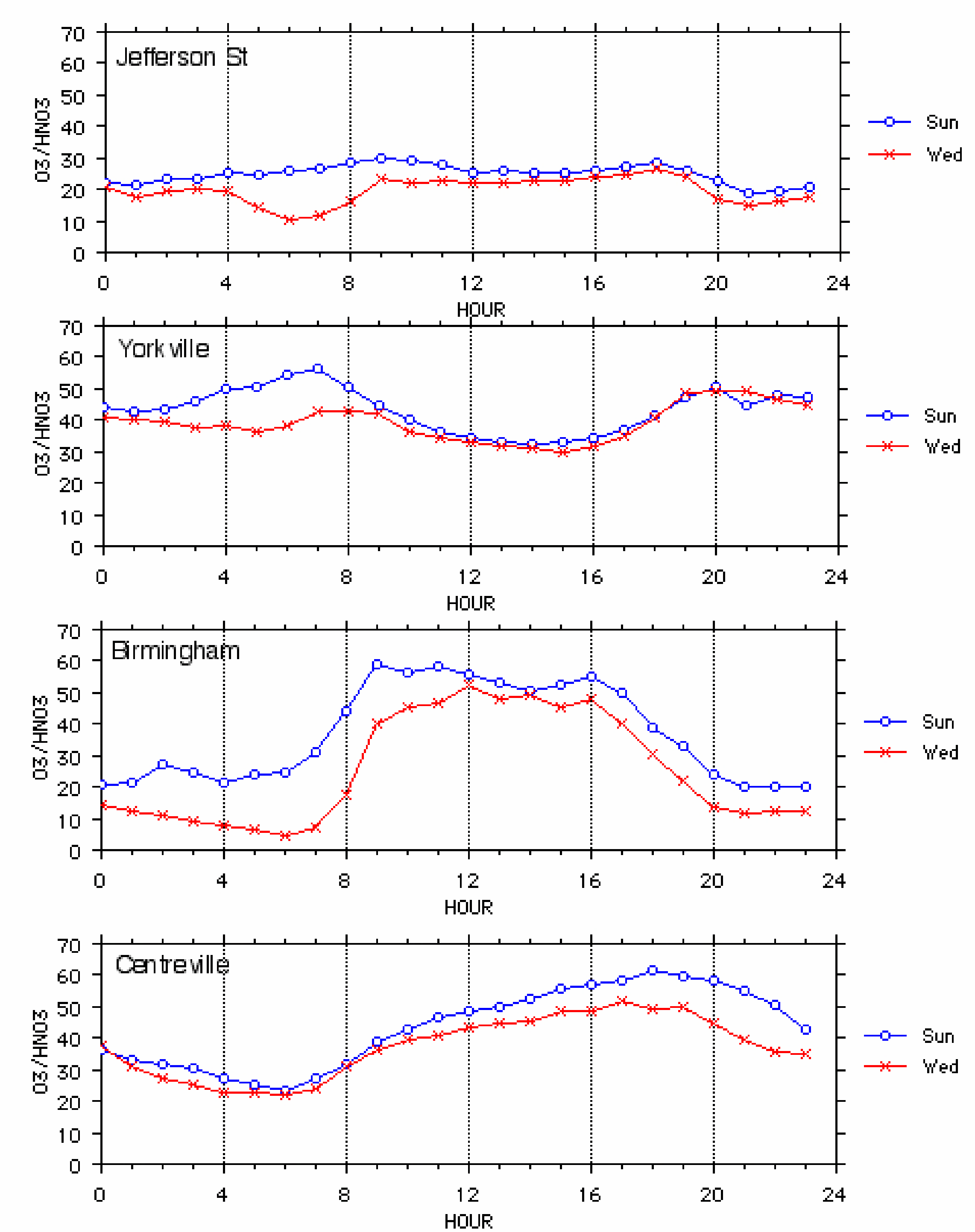


Figure 8. Hourly ratios of the mean concentrations of ozone and HNO_3 on Wednesdays and Sundays. Hourly averages were determined from measurements made at the SEARCH sites at Jefferson Street (Atlanta) (99-02), Yorkville (GA) (98-02), Birmingham (AL) (00-02) and Centreville (AL) (98-02) during the months of March through October, with each point representing approximately 30 hourly measurements per year.

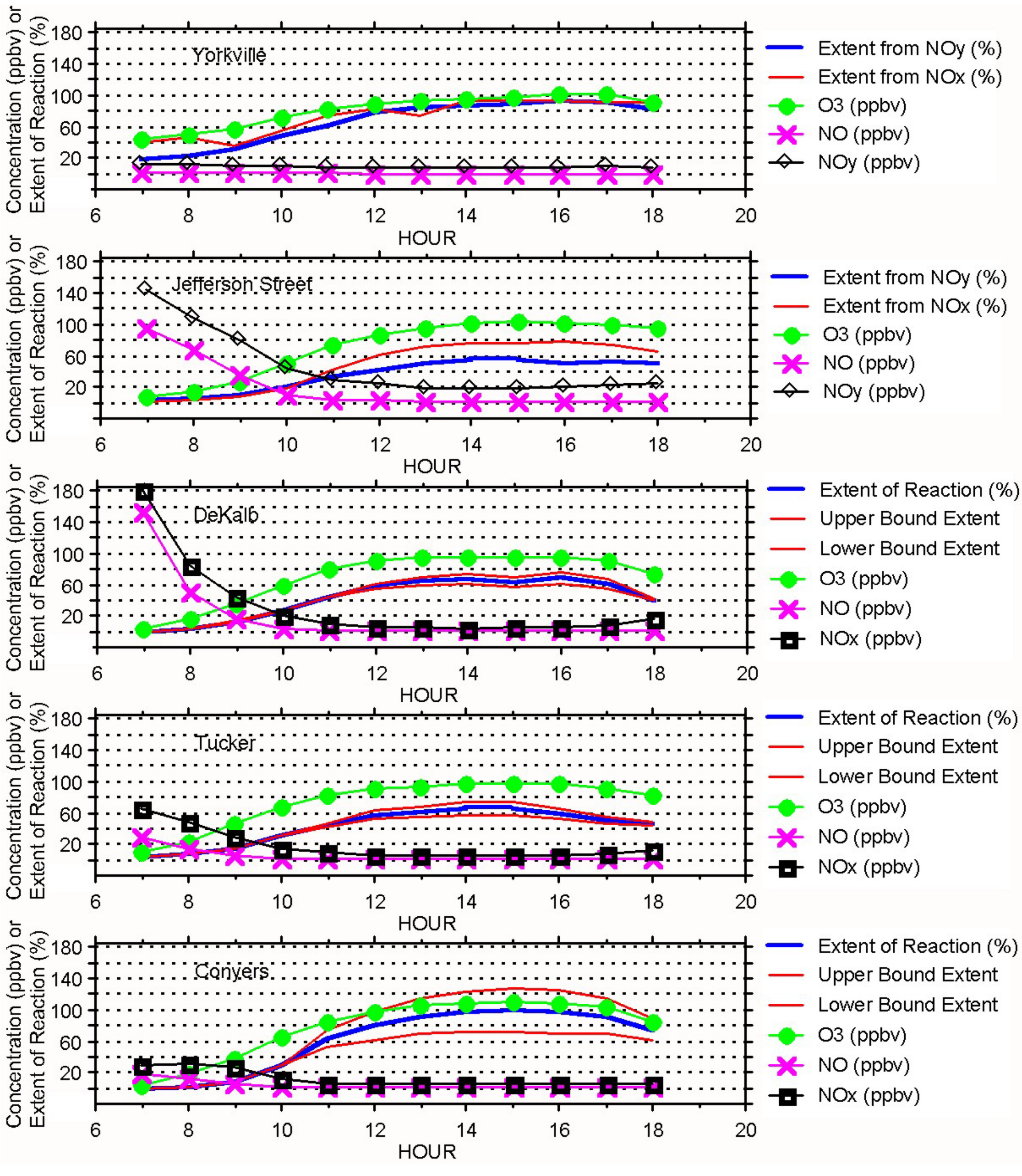


Figure 9. Hourly mean extent of reaction, ozone, NO, NO_x, and NO_y concentrations on high-ozone Wednesdays (top 3 peak 8-hour ozone-concentration Wednesdays per year), 1998-2002. For Yorkville and Jefferson Street, two alternative formulations of the extent of reaction were calculated using the measurements of NO_y and NO_x; the NO_x data were available only for 2001 and 2002 at Jefferson Street and 2002 at Yorkville. For the remaining three sites, upper and lower bounds of the extent of reaction were calculated using the available NO_x measurements and a best estimate is presented as the mean of the bounds.

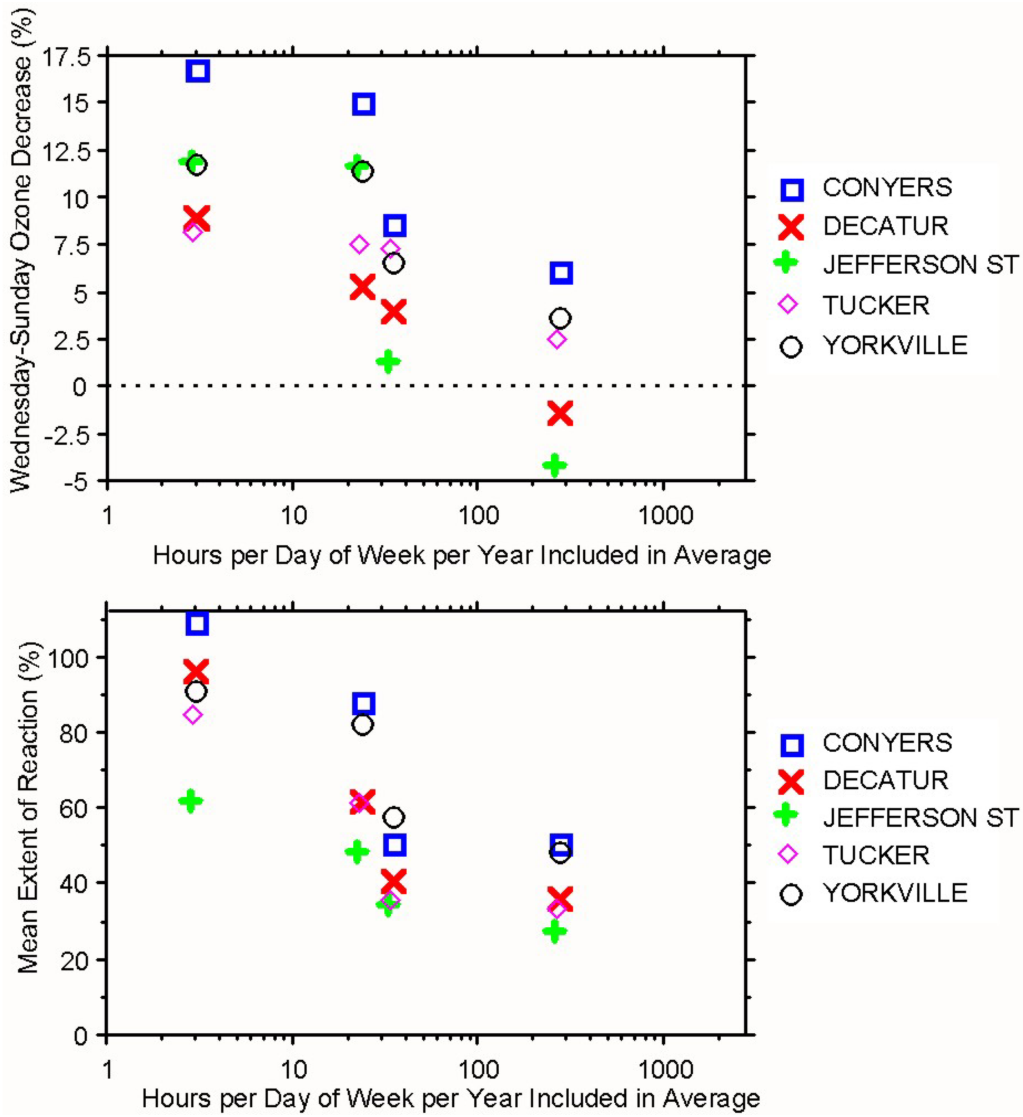


Figure 10. Mean Wednesday-to-Sunday decrease in peak ozone concentrations (top) and mean extent of reaction during peak ozone hours (bottom) versus the number of hours per day of week per year included in each average. From left to right, the number of hours correspond to peak 1-hour ozone averages on high-ozone days (top 3 days per day of week per year), peak 8-hour ozone on high-ozone days, peak 1-hour ozone on all ozone season days, and peak 8-hour ozone on all ozone season days.

APPENDIX A. WEEKDAY/WEEKEND CHANGES IN AMBIENT CONCENTRATIONS OF PRIMARY POLLUTANTS

Table A-1. Differences between mean Wednesday and Saturday NO and NO_x or NO_y concentrations at 6 am and 12 noon (percent declines relative to mean Wednesday levels). Positive numbers represent higher Wednesday concentrations. Statistically significant ($p<0.01$) differences are shown in bold. Statistical tests were not applied to the means and medians. The averages were determined from all days during March through October of 1998 through 2002. Mean and median were determined from AIRS sites. The number of observations for Wednesday NO 6am means are listed after the city name.

AIRS/ SEARCH	**CITY**	**Wednesday – Saturday Decrease (percent)**					
		NO 6am	NO Noon	NO_x 6am	NO_x noon	NO_y 6am	NO_y noon
130890002	So. DeKalb/Decatur GA (140)	**38.3**	18.2	**36.4**	31.2		
130893001	Tucker/Atlanta GA (149)	**72.8**	21.0	**51.7**	**26.6**		
131210048	GA Tech/Atlanta GA (160)	38.3	**55.2**	**31.8**	**37.5**		
132470001	Conyers/Atlanta GA (164)	64.5	**21.4**	49.0	31.5		
	Mean	53.5	28.9	42.2	31.7		
	Median	51.4	21.2	42.7	31.3		
CTR*	Centreville AL (134)	17.8	35.2			4.9	20.4
JST*	Jefferson St/Atlanta GA (133)	**41.7**	**50.2**			**32.3**	**37.3**
YRK*	Yorkville GA (133)	27.1	**45.8**			19.6	**21.7**

*1999-2002

Table A-2. Differences between mean Wednesday and Sunday NO, NO_x , or NO_y concentrations at 6 am and 12 noon (percent declines relative to mean Wednesday levels). Positive numbers represent higher Wednesday concentrations. Statistically significant ($p<0.01$) differences are shown in bold. Statistical tests were not applied to the medians. The averages were determined from all days during March through October of 1998 through 2002. Mean and median were determined from AIRS sites. The number of observations for Wednesday NO 6am means are listed after the city name.

AIRS/ SEARCH	**CITY**	**Wednesday – Sunday Decrease (percent)**					
		NO 6am	NO noon	NO_x 6am	NO_x noon	NO_y 6am	NO_y noon
130890002	So. DeKalb/Decatur GA (140)	**62.6**	**57.3**	**60.1**	**53.1**		
130893001	Tucker/Atlanta GA (149)	**83.1**	**55.2**	**65.2**	**51**		
131210048	GA Tech/Atlanta GA (160)	**58.6**	**81.5**	**50.8**	**59.7**		
132470001	Conyers/Atlanta GA (164)	**80.0**	37.4	**66.6**	**49.1**		
	Mean	71.1	57.8	60.7	53.2		
	Median	71.3	56.3	62.6	52.0		
CTR*	Centreville AL (134)	33.5	37.2			20.8	**26.5**
JST*	Jefferson St/Atlanta GA (133)	**55.8**	**64.0**			**46.0**	**50.9**
YRK*	Yorkville GA (133)	53.7	**62.3**			**33.1**	**34.8**

*1999-2002

Table A-3. Differences between mean Wednesday and Sunday NO, NO_x , or NO_y concentrations at 6 am and 12 noon on high-ozone days (percent declines relative to mean Wednesday levels). Averages were determined from the top three peak 8-hour ozone days per day of week per year. The data are from March through October of 1998 through 2002. Mean and median were determined from AIRS sites only. Sites having fewer than three years of data were excluded. Positive numbers represent higher Wednesday concentrations. Statistically significant ($p<0.01$) differences are shown in bold. Statistical tests were not applied to the medians.

AIRS/ SEARCH	**CITY**	**Wednesday – Sunday Decrease (percent)**					
		NO 6am	NO noon	NO_x 6am	NO_x noon	NO_y 6am	NO_y noon
130890002	So. DeKalb/Decatur GA	**69.6**	51.0	**63.4**	39.3		
130893001	Tucker/Atlanta GA	**84.1**	-50.0	**66.4**	20.6		
132470001	Conyers/Atlanta GA	21.1	52.7	11.7	37.3		
	Mean	58.2	17.9	47.2	32.4		
	Median	69.6	51.0	63.4	37.3		
CTR*	Centreville AL	1.7	35.8			7.5	38.2
JST*	Jefferson St/Atlanta GA	71.5	52.9			56.0	33.6
YRK*	Yorkville GA	42.9	-52.5			42.6	11.1

*1999-2002

Table A-4. Differences between mean Wednesday and Sunday CO concentrations at 6 am and 12 noon (percent declines relative to mean Wednesday levels). Positive numbers represent higher Wednesday concentrations. Statistically significant ($p<0.01$) differences are shown in bold. The averages were determined from all days during March through October of 1998 through 2002 (AIRS: DeKalb and Roswell) or 1999 through 2001 (SEARCH: Centreville, Jefferson St., and Yorkville).The number of observations for Wednesday CO 6am means are listed after the city name.

AIRS/ SEARCH	**CITY**	**Wednesday – Sunday Decrease (percent)**	
		CO 6am	CO noon
130891002	So. DeKalb/Decatur GA (101)	**30.0**	14.4
131210099	Roswell/Atlanta GA (103)	**46.9**	**32.2**
CTR	Centreville AL (134)	2.6	7.7
JST	Jefferson St/Atlanta GA (133)	**36.3**	35.4
YRK	Yorkville GA (134)	5.7	9.1

Table A-5. Differences between mean 24-hour Wednesday and Sunday black carbon and organic carbon concentrations (percent declines relative to mean Wednesday levels). Positive numbers represent higher Wednesday concentrations. Statistically significant ($p<0.01$) differences are shown in bold. The averages were determined from all days during 2000-2002 for AIRS/PM-STN sites (So. DeKalb/Atlanta GA, No. Birmingham and Wylam/ Birmingham AL) or 1998-2002 for SEARCH sites (Birmingham AL, Centreville AL, Jefferson St./Atlanta GA, and Yorkville GA). The number of observations for Wednesday OC means are listed after the city name.

AIRS/ SEARCH	**CITY**	**Wednesday – Sunday Decrease (percent)**	
		Black Carbon	Organic Carbon
10730023	No. Birmingham/Birmingham AL (32)	35.4	13.1
10732003	Wylam/Birmingham AL (11)	23.0	4.5
130890002	So. DeKalb/Decatur GA (30)	**37.3**	4.6
BHM	Birmingham AL (105)	**31.3**	**19.1**
CTR	Centreville AL (122)	15.8	10.4
JST	Jefferson St/Atlanta GA (219)	**31.1**	7.8
YRK	Yorkville GA (126)	13.0	0.9

Table A-6. Differences between mean Wednesday and Sunday black carbon concentrations computed at different temporal resolutions (percent declines relative to mean Wednesday levels). Positive numbers represent higher Wednesday concentrations. Statistically significant ($p<0.01$) differences are shown in bold. The averages were determined from all days during 2001-2002 with continuous carbon measurements at four SEARCH sites. The number of observations for Wednesday 6 AM black carbon means are listed after the city name.

Site	CITY	**Wednesday – Sunday Decrease (percent)**					
		6 am	12 noon	6-9 am	9 am – 12 noon	12 noon – 3 pm	6 am – 3 pm
BHM	Birmingham (87)	**42.0**	**47.0**	**43.7**	**50.2**	**46.0**	**43.4**
CTR	Centreville (39)	36.7	**49.8**	31.3	41.3	**55.4**	**41.7**
JST	Jefferson St (98)	**55.1**	**55.7**	**56**	**62.3**	**55.5**	**57.8**
YRK	Yorkville (42)	**34.1**	**47.8**	**39.2**	**43.9**	**47.9**	**43.9**

Table A-7. Differences between mean Wednesday and Sunday organic carbon concentrations computed at different temporal resolutions (percent declines relative to mean Wednesday levels). Positive numbers represent higher Wednesday concentrations. Statistically significant ($p<0.01$) differences are shown in bold. The averages were determined from all days during 2001-2002 with continuous carbon measurements at four SEARCH sites. The number of observations for Wed 6 AM organic carbon means are listed after the city name.

Site	CITY	**Wednesday – Sunday Decrease (percent)**					
		6 am	12 noon	6-9 am	9 am – 12 noon	12 noon – 3 pm	6 am – 3 pm
BHM	Birmingham (79)	-2.8	20.1	-0.2	-2.2	-17.5	-7.7
CTR	Centreville (35)	16.0	33.3	13.7	18.5	52.8	34.3
JST	Jefferson St (88)	-13.5	**33.0**	4.9	51.1	**28.6**	28.7
YRK	Yorkville (22)	6.4	-20.2	7.4	-4.3	1.0	3.7

Table A-8. Mean ambient concentrations (6 am – 3 pm) and standard error (SE) of alkanes, alkenes, aromatics, benzene, isoprene and the sum of species (denoted "total"), and percent decreases from Wednesday to Sunday. Positive differences represent higher Wednesday concentrations. Statistically significant differences are in bold ($p<0.01$). Data are from 1996-2003. The number of daily observations for Wednesday means are listed after the site name.

Site/Airs Code	Species	Wednesday – Sunday Decrease (percent)	Wednesday Mean (SE) (ppbC)	Sunday Mean (SE) (ppbC)
South DeKalb 130890002 (90)	ALKANES	**23.6**	33.7 (2.30)	25.7 (1.84)
	ALKENES	15.4	10.1 (0.59)	8.6 (0.54)
	AROMATIC	**31.7**	17.2 (1.29)	11.7 (1.01)
	BENZENE	21.7	1.9 (0.13)	1.5 (0.11)
	ISOPRENE	1.9	5.3 (0.26)	5.1 (0.27)
	TOTAL	**24.6**	62.3 (4.11)	47.0 (3.38)
Tucker 130893001 (64)	ALKANES	**32.5**	32.5 (2.00)	21.9 (1.33)
	ALKENES	26.3	11.6 (0.89)	8.6 (0.80)
	AROMATIC	**57.6**	20.2 (1.41)	8.6 (0.58)
	BENZENE	**39.2**	1.8 (0.09)	1.1 (0.06)
	ISOPRENE	17.0	7.7 (0.87)	6.4 (0.76)
	TOTAL	**39.5**	65.2 (3.77)	39.4 (2.42)
Yorkville 132230003 (37)	ALKANES	-8.0	9.2 (0.60)	9.9 (0.79)
	ALKENES	-12.6	6.0 (0.53)	6.8 (0.56)
	AROMATIC	-0.1	3.3 (0.42)	3.3 (0.50)
	BENZENE	-23.8	0.5 (0.10)	0.6 (0.13)
	ISOPRENE	-8.9	5.7 (0.53)	6.2 (0.55)
	TOTAL	-7.8	18.9 (1.18)	20.4 (1.40)
Conyers 132470001 (46)	ALKANES	8.5	20.1 (1.89)	18.4 (1.43)
	ALKENES	11.5	8.8 (0.61)	7.8 (0.51)
	AROMATIC	24.6	7.8 (0.86)	5.9 (0.62)
	BENZENE	20.1	1.0 (0.10)	0.8 (0.08)
	ISOPRENE	7.7	6.7 (0.44)	6.1 (0.40)
	TOTAL	12.8	37.5 (3.24)	32.6 (2.43)
Mean	ALKANES	14.2	23.8	19.0
	ALKENES	10.1	9.1	7.9
	AROMATIC	28.5	12.1	7.4
	BENZENE	14.3	1.3	1.0
	ISOPRENE	4.4	6.3	6.0
	TOTAL	17.3	46.0	34.9
Median	ALKANES	16.0	26.3	20.1
	ALKENES	13.4	9.5	8.2
	AROMATIC	28.2	12.5	7.2
	BENZENE	20.9	1.4	0.9
	ISOPRENE	4.8	6.2	6.2
	TOTAL	18.7	49.9	36.0

Table A-9. Differences between mean Wednesday and Sunday HNO_3 concentrations at 6 am, noon, 6-9am, 9am-12 noon, 12 noon-3pm and 6am-3pm (percent declines relative to mean Wednesday levels). Positive numbers represent higher Wednesday concentrations. None of the differences are statistically significant. The averages were determined from days during March through October of 1999 through 2002. All locations are SEARCH sites.

SITE	**CITY**	**HNO_3 Wednesday – Sunday Decrease (percent)**					
		6am	noon	6-9 am	9am-noon	Noon-3pm	6am-3pm
BHM	Birmingham AL*	53.6	2.7	51.8	15.7	8.8	27.1
CTR	Centreville AL	19.5	19.9	22.0	20.5	18.8	20.4
JST	Jefferson St/Atlanta GA	30.3	17.0	22.0	11.6	21.5	18.6
YRK	Yorkville GA	27.4	18.8	25.7	**23.4**	19.1	21.8

*Oct 2000 – Dec 2002

Table A-10. Differences between mean Wednesday and Sunday nitrate and sulfate concentrations (percent declines relative to mean Wednesday levels). Positive numbers represent higher Wednesday concentrations. None of the differences are statistically significant ($p<0.01$). The averages were determined from all days during 2000-2002 (AIRS/PM-STN: So. DeKalb/Atlanta GA and No. Birmingham) and 1998-2002 (SEARCH: Birmingham AL, Centreville AL, Jefferson St./Atlanta GA, and Yorkville GA).

AIRS or SEARCH	**CITY**	**Wednesday – Sunday Decrease (percent)**	
		Nitrate	Sulfate
010730023	No. Birmingham AL	8.7	-1.2
130890002	So. DeKalb/Atlanta GA	25.2	7.8
BHM	Birmingham AL	19.2	4.0
CTR	Centreville AL	20.8	-1.2
JST	Jefferson St/Atlanta GA	18.8	5.1
YRK	Yorkville GA	15.6	-5.4

APPENDIX B. SPATIAL AND TEMPORAL PATTERNS OF WEEKDAY/WEEKEND OZONE CHANGES

When determined from all days during March through October, the ratios of mean Sunday to mean Wednesday peak 8-hour ozone concentrations were in the range of 90 to 105 percent (Figure B-1). Two of the three sites with higher mean Sunday levels (ratio of mean Sunday to mean Wednesday exceeding 100 percent) were central (Confederate Avenue) or high-emissions sites (DeKalb, PAMS type 2).

When determined from high-ozone days during March through October, all sites showed lower mean levels on Sundays than on Wednesdays: the ratios of mean Sunday to mean Wednesday peak 8-hour ozone concentrations were in the range of 80 to 95 percent (Figure B-2).

The analysis of spatial patterns reveals an additional feature of interest: the average maximum high-ozone levels occurred on either Wednesdays or Thursdays according to location. At sites west of Atlanta, the highest mean 8-hour ozone concentrations occurred on Wednesdays, whereas at sites within and east of Atlanta, the highest mean 8-hour concentrations occurred on Thursdays (Figure B-3). The day-of-week differences in mean peak concentrations were typically larger for the high-ozone days than for means that were determined from all ozone-season days (Figures B-4 through B-6).

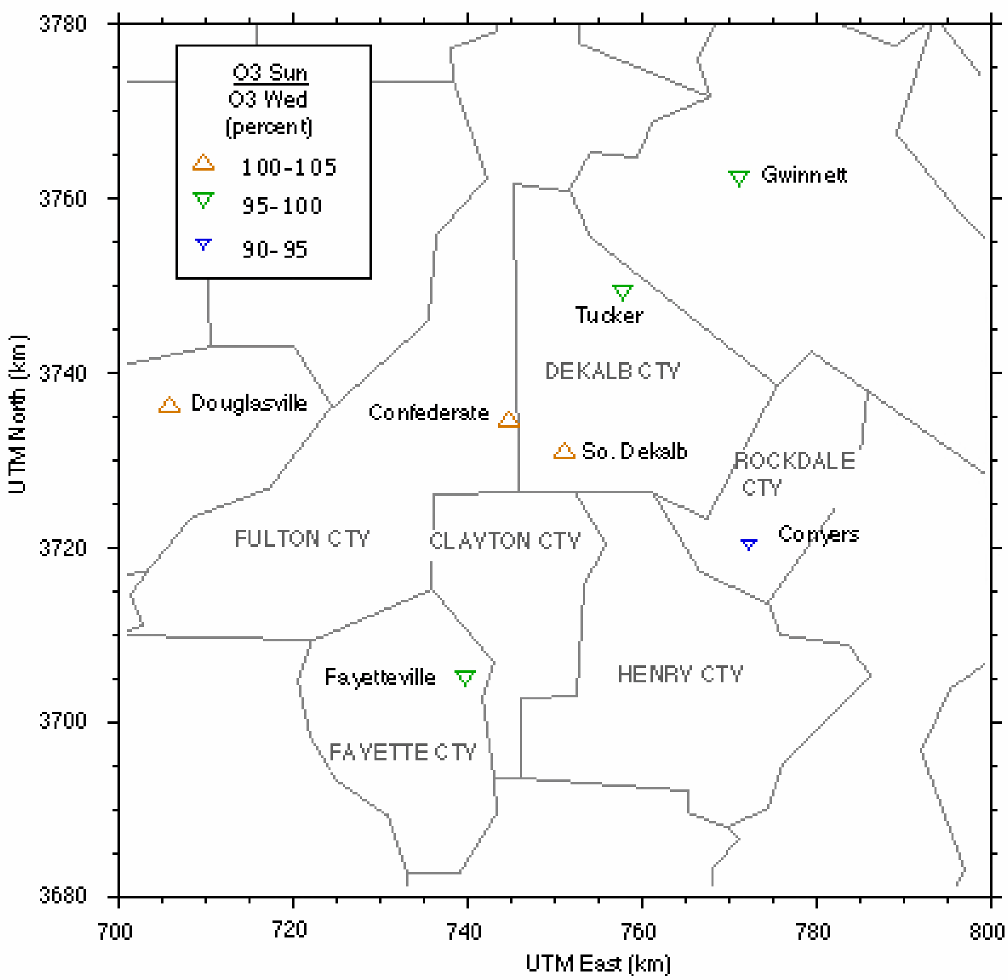


Figure B-1. Ratios of mean eight-hour ozone concentrations on Wednesdays to Sundays at sites in the Atlanta area. The differences were determined from all days, March-October 1998-2002. Ratios less than 100 percent indicate that the mean Sunday concentrations were lower than the mean Wednesday concentrations.

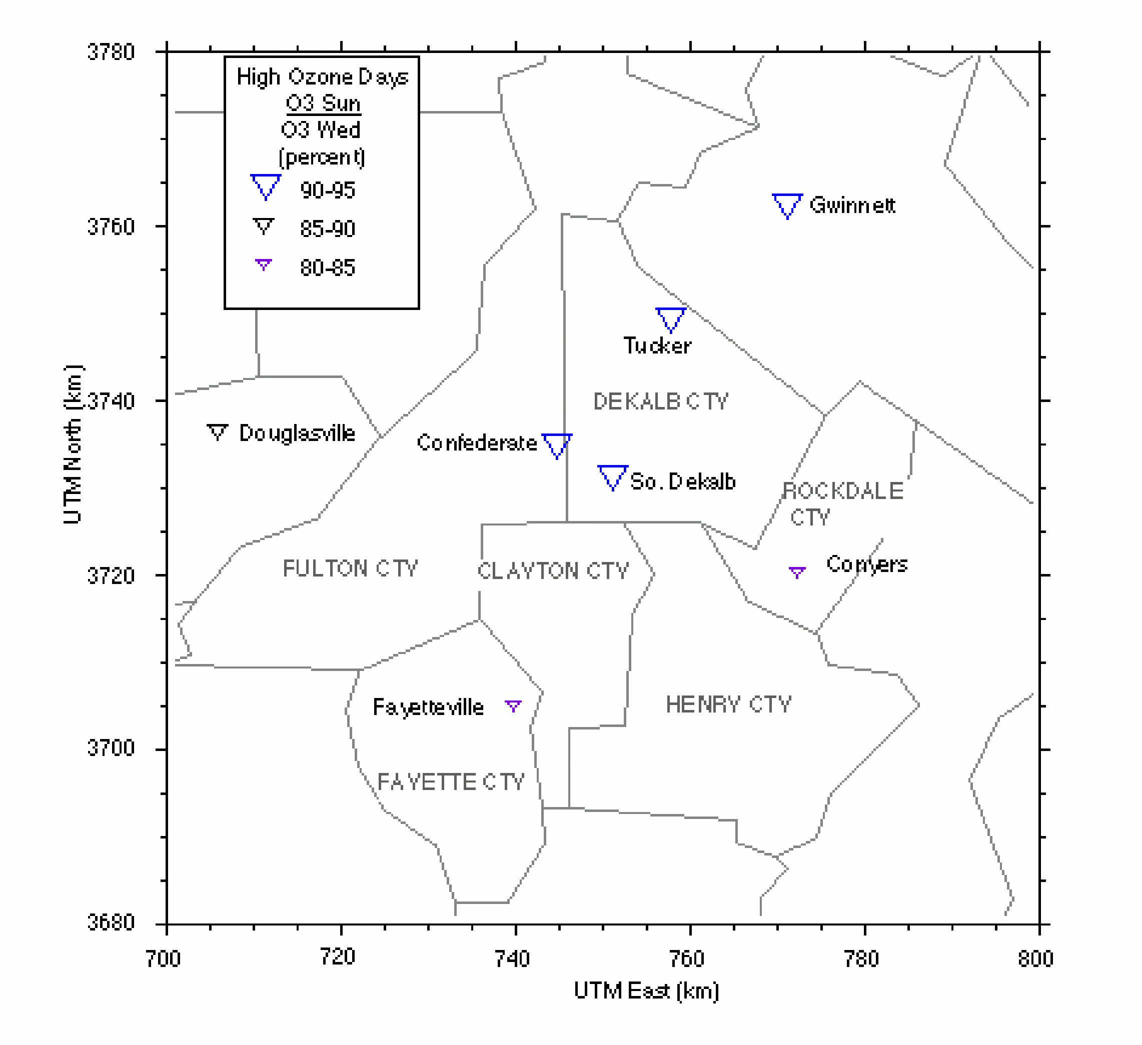
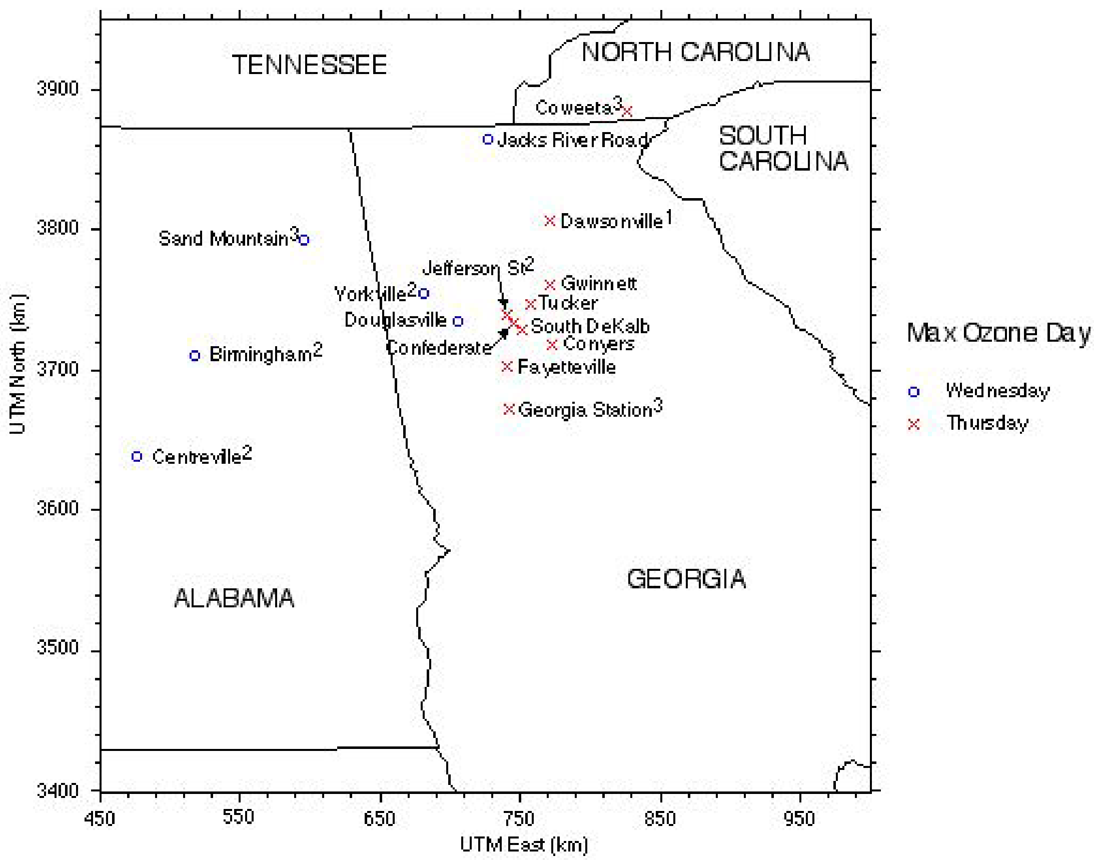


Figure B-2. Ratios of mean eight-hour ozone concentrations on Wednesdays to Sundays at sites in the Atlanta area on high-ozone days. The differences were determined from the top three peak 8-hour ozone days per day of week per year, March-October 1998-2002. Ratios less than 100 percent indicate that the mean Sunday concentrations were lower than the mean Wednesday concentrations.



[1]data limited to 2001-02
[2]SEARCH site, 1999-2001
[3]CASTNet site, 1998-2001

Figure B-3. Mean peak 8-hour ozone by day of week (from top three ozone days for each day of week) during the period March-October, 1998-2002 (unless noted) in the Atlanta area.

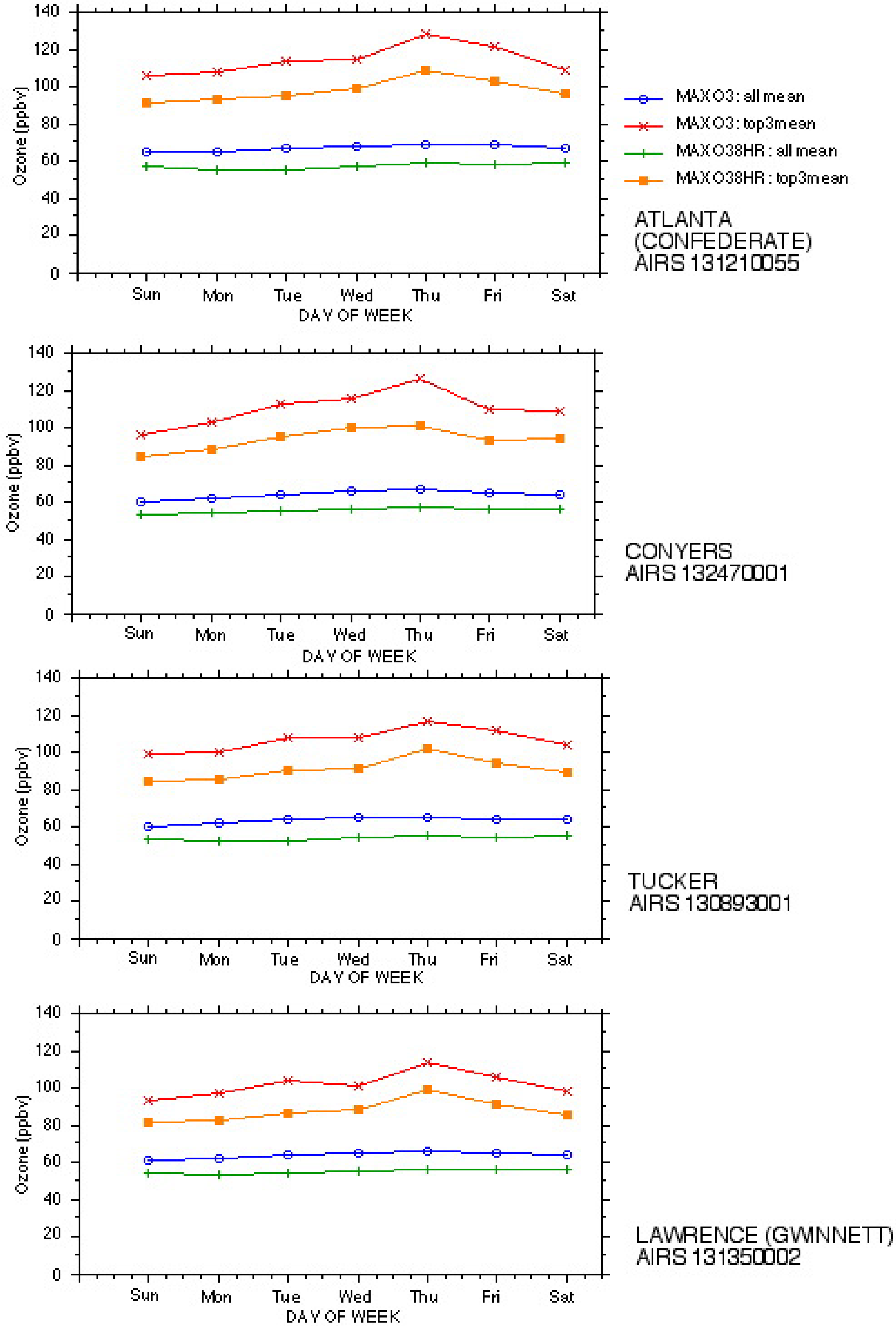


Figure B-4. Maximum 1-hour and 8-hour ozone means for all days and for top 3 days per day of week at four sites (Confederate/Atlanta, Conyers, Tucker and Lawrenceville/Gwinnett) for the period March-October, 1998-2002.

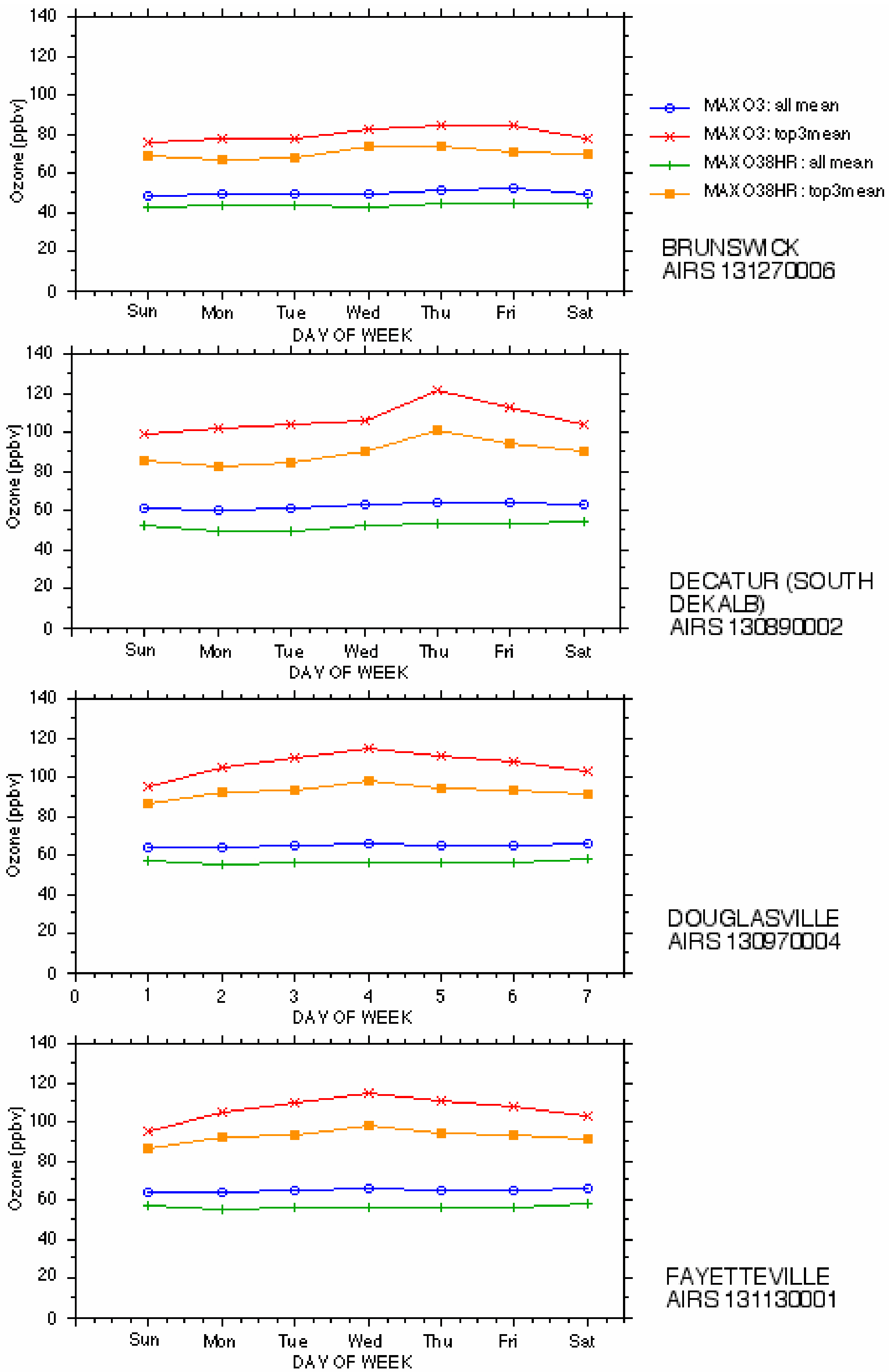


Figure B-5. Maximum 1-hour and 8-hour ozone means for all days and for top 3 days per day of week at four sites (Brunswick, Decatur/S. DeKalb, Douglasville, Fayetteville) for the period March-October, 1998-2002.

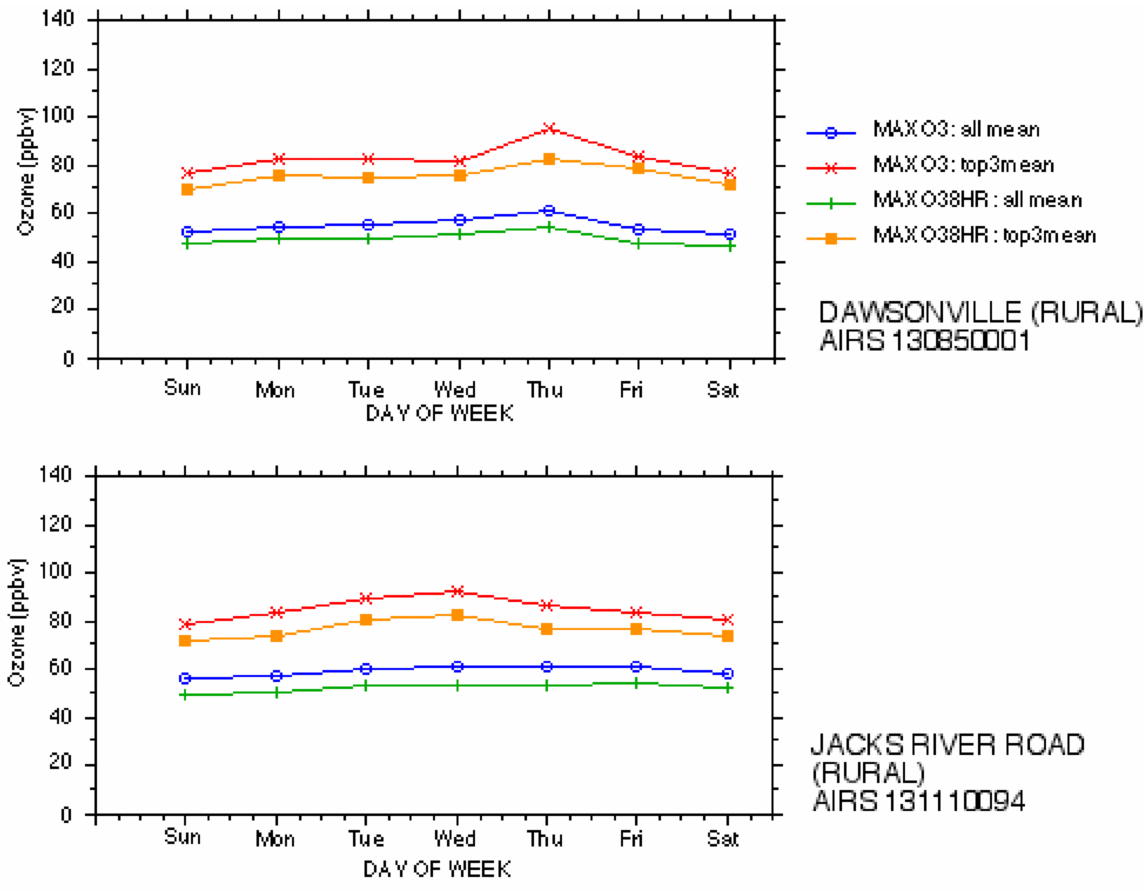


Figure B-6. Maximum 1-hour and 8-hour ozone means for all days and for top 3 days per day of week at two rural sites (Dawsonville and Jacks River Road) for the period March-October, 1998-2002.

APPENDIX C. DAY-OF-WEEK CHANGES IN MEAN HOURLY POLLUTANT CONCENTRATIONS

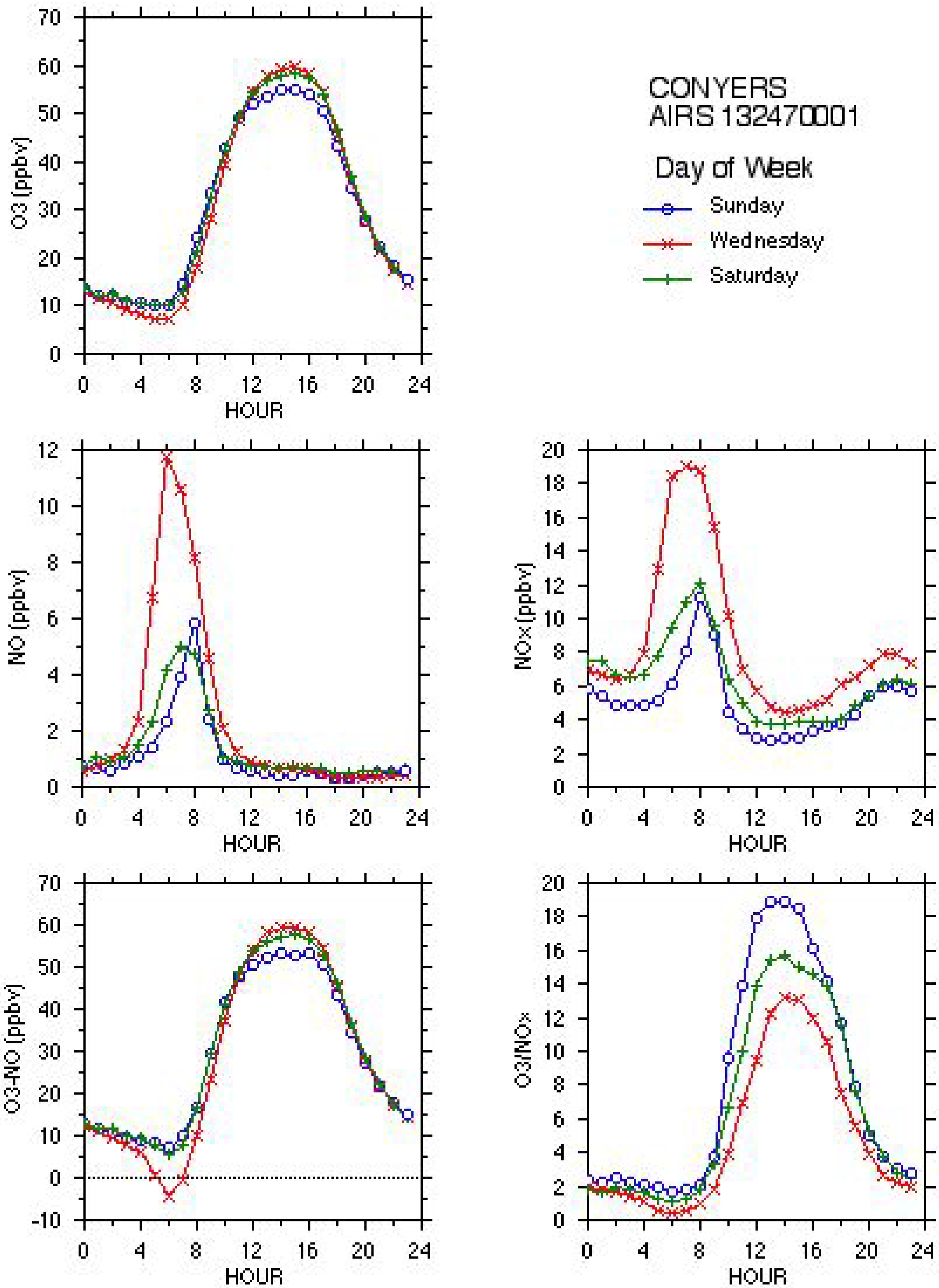


Figure C-1. Diurnal profiles comparing Sunday, Saturday and Wednesday for O_3, NO, NO_x, O_3-NO, and O_3/NO_x during the period March-October 1998-2002 at Conyers.

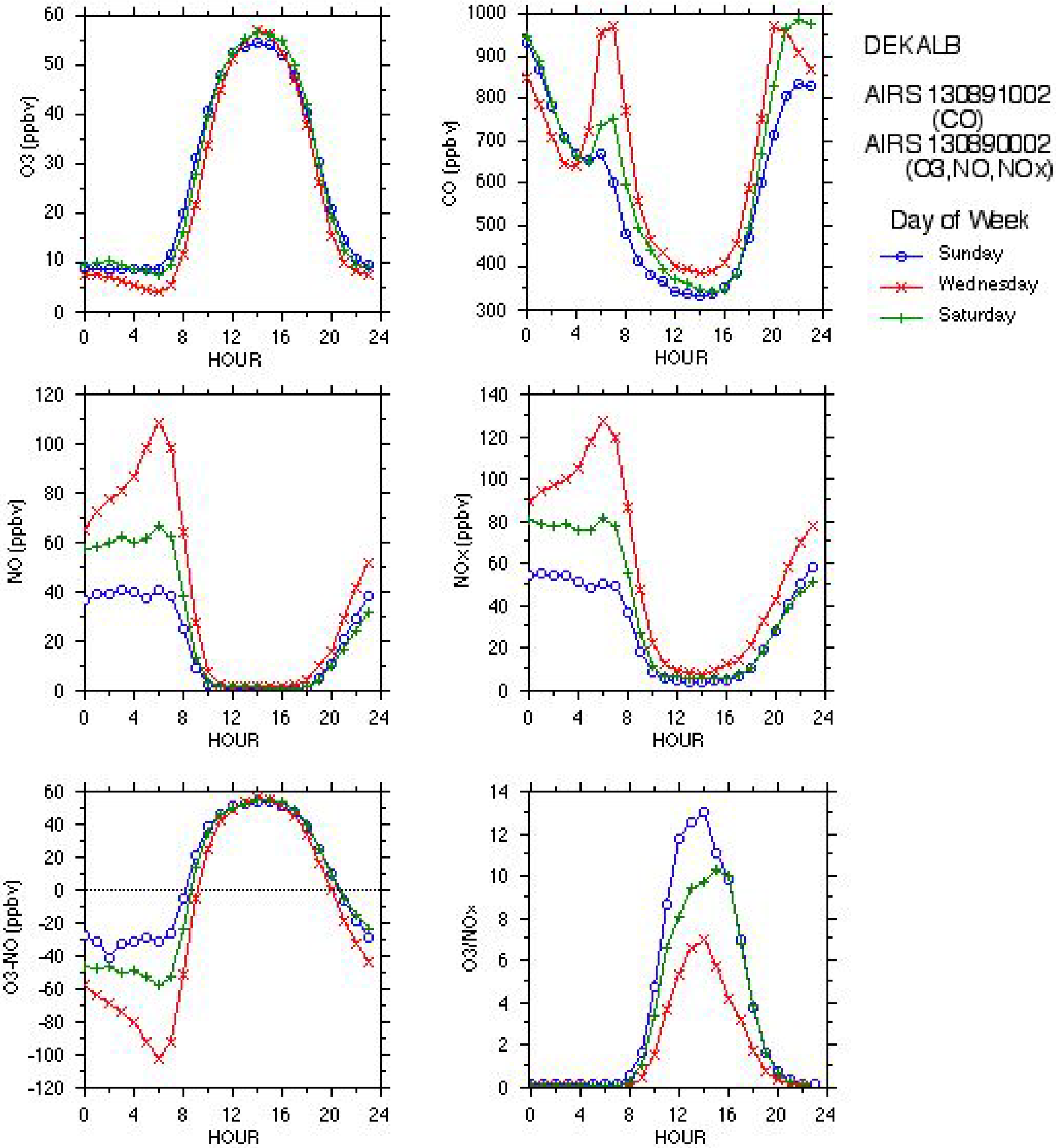


Figure C-2. Diurnal profiles comparing Sunday, Saturday and Wednesday for O_3, NO, NO_x, O_3-NO, and O_3/NO_x during the period March-October 1998-2002 at So. DeKalb/Decatur (O_3, NO, NO_x) and DeKalb/Clarkston (CO).

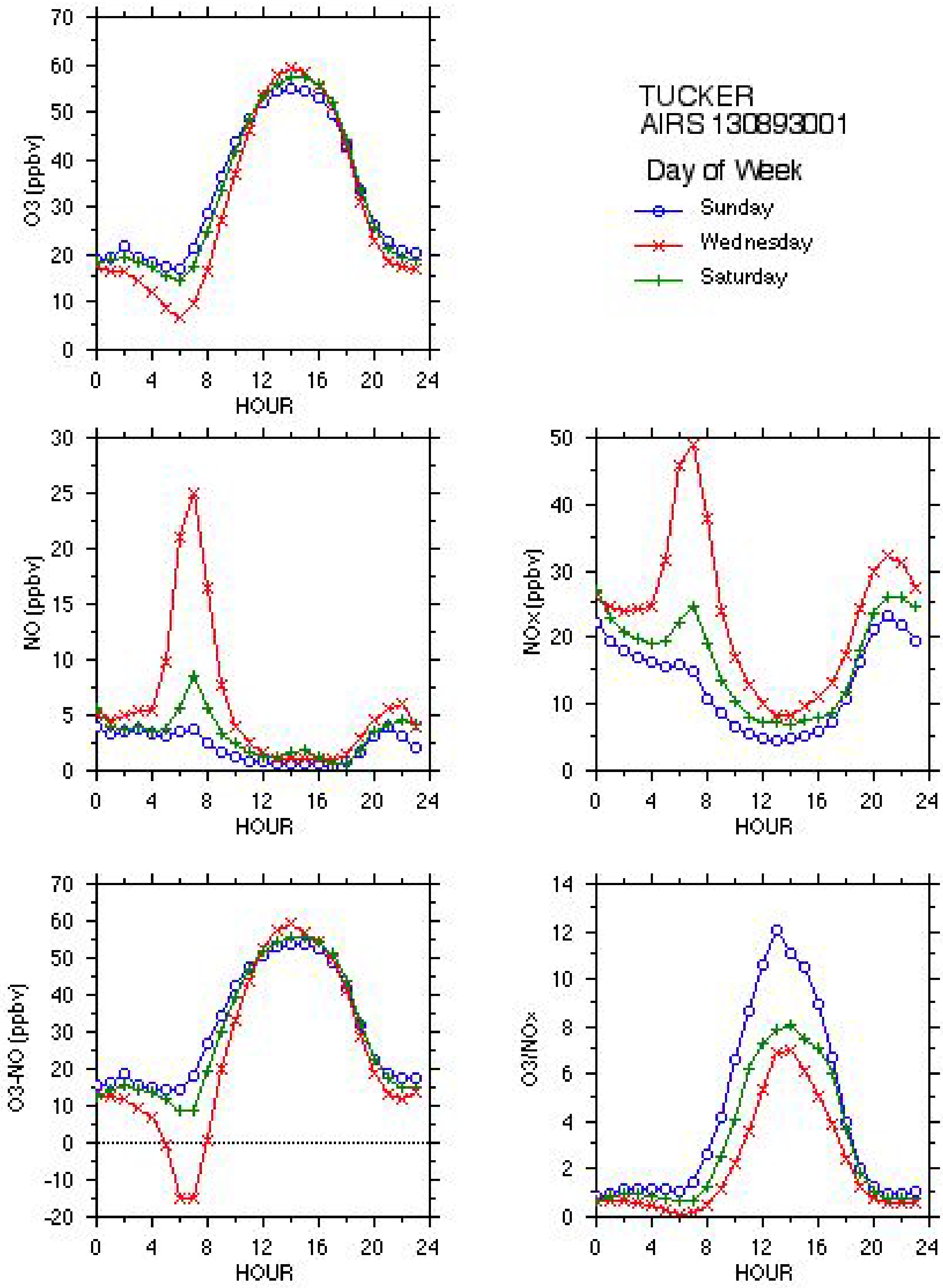


Figure C-3. Diurnal profiles comparing Sunday, Saturday and Wednesday for O_3, NO, NO_x, O_3-NO, and O_3/NO_x during the period March-October 1998-2002 at Tucker.

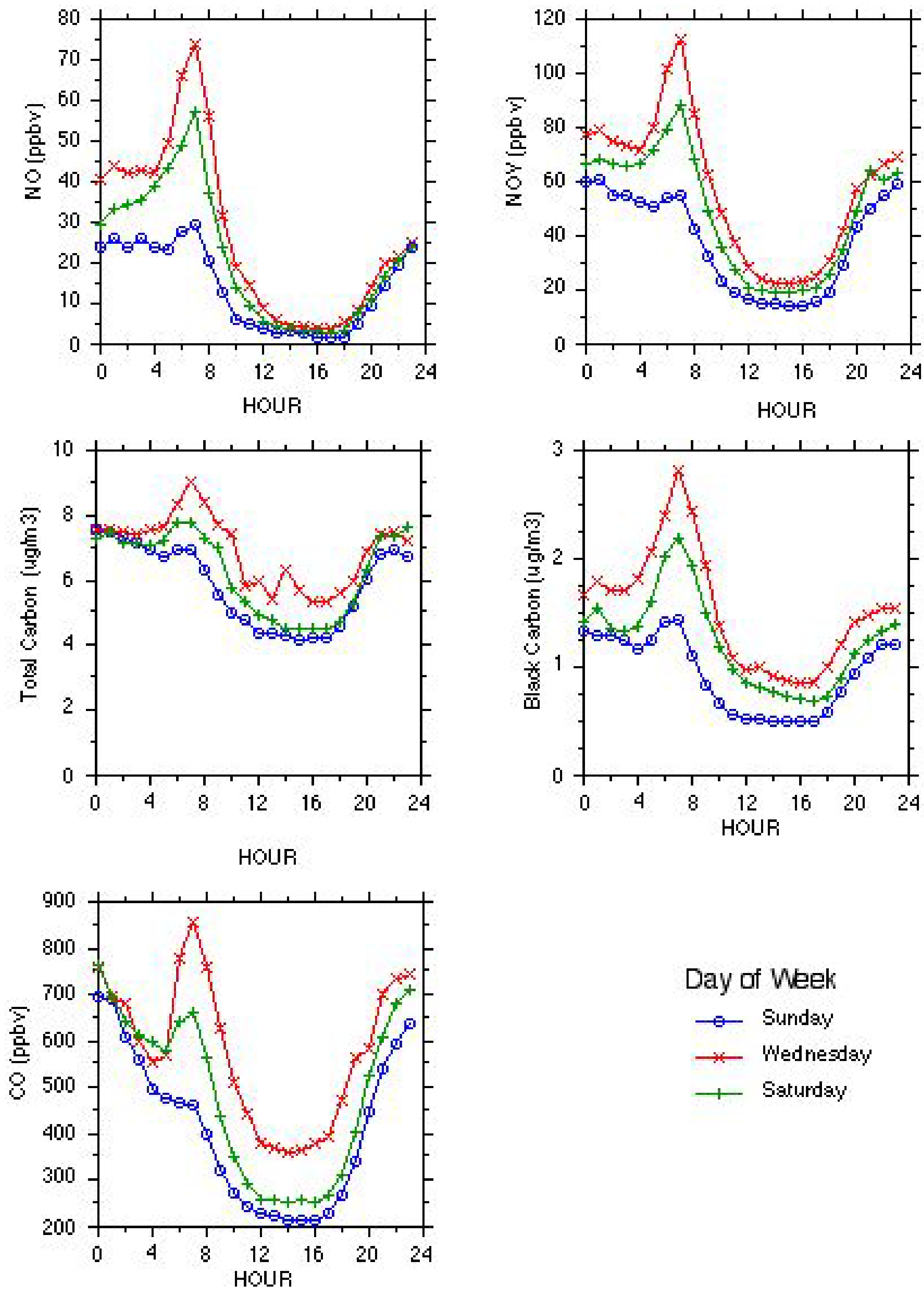


Figure C-4. Diurnal profiles comparing Sunday, Saturday and Wednesday during the period March-October 1999-2002 (NO, NO_y, CO and total carbon) and 2000-2002 (black carbon) at Jefferson St./Atlanta.

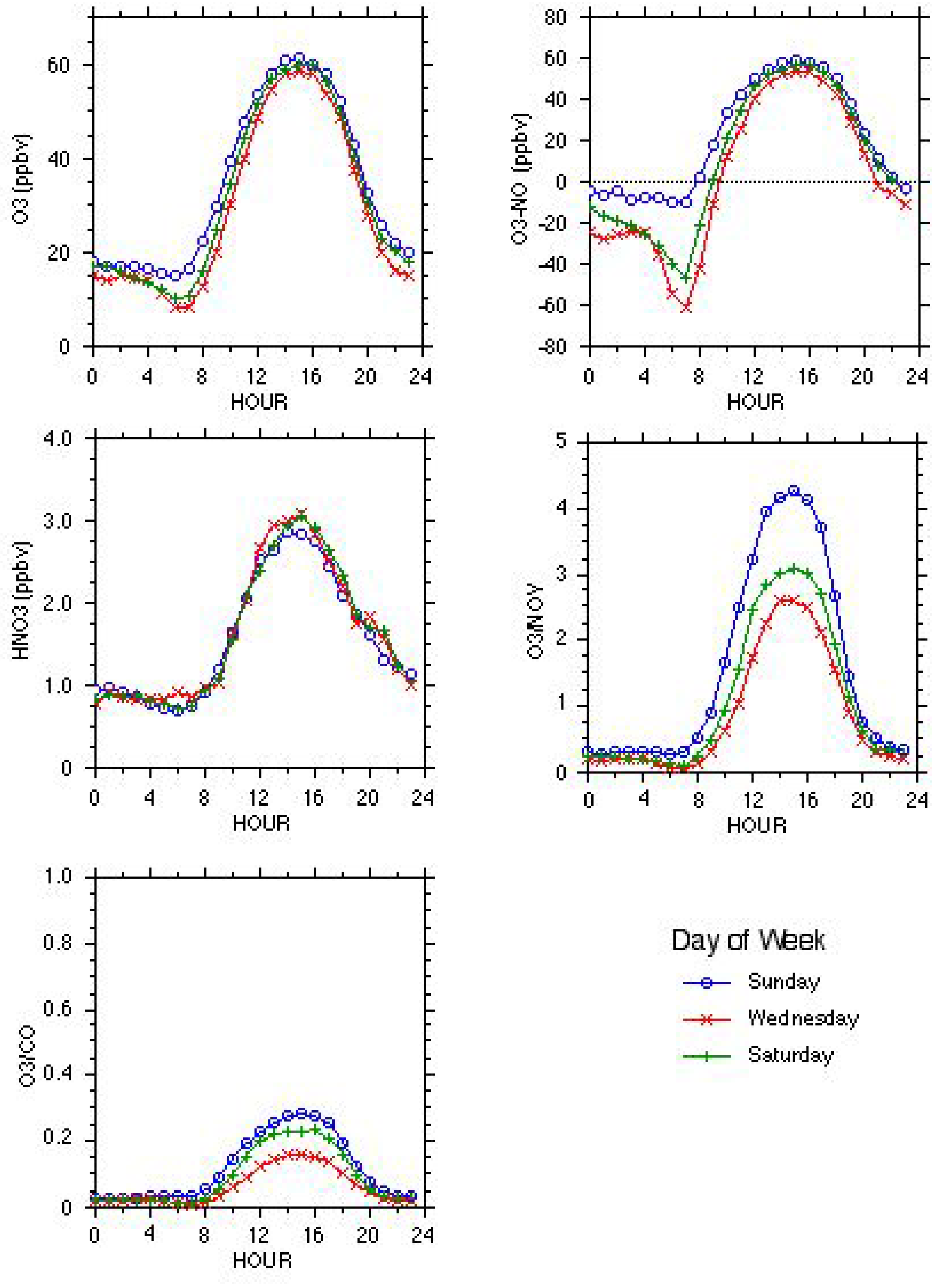


Figure C-5. Diurnal profiles comparing Sunday, Saturday and Wednesday for O_3, O_3-NO, HNO_3,O_3/NO_y and O_3/CO during the period March-October 1999-2001 at Jefferson St./Atlanta.

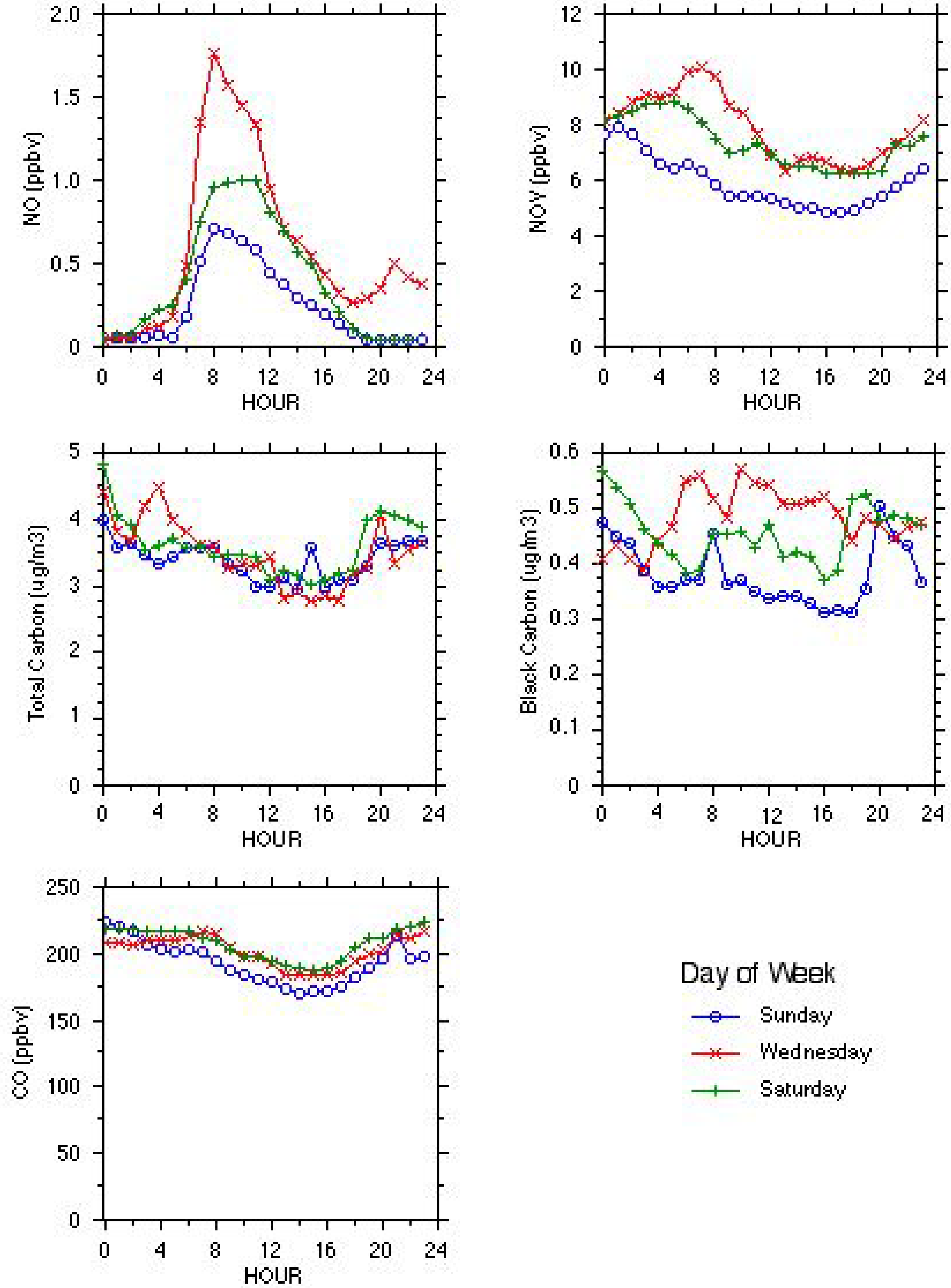


Figure C-6. Diurnal profiles comparing Sunday, Saturday and Wednesday during the period March-October 1998-2001 (NO, NO_y and CO), 2001-2002 (total carbon) and 2002 (black carbon) at Yorkville.

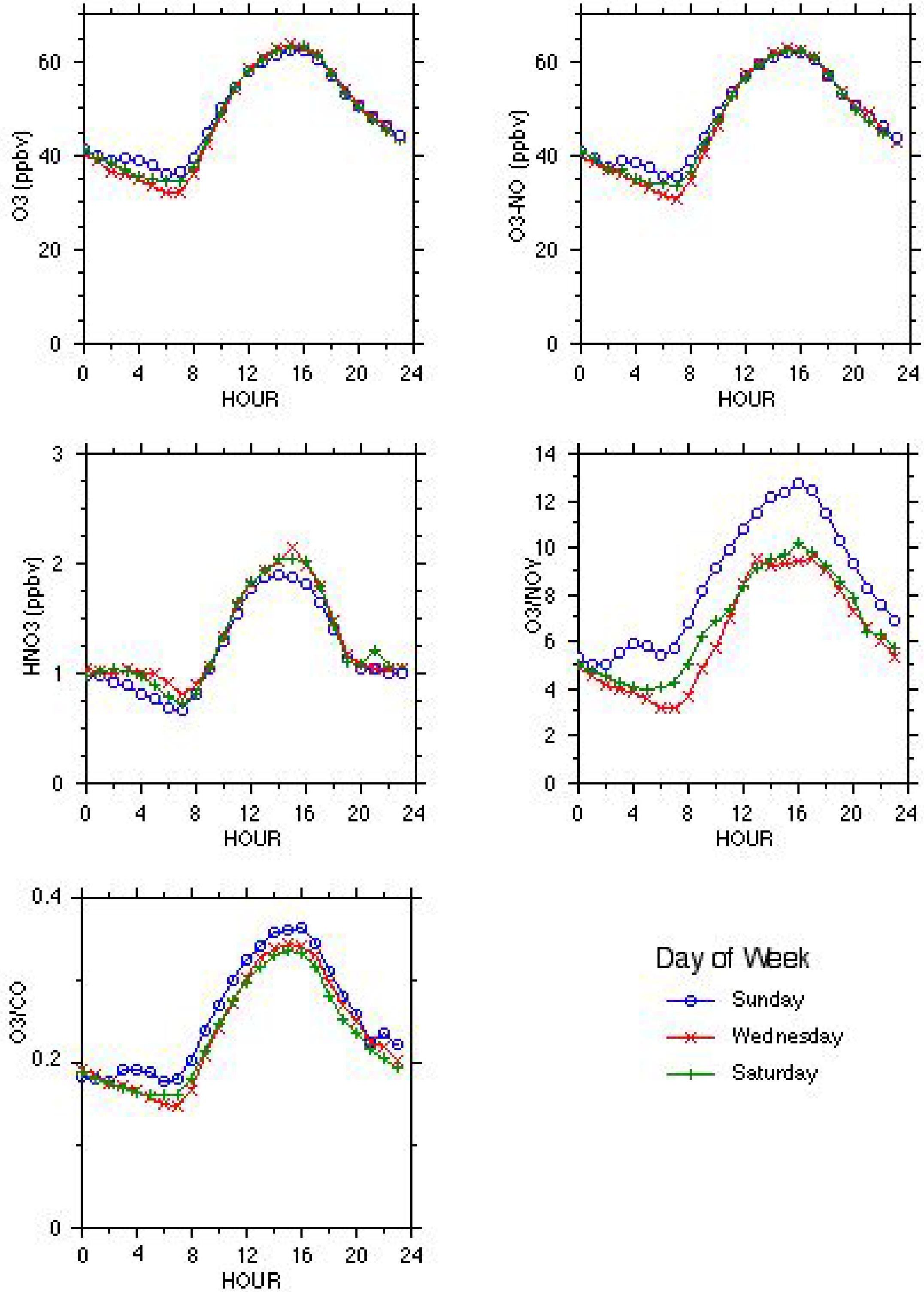


Figure C-7. Diurnal profiles comparing Sunday, Saturday and Wednesday for O_3, O_3-NO, HNO_3,O_3/NO_y and O_3/CO during the period March-October 1998-2001 at Yorkville.

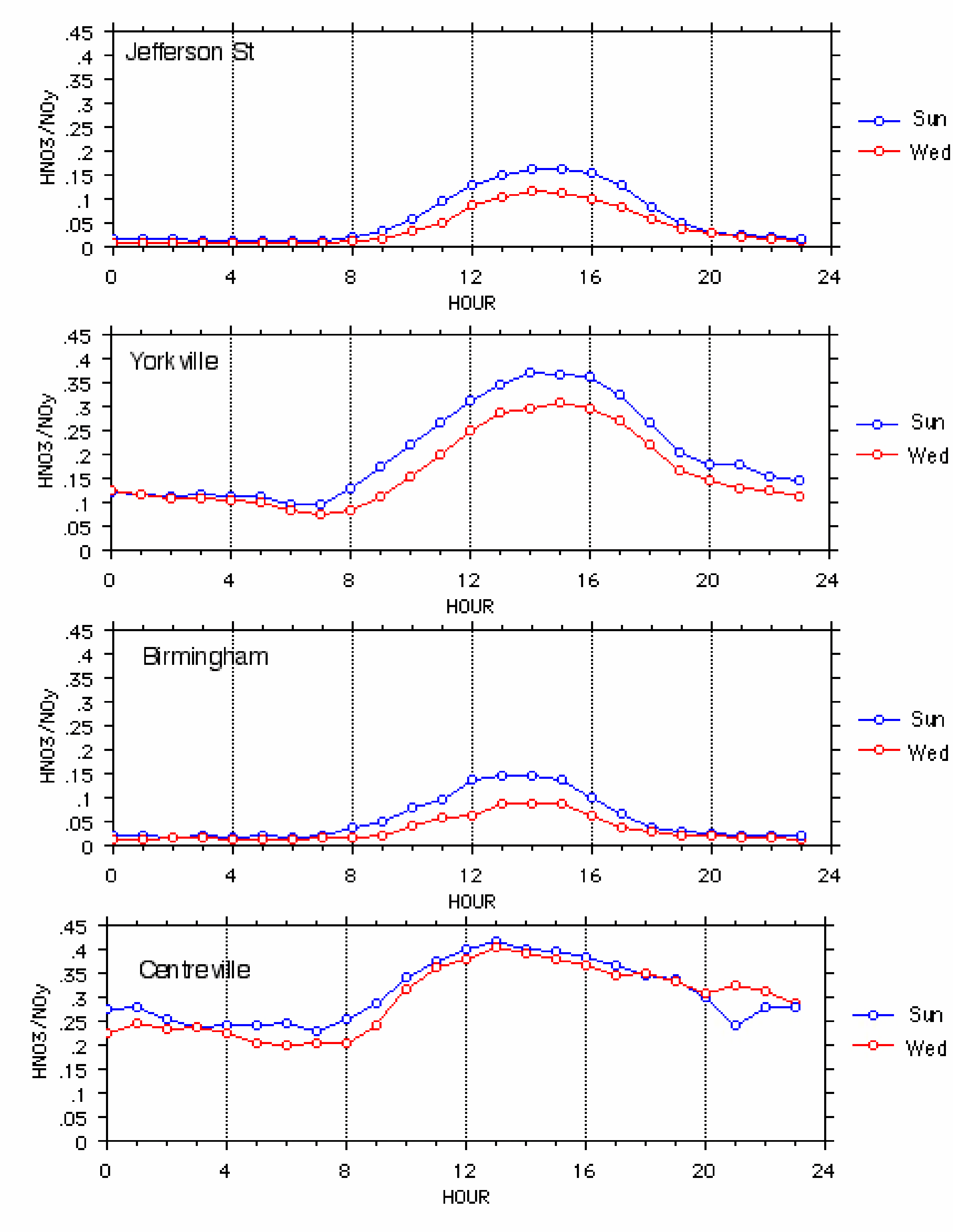


Figure C-8. Hourly ratios of the mean concentrations of HNO_3 to NO_y on Wednesdays and Sundays. Hourly averages were determined from measurements made at the SEARCH sites at Jefferson Street (99-02), Yorkville (98-02), Birmingham (00-02) and Centreville (98-02) during the months of March through October, with each point representing approximately 130 hourly measurements per year.

APPENDIX D. TRANSPORT OF OZONE AND PRECURSORS

Stagnation and transport are known to affect the occurrence of high ozone concentrations. For the purpose of the present task, the pertinent question is the extent to which these processes might account for differential ozone concentrations on weekdays and weekends. That is, could stagnation or transport yield high (or low) ozone concentrations more (or less) frequently on weekends than on weekdays?

We considered contrasts between urban, suburban, and regional monitoring locations, using surface meteorological information to characterize “upwind” and “downwind” directions on specific days. The transport analyses were carried out for high-ozone days (top three peak 8-hour daily maximum days per day of week per year for each site). For each high-ozone day, hourly surface wind speed and direction were obtained for three SEARCH sites (Jefferson Street, Yorkville, and Centreville) and three CASTNet sites (Georgia Station, Sand Mountain, and Coweeta). These data were also assigned to ozone sites lacking meteorological measurements. We computed 24-hour vector average wind speed and direction for each site’s set of high-ozone days. The 24 hours used were 7 pm of each preceding day through 6 pm of each high-ozone day. For each monitoring site, we then classified the 24-hour transport direction according to quadrants (NE, SE, SW, NW).

We checked our transport classifications using the NOAA HYSPLIT model (www.arl.noaa.gov/ready). An example HYSPLIT back-trajectory using the DeKalb County airport as a starting point is shown in Figure D-1. We specified starting heights of 100 m, 500 m, and 1000 m to provide an indication of the potential magnitudes of vertical shear in each case. The three trajectory levels (100, 500, and 1000 m) remained reasonably coherent (within the classification of transport quadrants). Ten dates with 24-hour vector-average surface winds from the northwest quadrant were chosen from high ozone days (top 3 8-hour days per day of week) during June-August, 1999-2002. Trajectories were carried back for 48 hours at 6-hour time intervals for each trajectory. For five of these ten dates, all trajectory points were within the northwest quadrant. Four of the remaining five dates exhibited 1 to 4 time steps outside the northwest quadrant at one or more heights, but falling no more than 20 degrees east of north or south of west. On one date, six time steps at two levels fell outside the northwest quadrant, again deviating by no more than 20 degrees.

A similar analysis was carried out for dates with 24-hour vector-average surface winds from the southwest quadrant during high ozone days. Agreement between vector-average winds and back trajectories when vector-average winds were from the southwest was comparable to the northwest case. For six of the ten days when surface winds were from the southwest quadrant, the HYSPLIT trajectory positions for all but 1 to 5 time steps were within the southwest quadrant at all heights. On three of the four remaining dates, trajectories were consistent with the presence of a high pressure pattern (back trajectories were initially from the southwest but rotated to an easterly origin). On the two dates, fewer than half of the positions fell within the southwest quadrant. On the remaining 2 dates, none of the trajectory positions fell within the southwest quadrant.

The ozone monitoring sites are located so that approximate transects are possible for the most common transport direction (from the NW) and the second most common direction (from the SW). For northwesterly transport, we defined our transect sites from far upwind to downwind as Sand Mountain, Yorkville, Douglasville, Jefferson Street, Confederate Avenue (Atlanta), Decatur (DeKalb), and Conyers (Figure 1). For southwesterly transport, we defined our transect sites from far upwind to downwind as Centreville, Douglasville, Jefferson Street, Tucker, and Gwinnett (Figure 1). The HYSPLIT back-trajectories suggest that transport times from the far upwind sites (Sand Mountain and Centreville) to downwind sites (Conyers and Gwinnett) were typically 12 to 18 hours (Figure D-1). However, we did not attempt to trace air masses backwards. Rather, we used the wind directions and trajectories to select subsets of days when it was reasonable to characterize one group of sites as upwind from Atlanta and another as downwind.

High-ozone days had previously been selected for each monitoring site as its top three days per day of week per year, and, therefore, each site had a possibly unique set of 21 high-ozone days per year. However, for evaluating ozone formation along the transects, we needed a data subset that included exactly the same days for each site along the northwesterly transect, and a second subset that included the same days for each site along the southwesterly transect. We used the days within the Conyers high-ozone subset to select a set of days for the northwest-transect analysis, and the days within the Gwinnett high-ozone subset for the southwest-transect analysis. In each case, the days analyzed represented the highest ozone days at the furthest downwind site in each trajectory, totaling ~105 days (5 years, 21 days per year).

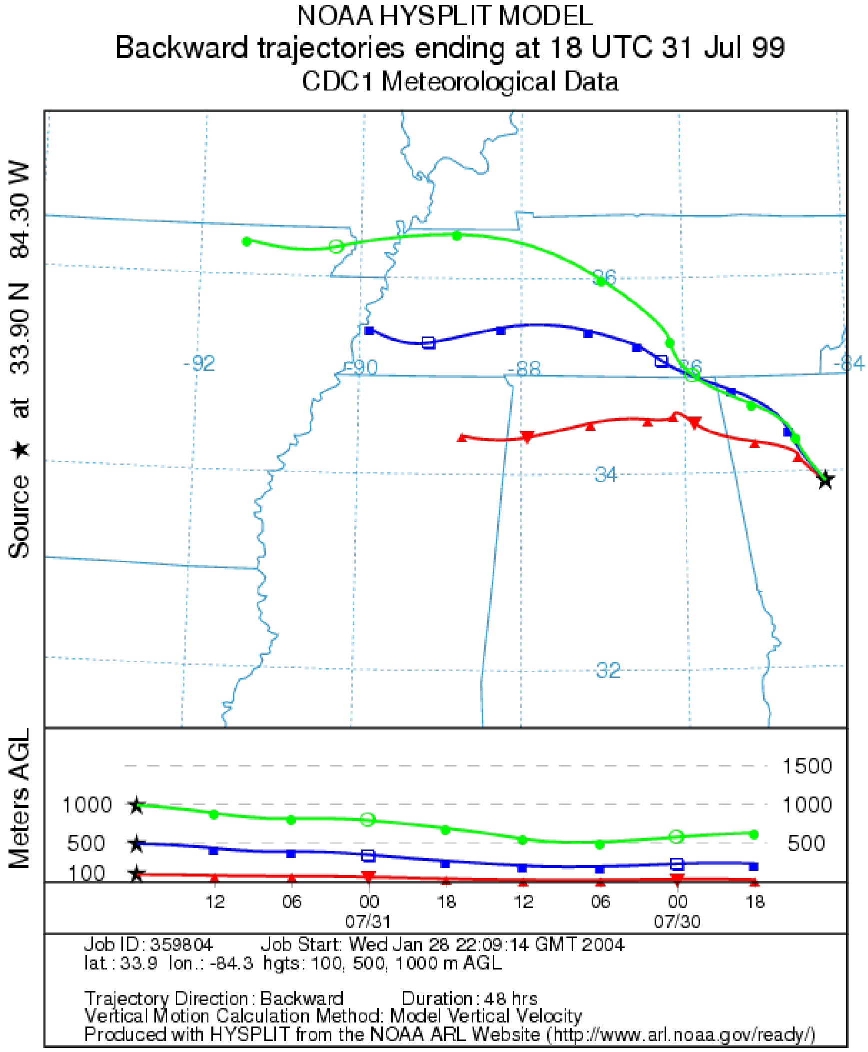


Figure D-1. Example HYSPLIT trajectory. All back-trajectories were initiated from DeKalb County airport at 1800 UT (1 pm EST), approximately at the midpoint of typical 8-hour daily maxima.

The mean day-of-week 8-hour ozone maxima were highest on Thursdays at all sites for northwesterly transport transect, and on Thursdays or Fridays for southwesterly transport (Figure D-2). Under northwesterly transport, Douglasville and Yorkville showed essentially identical means. The means at the urban and downwind sites varied more, but were almost always greater than the means for the upwind and far upwind sites. The mean concentrations from the far upwind, upwind, and urban/downwind sites followed approximately parallel lines, with some day-to-day variations. The results demonstrate that:

- Day-of-week differences in mean concentrations are partially or wholly driven by day-of-week differences in upwind transport concentrations, rather than by day-of-week differences in ozone production within Atlanta;
- The maximum mean upwind ozone levels show different day-of-week patterns for southwesterly and northwesterly transport, suggesting differences in the relative influences of closer and more distant source regions;
- For both southwesterly and northwesterly transport, one day exhibits the highest mean peak ozone levels (Friday under southwesterly, Thursday under northwesterly transport), five days show comparable mean peak ozone concentrations, and the day preceding the maximum mean ozone day exhibits intermediate ozone levels.

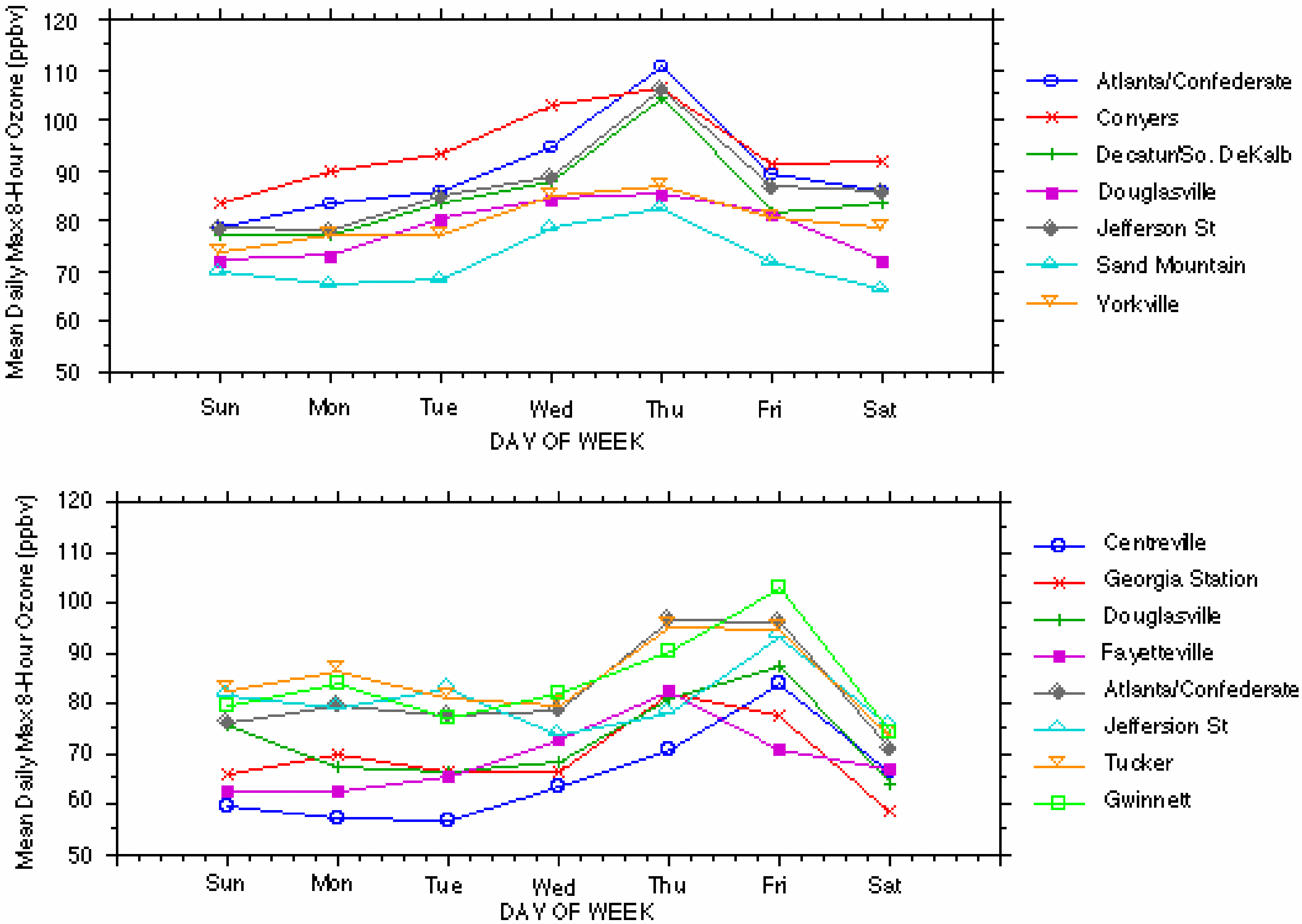


Figure D-2. Mean daily 8-hour ozone maxima by day of week and monitoring location for high-ozone days, 1998-2002. The top panel shows days when 24-hour vector-average wind directions were within the northwest quadrant and 8-hour ozone maxima at Conyers were among the top three days per day of week per year. The bottom panel shows days when 24-hour vector-average wind directions were within the southwest quadrant and 8-hour ozone maxima at Gwinnett were among the top three days per day of week per year.

After averaging the data from sites within each group (far upwind, upwind, urban), we determined the differences between mean daily maximum ozone levels for each of three pairwise combinations: near upwind minus far upwind, urban/downwind – near upwind, and urban/downwind – far upwind. The differences were computed as both the differences of the means and the means of differences (i.e., differences of maxima paired by day, then averaged). The results are shown in Figures D-3 and D-4. No significant day-of-week variations were found in the differences between urban and upwind concentrations, implying that the amounts of local ozone formation did not vary by day of week.

The levels of sulfate, nitrate, and organic carbon at upwind sites approached those measured at Jefferson Street, Atlanta (Figures D-5, D-6, D-7), indicating that transport contributed substantially to the urban levels of those compounds. In contrast, black carbon exhibited a stronger local than transport component, with day-of-week variations attributable to the local component (Figure D-5).

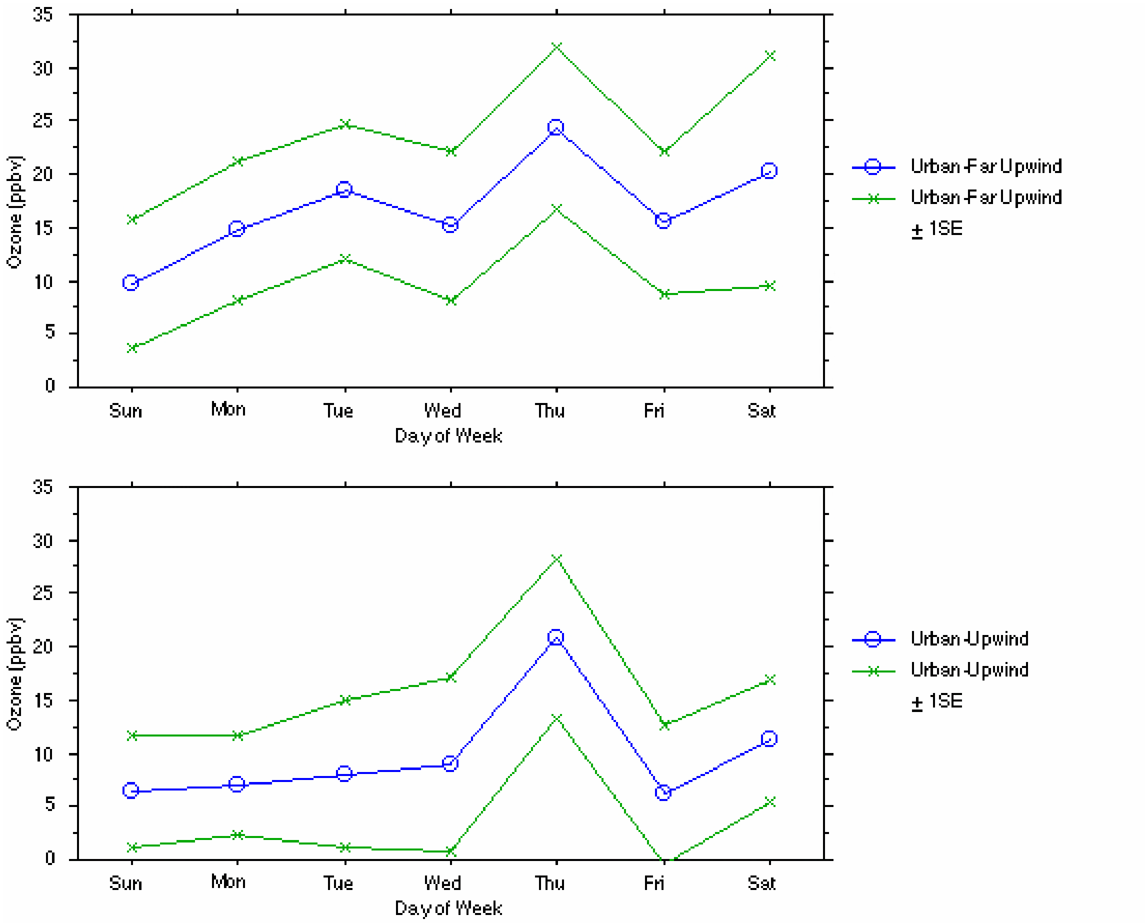


Figure D-3. Northwesterly transport differences between mean daily maximum ozone levels for each of two pairwise combinations: urban/downwind – near upwind, and urban/downwind – far upwind. The green lines show these differences plus and minus first order standard errors.

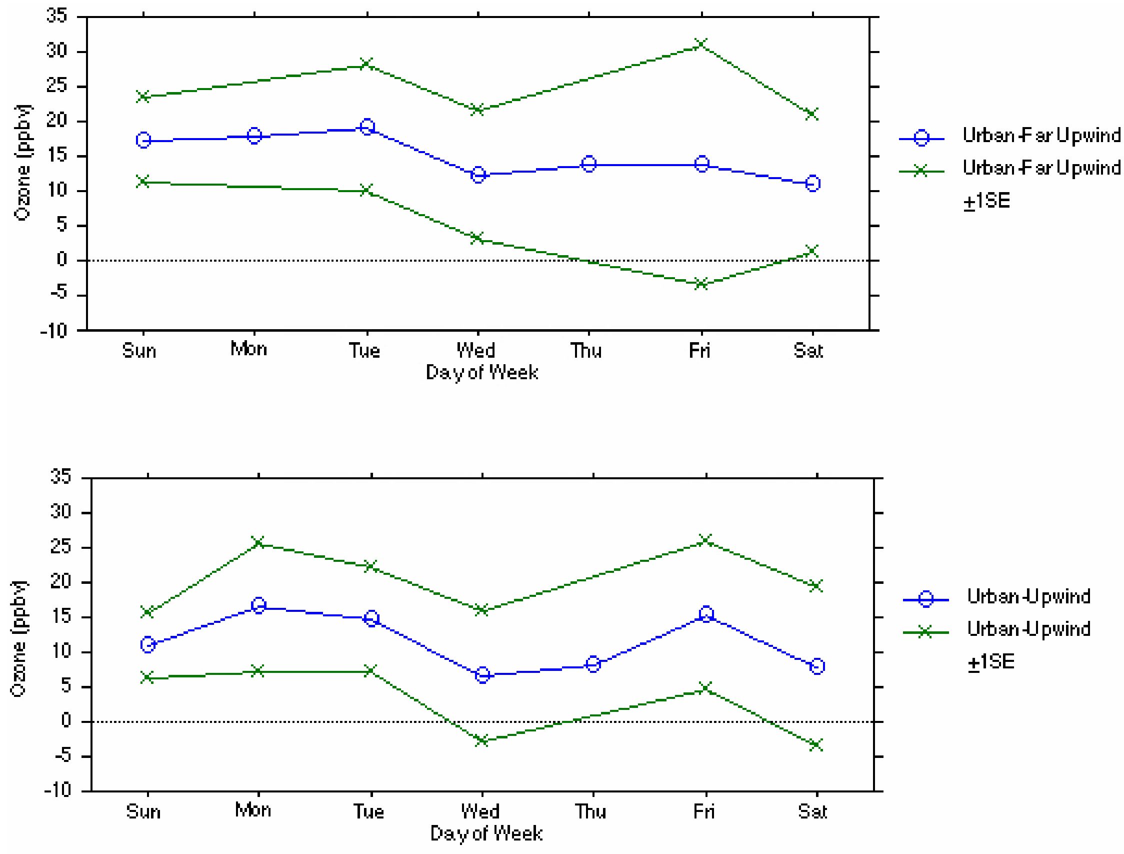


Figure D-4. Southwesterly transport differences between mean daily maximum ozone levels for each of two pairwise combinations: urban/downwind – near upwind, and urban/downwind – far upwind. The green lines show these differences plus and minus first order standard errors.

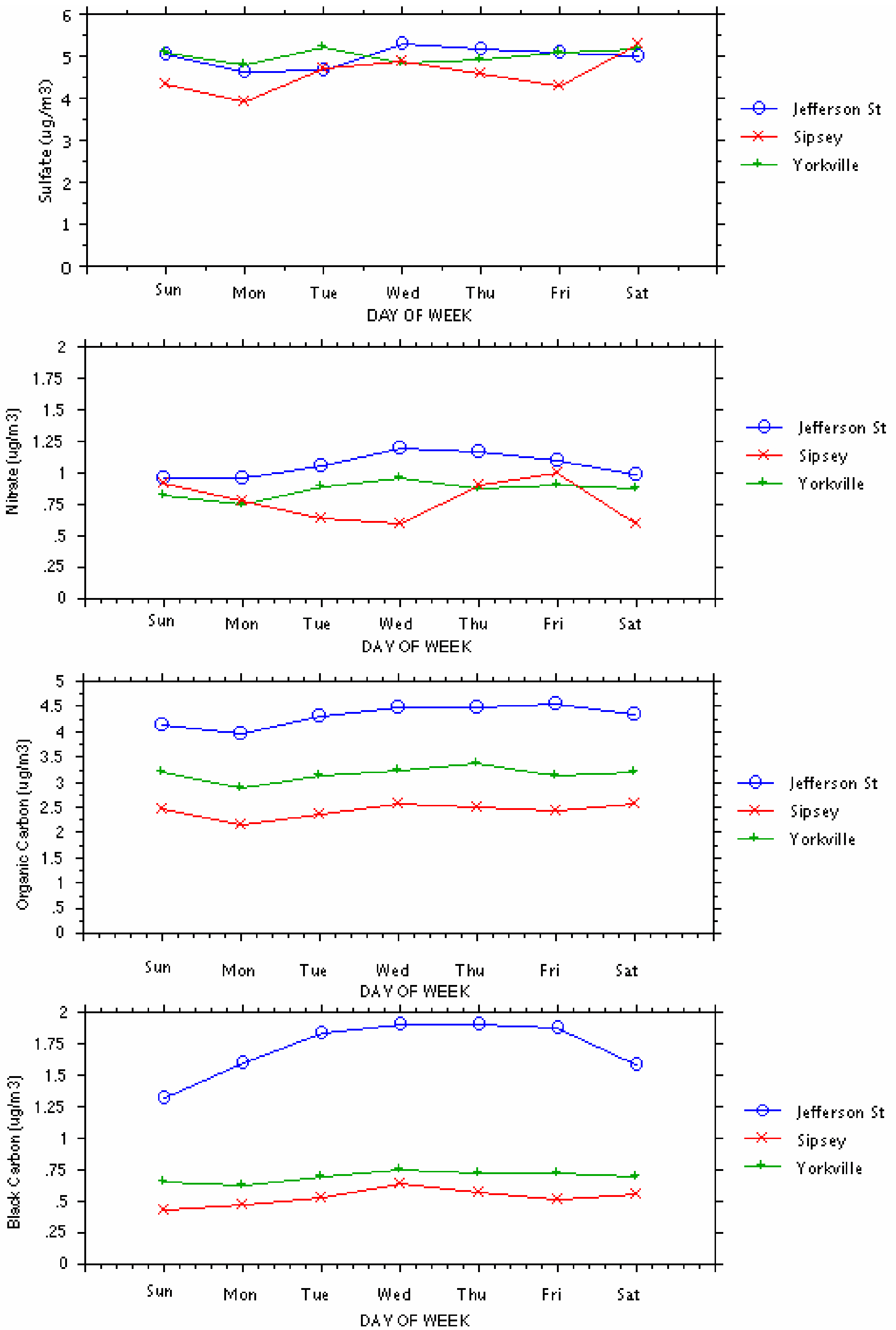


Figure D-5. Day of week means for sulfate, nitrate, organic carbon and black carbon at Sipsey, Yorkville and Jefferson St. for the period 1998-2002. The number of samples at each site are as follows: Jefferson St - SO_4 (195-211), NO_3 (196-210), Organic and Black Carbon (216-225); Yorkville - SO_4 (123-128), NO_3 (125-132), Organic and Black Carbon (112-123); Sipsey – SO_4 (35-38 Su,M,Tu,Th,F, 141 W, 165 Sa), NO_3 (34-37 Su,M,Tu,Th,F, 113 W, 129 Sa), Organic and Black Carbon (34-37 Su,M,Tu,Th,F, 140 W, 160 Sa).

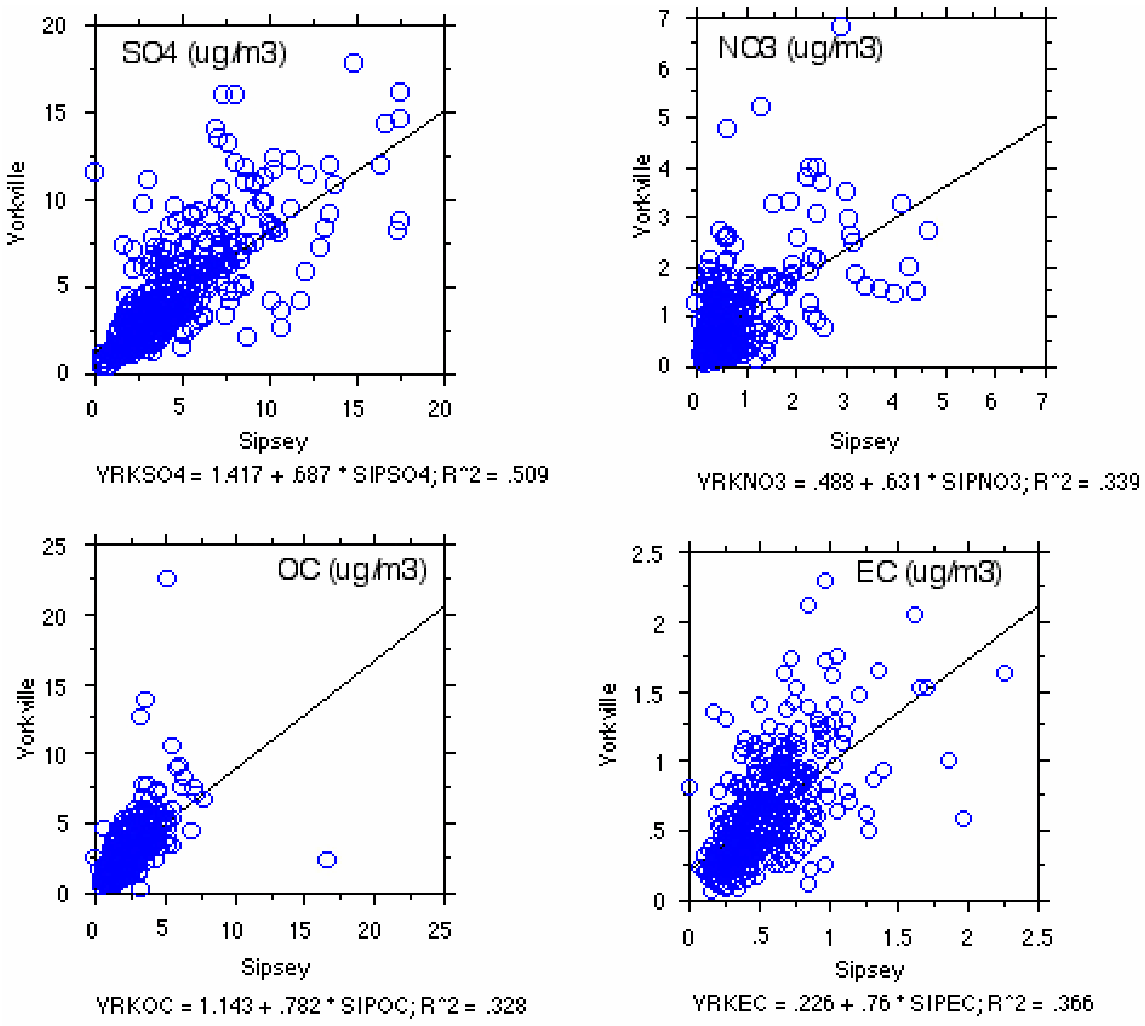


Figure D-6. Comparison of sulfate, nitrate, organic carbon and black carbon at Yorkville and Sipsey during the period 1998-2002.

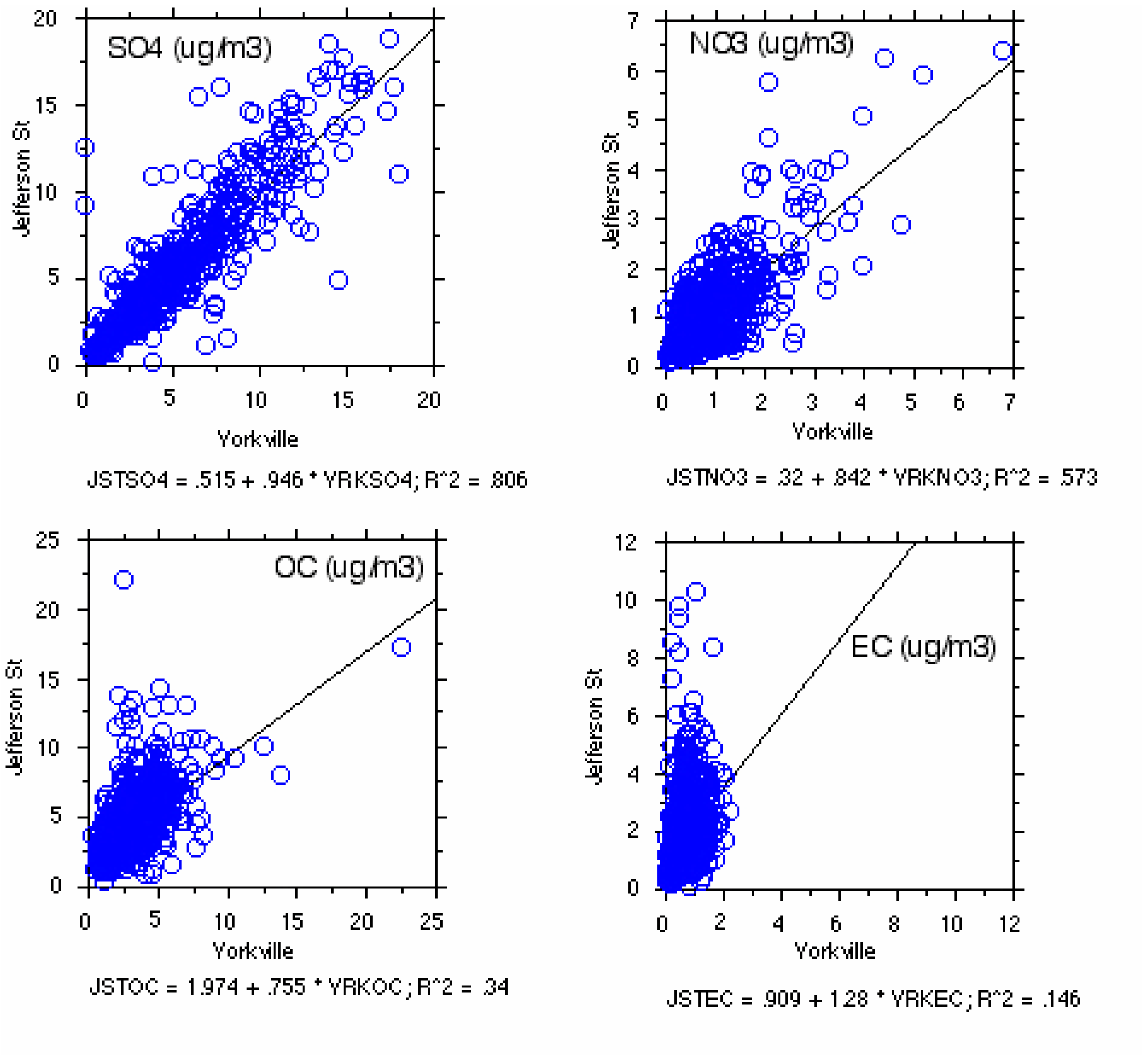


Figure D-7. Comparison of sulfate, nitrate, organic carbon and black carbon at Jefferson St. and Yorkville during the period 1998-2002.

APPENDIX E. EXTENT OF REACTION

Various studies have examined the sensitivity of Atlanta ozone levels to changes in VOC or NO_x emissions. Here, we add to previous results by applying the Smog Production (SP) algorithm (Blanchard et al., 1999) to all ozone-season days (March through October) during 1998-2002. Calculation of the extent of reaction, its use in delineating VOC- and NO_x-limitation, and comparisons with modeling studies are described in Blanchard et al. (1999), Blanchard (2000), and Blanchard and Stoeckenius (2001).

Measurements of hourly ambient concentrations of ozone, NO, NO_x, NO_2, and NO_y were obtained from the AIRS database for all monitoring locations for the period 1998-2002 and from the SEARCH database for 1999-2001 (2002 data were not available at the time of the analysis). The SP algorithm was applied to the data from all sites having measurements of ozone, NO, and either NO_2, NO_x, or NO_y. In summary, the extent of reaction is defined as:

(1) $\text{Extent}(t) = SP(t)/SP_{max}$

Smog Produced (SP) is defined as (Johnson, 1984):

(2) $SP(t) = O_3(t) + DO_3(t) - O_3(0) + NO(0) - NO(t)$

In application to ambient measurements, Blanchard et al. (1999) describe procedures for estimating the background ozone and ozone lost to deposition, i.e., $O_3(0)$ and $DO_3(t)$. The initial NO, or the NO input, i.e., NO(0), is estimated as $F{*}NO_x(0)$, where F=0.95, and additional equations are used to estimate $NO_x(0)$. The estimated $NO_x(0)$ is also used for calculating the denominator of the extent of reaction, namely, SP_{max}:

(3) $SP_{max} = B{*}NO_x(0)^a$

where B = 19 and a = 2/3 (Blanchard et al., 1999).

When NO_y data are available, the $NO_x(0)$ is estimated as the sum of NO_y and the cumulative mass of NO_y lost to deposition (Blanchard et al., 1999):

(4) $NO_x(0) = NO_y(t) + DNO_y(t)$

When true NO_x ($NO + NO_2$) data are available, the $NO_x(0)$ is estimated from:

(5) $NO_x(0) = NO_x(t) + [B/3F]^3 * [2X + 1]^3$

where:

$X = \cos[(4\pi + \cos^{-1}C)/3]$

$C = 1 - (27\gamma/F)/\{2*(B/F)^3\}$ for $-1 <= C <= 1$

$\gamma = \{O_3(t) + DO_3(t) - O_3(0) + B*NO_x(t) - NO(t) \}/ (B - F)$

There are typographical errors in these equations as published in Blanchard et al., (1999), and the correct version (above) was used for this project.

As indicated by Equations 1 through 5, the SP algorithm requires accurate measurements of ozone, NO, and either NO_x or NO_y. However, measurements of true NO_x ($NO + NO_2$) or NO_y (the sum of NO_x and NO_x reaction products) are not routinely available from compliance monitors. The standard NO_x monitor measures NO_x plus unquantified fractions of NO_x reaction products, such as peroxyacetylnitrate (PAN) and nitric acid (HNO_3) (Winer et al., 1974). For AIRS sites, these routine "NO_x" data were used to provide upper and lower bounds on the extent of reaction. The lower bound for extent was computed by using the measurements of "NO_x" as if they were true NO_x in Equation 5 above. The upper bound for extent was computed by using the measurements of "NO_x" as if they were true NO_y in Equation 4 above. The extent of reaction was estimated as the mean of the upper and lower bounds. In previous work, we have found good agreement between the mean of the upper and lower bounds and the extent of reaction calculated from true NO_y. For SEARCH sites, it was possible to compute the extent of reaction obtained from true NO_y.

The mean afternoon (12 noon through 5 pm) extents of reaction on high-ozone days (top three peak 8-hour concentrations per day of week per year at each site) show differences among monitoring locations (Figure E-1). Jefferson Street, the only central-city site, shows low (< 0.6) mean extent of reaction on all days, indicative of VOC-limited conditions. The remaining sites, which are all suburban or rural, exhibit a range of mean extents of reaction, nearly all of which are high (> 0.8) and indicative of NO_x-limited conditions. The statistical significance of day-to-day differences was not evaluated. When determined from all ozone-season days, nearly all the mean extents of reaction were less than 0.6 (VOC-limited) and the extents of reaction increased on weekends compared with weekdays (Figure E-2).

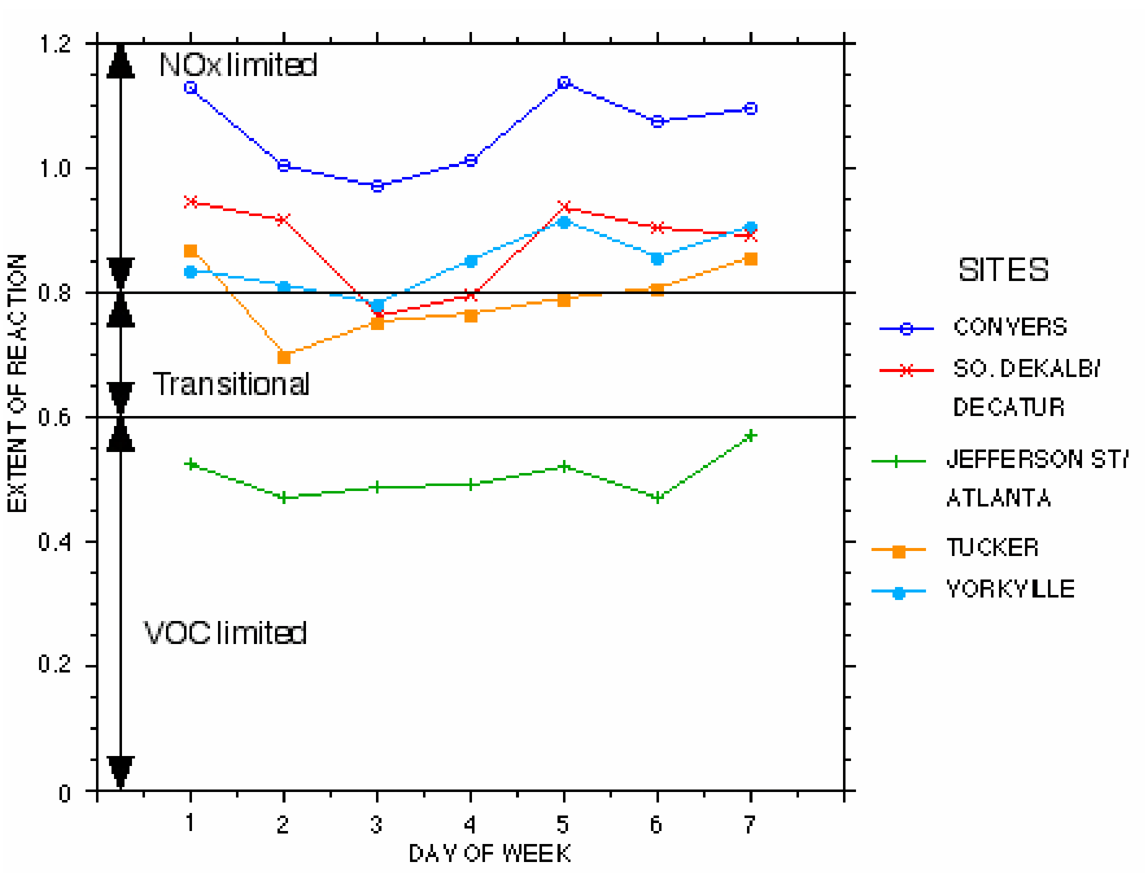


Figure E-1. Mean afternoon (12 noon through 5 pm) extent of reaction on high-ozone days (top three peak 8-hour concentrations per day of week per year at each site). The data are from the period March-October 1998-2002 (Conyers, So. DeKalb and Tucker), 1998-2001 (Yorkville) and 1999-2001 (Jefferson St.).

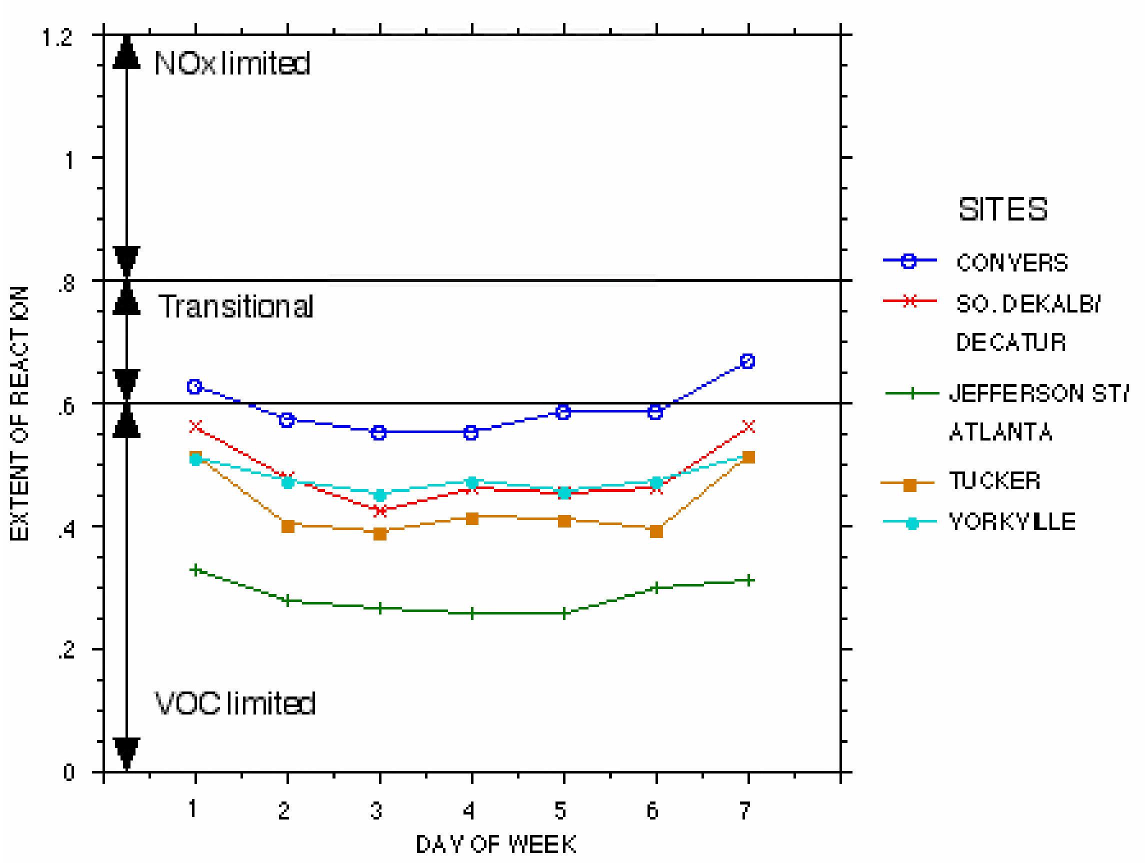


Figure E-2. Mean afternoon (12 noon through 5 pm) extent of reaction determined from all ozone-season days. The data are from the period March-October 1998-2002 (Conyers, So. DeKalb and Tucker), 1998-2001 (Yorkville) and 1999-2001 (Jefferson St.).

APPENDIX F. EFFECTS OF SO_2 AND NO_X EMISSION REDUCTIONS ON $PM_{2.5}$ MASS AND NITRATE CONCENTRATIONS IN THE SOUTHEASTERN UNITED STATES

This appendix summarizes relevant findings from Blanchard and Hidy (2003; 2005). Measurements from sites of the SEARCH program, made from 1998-2001, were used with a thermodynamic equilibrium model, SCAPE2, to study the responses of fine particulate nitrate and $PM_{2.5}$ mass concentrations to changes in concentrations of nitric acid and sulfate. The responses were determined for a projected range of variations of sulfate and nitric acid concentrations resulting from adopted and proposed regulatory initiatives.

The predicted mean $PM_{2.5}$ mass concentration decreases averaged 1.8 to 3.9 $\mu g\ m^{-3}$ for sulfate decreases of 46 to 63 percent from current concentrations. Combining the sulfate decrease with a 55 percent nitric acid decrease from current concentrations yielded incremental reductions of mean predicted $PM_{2.5}$ mass concentration of 0.2 – 0.3 $\mu g\ m^{-3}$ for three nonurban sites and 1.0 to 1.5 $\mu g\ m^{-3}$ for one nonurban (Yorkville) and two urban (Birmingham and Jefferson Street, Atlanta) sites.

PM mass concentration isopleths computed separately for warmer and cooler months showed that $PM_{2.5}$ mass concentrations would decrease more in response to HNO_3 decreases during October through March than during April through September (Figure F-1). The warm-season isopleths for Centreville were essentially vertical, indicating no response of mean $PM_{2.5}$ mass concentrations to changes in HNO_3 levels during these months. For Atlanta (Jefferson Street) and Yorkville, 55 percent reductions of HNO_3 yielded mean cool-season reductions of $PM_{2.5}$ mass concentrations of about 1.5 $\mu g\ m^{-3}$ across a range of reductions of sulfate (Figure F-1).

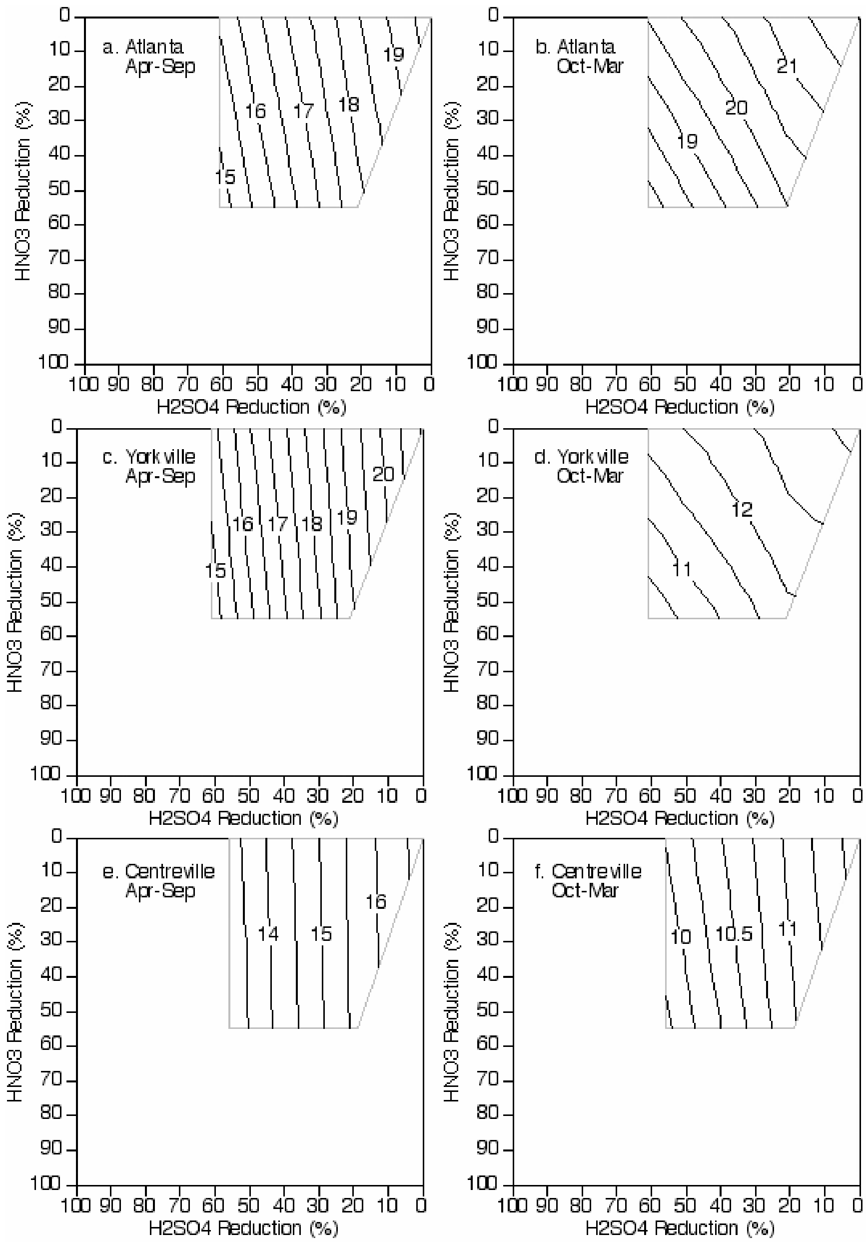


Figure F-1. Predicted mean $PM_{2.5}$ mass concentrations during the months of April through September and October through March as functions of the reductions of sulfate and nitric acid from current concentrations (Blanchard and Hidy, 2005). The isopleths were drawn from 22 sets of specified reductions of sulfate and nitric acid. The predicted mean concentrations for each of the 22 sets were determined from the predictions for 95 to 251 individual samples. For each sample, predicted PM mass concentration was computed as current FRM fine mass concentration minus the predicted changes in sulfate, nitrate, and ammonium concentrations.

We determined day-of-week averages for current conditions and model predictions (Table F-1). Under current conditions, the mean fine mass concentrations were greater on Sundays than on Wednesdays at Birmingham and Yorkville, while mean fine mass concentrations were lower on Sundays than on Wednesdays at Atlanta and Centreville; none of these differences was significant. In the model simulations, the reductions of sulfate and nitric acid reduced fine PM mass concentrations on both Sundays and Wednesdays.

Table F-1. Mean FRM mass by site and day of week at four SEARCH sites under current conditions and for model predictions. The predictions were based upon ~60 percent reduction of sulfate (61 percent for Atlanta and Yorkville; 56 percent for Birmingham and Centreville) and 55 percent reduction of HNO_3. Each entry is the average of 8 to 23 24-hour measurements or model predictions. The uncertainties are one standard error of the mean.

Site	Day of Week	FRM Mass ($\mu g\ m^{-3}$)	Predicted FRM Mass ($\mu g\ m^{-3}$)
Atlanta	Sunday	19.7 +/ -1.7	15.4 +/- 1.5
	Wednesday	22.5 +/ -2.2	17.5 +/- 1.9
Birmingham	Sunday	19.3 +/ -2.1	14.3 +/- 1.8
	Wednesday	17.8 +/ -2.2	13.3 +/- 1.7
Centreville	Sunday	9.8 +/- 1.6	8.4 +/- 1.4
	Wednesday	13.3 +/- 1.7	11.0 +/- 1.5
Yorkville	Sunday	17.0 +/- 3.6	12.3 +/- 2.5
	Wednesday	16.7 +/- 2.3	12.8 +/- 1.6