Atmospheric and Environmental Research, Inc.

DATA ANALYSIS FOR A BETTER UNDERSTANDING OF THE WEEKDAY/WEEKEND OZONE AND PM DIFFERENCES

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GLOSSARY OF ACRONYMS

AER	Atmospheric and Environmental Research
AIRS	Aerometric Information Retrieval System
CARB	California Air Resources Board
CRC	Coordinating Research Council
EC	Elemental Carbon
IMPROVE	Interagency Monitoring of Protected Visual Environments
LADCO	Lake Michigan Air Directors Consortium
NAAQS	National Ambient Air Quality Standard
NAMS	National Air Monitoring Stations
NREL	National Renewable Energy Laboratory
OC	Organic Carbon
PAMS	Photochemical Assessment Monitoring Stations
PM	Particulate Matter
SLAMS	State and Local Air Monitoring Stations
TEOM	Tapered Element Oscillating Microbalance
TNMOC	Total Non-Methane Organic Compounds
UV	Ultra Violet Radiation
VOC	Volatile Organic Compounds

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EXECUTIVE SUMMARY

The weekly cycles of O_3 and PM are of interest because they provide insights into how these pollutants respond to changes in anthropogenic emissions from weekdays to weekends. Several studies are in progress or are being completed that analyze the weekly behavior of O_3 in the South Coast Air Basin in California. The focus of this project is on three areas outside of California. Two areas, Chicago, IL and Philadelphia, PA, exhibit weekend increases in O_3 formation, and conclusions drawn about the causes of this O_3 behavior may be compared to those in the South Coast Air Basin. A third area, Atlanta, GA, shows a different weekly cycle, and enables us to investigate alternative responses to the weekly cycle of anthropogenic emissions.

This report presents in detail our analysis of the weekly behavior of O_3 and PM in these three metropolitan areas, using data from 1995 to 1999. The statistical significance of the differences between weekday and weekend concentrations is tested using the bootstrap resampling technique. Several hypotheses are presented to explain the weekly behavior of O_3. Available ambient data are used to test these hypotheses. We also identified changes in the weekly behavior of O_3 from the late eighties to the late nineties.

Weekly behavior of O_3 and PM (1995 – 99)

O_3 diurnal profiles. The average diurnal profiles of O_3 were plotted at different monitoring sites in Atlanta, Chicago, and Philadelphia for each day of the week. Afternoon O_3 concentrations were highest on Sundays in Chicago and on Saturdays at most sites in Philadelphia. High concentrations were observed during weekends at all sites in these urban areas. In Atlanta, afternoon O_3 concentrations built up from Mondays to Fridays and recovered during the weekends. During morning rush hours, O_3 concentrations were consistently lower on weekdays than on weekends in all three cities. This is due to O_3 titration by NO emitted by traffic. In fact, when both O_3 and NO are measured at the same location, the NO-O_3 cross-over time was delayed, by one hour in Atlanta and one to two hours in Chicago and Philadelphia, on weekdays relative to weekends. In Chicago and Philadelphia, the earlier start in O_3 accumulation and the higher morning concentrations translated into higher afternoon peak O_3 concentrations on

weekends. In Atlanta, NO titration seemed to have a smaller effect on the starting time of O_3 accumulation in the morning, possibly due to lower NO concentrations relative to O_3.

One-hour average O_3. The maximum one-hour average O_3 concentrations were calculated and grouped by the day of the week. We tested the day-of-the-week differences in the mean, median, and 90th percentile of the maximum one-hour average concentrations for each of the three cities. At each site, the mean values of the maximum one-hour average concentrations showed the most consistent trend.

Highest concentrations were observed on Fridays in Atlanta at five O_3 monitoring sites with complete data records from 1995 to 1999. Lowest concentrations were observed on Mondays. The differences between the highest and lowest concentrations were significant at all sites. The median value and 90th percentile of the maximum one-hour average concentrations showed similar trends, with the largest plurality of sites showing high concentrations on Fridays. However, the median and 90th percentile concentrations on Saturdays were also high. Low concentrations were observed most frequently on Mondays, but some sites also showed low median or 90th percentile values on Sundays and Tuesdays. Exceedances of the one-hour average O_3 National Ambient Air Quality Standard (NAAQS) of 120 ppb occurred most frequently on Fridays, followed by Thursdays and Saturdays. The days of the week when the NAAQS was exceeded the least number of times were Mondays and Sundays in Atlanta.

Weekend increases in O_3 were observed in the daily maximum one-hour average concentration data in Chicago. The mean of the maximum one-hour concentrations showed maximum values on Sundays at 18 monitoring sites with complete O_3 season data records between 1995 and 1999. The lowest concentrations were observed on Tuesdays and Wednesdays. The weekend-weekday differences in the mean values of the daily maximum one-hour concentrations were statistically significant at the 5% level. The median values of the maximum one-hour concentrations were also highest on Sundays, and lowest primarily on Tuesdays, Wednesdays, and Thursdays. The trends were less consistent in the median than in the mean values. The days with the highest 90th percentile concentrations were Saturdays (at 15 sites) and Sundays (at only three sites). Tuesdays and Mondays recorded most of the low 90th percentile concentrations. The 90th percentile results seemed to represent a shift of the weekly cycle relative to the mean and median values. Chicago exceeded the one-hour O_3 NAAQS infrequently, but more than half of the exceedances occurred on Saturdays, consistent with their high 90th percentile concentrations.

An increase in weekend O_3 was also apparent in the daily maximum one-hour average concentration data from Philadelphia, PA. All four monitoring sites with complete O_3 season data records between 1995 and 1999 showed maximum concentrations on Saturdays. Lowest concentrations were observed primarily on Fridays. The highest median values were observed on Saturdays and Sundays. The lowest median concentrations were also observed on Fridays. At two sites, low median concentrations were observed on other days of the week in addition to Fridays. The weekday-weekend differences in the median values were significant. The 90th percentile of the daily maximum one-hour average O_3 was highest on Saturdays. At one site, Mondays tied with Saturdays for the highest 90th percentile values. Low 90th percentile concentrations occurred on different weekdays at different sites. The weekend-weekday differences in the 90th percentile concentrations were significant at all sites. The one-hour O_3 NAAQS was exceeded 8 times each on Saturdays and Mondays in the Philadelphia area during 1995 to 1999.

8-hour average O_3. The daily maximum 8-hour average O_3 concentrations were also calculated for the time period 1995 to 1999 in Atlanta, Chicago, and Philadelphia. With smaller weekday-weekend differences, the mean values of the daily maximum 8-hour average concentrations in Atlanta showed a less consistent trend than the mean of the maximum one-hour average concentrations. The sites with complete records for the years 1995 through 1999 were split between having high 8-hour average O_3 on Fridays and Saturdays. Low 8-hour O_3 concentrations were observed on Mondays. In Chicago, the day-of-the-week behavior of the 8-hour O_3 concentrations was quite similar to that of the one-hour concentrations. Highest concentrations were observed on Sundays. Low concentrations were observed most frequently on Tuesdays and Wednesdays. On average, the weekday-weekend differences in the one-hour concentrations were slightly higher than those in the 8-hour concentrations, but at individual sites the difference may be higher or lower. The day-of-the-week behavior of the daily maximum 8-hour average concentrations was also similar to that of the one-hour concentrations in Philadelphia. High 8-hour O_3 concentrations were observed on Saturdays at three sites and on Sundays at the remaining site, while low 8-hour O_3 concentrations were observed on Fridays. The weekly differences in the maximum 8-hour concentrations were lower than those in the one-hour concentrations at all monitoring sites.

PM_{10}. Due to shorter PM_{10} records, smooth diurnal profiles were not observed in Atlanta and Chicago. In Philadelphia, diurnal PM_{10} profiles showed some characteristics of primary emissions associated with morning traffic. The profiles on Saturdays and Sundays were much lower in concentration during the day than those on weekdays; the difference was especially significant during the 5 a.m. to 8 a.m. period. Day-of-the-week-specific 24-hour average PM_{10} concentrations were compared. In Atlanta, high concentrations were observed on Tuesdays and low concentrations on Sundays. The difference was significant at the 10% level when tested with bootstrap resampling. Chicago's PM_{10} exhibited a weekly cycle of high concentrations on weekdays (Fridays or Tuesdays) and low concentrations on weekends. The maximum weekend-weekday differences were statically significant at the 5% level. Philadelphia showed low PM_{10} concentrations on Sundays, followed by Saturdays. Relatively high PM_{10} concentrations were very similar on all weekdays, and the difference between all weekday-weekend differences were significant at the 5% level.

$PM_{2.5}$. $PM_{2.5}$ monitoring was initiated in 1999; therefore, data were somewhat more limited than for PM_{10}. Atlanta and Chicago reported 24-hour average concentrations. In Atlanta, high 24-hour $PM_{2.5}$ concentrations were observed late in the week (Thursdays through Saturdays), while low concentrations were observed on Sundays or Mondays. In Chicago, the weekly trend was somewhat peculiar: high concentrations were observed on Wednesdays, Fridays, and Saturdays, and low concentrations were observed on Tuesdays or Thursdays. We questioned the representativeness of these data due to the small sample size (7 to 9 samples per day of the week). In Philadelphia, $PM_{2.5}$ concentrations were reported as one-hour average concentrations. The diurnal profiles did not show any day-of-the-week trends. 24-hour average concentrations were highest on Saturdays, followed by Tuesdays, and lowest on Thursdays.

Hypothesis Testing

Several hypotheses were proposed to explain the weekday-weekend differences in O_3 in Atlanta, Chicago, and Philadelphia. We tested the hypotheses using available ambient data. Identified changes were correlated to the day-of-the-week-specific mean values of the maximum one-hour average O_3 concentrations.

Hypothesis 1. Greater than proportionate reduction in NO_x relative to VOC leads to an increase in the VOC/NO_x ratio. In a VOC-sensitive airshed, O_3 formation potential increases with the VOC/NO_x ratio. In a NO_x-sensitive airshed, O_3 formation will decrease with reduced NO_x emissions. We identified statistically significant increases in the VOC/NO_x ratios on weekends relative to those on weekdays. These ratios are listed in Table E-1.

Table E-1. Summary of Hypothesis 1.

	Atlanta, GA	Chicago, IL	Philadelphia, PA
24-hour average VOC/NO_x ratios			
Weekday ratios	5.6 – 6.6	2.3 – 2.6	9.4 – 10.5
Weekend ratios	7.9 – 8.4	3.1 – 3.4	11.0 – 14.1
Correlation coefficients between maximum one-hour average O_3 and ratio	0.04(1)	0.95(2)	0.72(3)
Morning (5-8 a.m. average) ratios			
Weekday ratios	4.6 – 5.8	1.9 – 2.4	6.6 – 9.9
Weekend ratios	7.5 – 9.5	2.9 – 3.9	10.3 – 11.3
Correlation coefficients between maximum one-hour average O_3 and ratio	- 0.2(1)	0.93(2)	0.58(3)

(1) Statistically insignificant at the 10% level.

(2) Statistically significant at the 5% level.

(3) Statistically significant at the 10% level.

In previous studies, Atlanta has been identified as either NO_x sensitive or in the transition regime between NO_x and VOC sensitivity. But instead of a reduction of O_3 during the weekend with decreased NO_x and increased VOC/NO_x ratio, no correlation was observed between O_3 and the ratio. Therefore, O_3 in Atlanta may be driven by factors other than same-day emissions of VOC and NO_x. Chicago had the lowest VOC/NO_x ratio of all three cities. As predicted by Hypothesis 1, O_3 correlated strongly with the VOC/NO_x ratio in this VOC-sensitive airshed. The VOC/NO_x ratios were higher in Philadelphia than in the other two cities, but photochemical indicators (NO_y, $HCHO/NO_y$, O_3/NO_y) predicted VOC sensitivity. The weak but statistically significant positive correlation between O_3 and the 24-hour VOC/NO_x ratio indicates that (1) O_3 production is sensitive to local NO titration and the increased availability of OH with reduced HNO_3 formation when NO_x is reduced, and (2) O_3 formation may take place in part in upwind locations that are VOC sensitive.

Hypothesis 2. Increased traffic emissions on Friday and Saturday evenings lead to increased precursors carried over to the next day, thereby increasing O_3 forming potential, and vice versa. Predawn (midnight to 4 a.m.) concentrations were used as a measure of nighttime emissions of NO_x and CO, a surrogate for vehicular VOC emissions. In all three locations, predawn concentrations of CO were higher on weekends than on weekdays. Predawn VOC did not show statistically significant weekday-weekend differences in Chicago and Philadelphia. In Atlanta, higher predawn VOC concentrations were observed on weekends relative to weekdays. Predawn NO_x showed a different weekly trend, which was lowest on Sunday mornings, second lowest on Monday mornings, and higher on other weekday mornings. The CO and NO_x concentrations are shown in Table E-2.

Table E-2. Summary of Hypothesis 2.

	Atlanta, GA		Chicago, IL		Philadelphia, PA	
	CO	NO_x	CO	NO_x	CO	NO_x
Predawn (midnight to 4 a.m. average) concentrations (ppb)						
Monday	780	28	730	38	660	27
Tuesday to Friday	760 – 830	34 – 38	720 – 760	44 – 51	620 – 680	28 – 35
Saturday	900	33	820	46	810	30
Sunday	990	26	800	36	820	24
Correlation coefficients between maximum one-hour average O_3 and predawn concentrations	0.11[(1)]	0.70[(2)]	0.85[(3)]	-0.52[(1)]	0.85[(3)]	-0.52[(1)]

(1) Statistically insignificant at the 10% level.

(2) Statistically significant at the 10% level.

(3) Statistically significant at the 5% level.

The difference in weekly cycles of NO_x and CO may reflect the different vehicular mix that makes up nighttime traffic. An increase in passenger car traffic on Friday and Saturday nights could explain the high predawn concentrations on Saturday and Sunday mornings. A decrease in heavy-duty vehicle traffic on Saturdays and Sundays, especially at night, could explain the reduced concentrations of NO_x observed on Sunday and Monday mornings. It should be noted that in addition to possibly different weekly cycles of NO_x and CO predawn emissions, the differences in the atmospheric chemistry and lifetimes of NO_x and CO may also help explain why these two pollutants correlate well for time periods dominated by emissions of both (e.g., morning average and 24-hour average) but not as well for the predawn time period with less fresh emissions.

The predawn concentrations were correlated to the daytime O_3, with results as shown in Table E-2. In Atlanta, the O_3 weekly cycle seemed to be positively correlated with predawn NO_x, and not correlated to predawn CO. The positive correlation with NO_x may indicate the predominant role of NO_x as fuel for photochemical O_3 production. In Chicago and Philadelphia, positive correlations with predawn CO were consistent with VOC sensitivity. (Despite limited data, positive correlations were also found between O_3 and the predawn VOC concentrations.) Although statistically insignificant, the negative correlations of O_3 in these two locations with predawn NO_x were consistent with titration of O_3 by NO_x.

Hypothesis 2a. Carry-over of precursors and/or O_3 from one day to the next drives the weekly cycle of O_3. The sensitivity of O_3 to predawn concentrations may indicate a correlation with carry-over, rather than just nighttime emissions. We tested the correlations between O_3 and 24-hour concentrations of O_3 and precursors from the previous day. The results are summarized in Table E-3. The only significant correlations in Atlanta were between O_3 and previous day's NO_x, NO_y, and CO. Since O_3 did not correlate with VOC, the correlation with CO was probably related to the correlation with NO_x (the correlation coefficient between 24-hour average CO and NO_x was 0.96). O_3 in Atlanta positively correlated with NO_x and NO_y carried over from the previous day. Chicago's O_3 correlated with VOC from the previous day. No statistically significant correlation was found between O_3 in Philadelphia and precursor concentrations during the previous 24 hours.

Table E-3. Summary of Hypothesis 2a

Correlation coefficients between maximum one-hour average O_3 and 24-hour average concentration from previous day	Atlanta, GA	Chicago, IL	Philadelphia, PA
O_3	0.02(1)	0.30(1)	0.15(1)
NO_x	0.75(2)	-0.12(1)	-0.18(1)
NO_y	0.87(2)	0.12(1)	0.59(1)
CO	0.81(2)	0.16(1)	0.25(1)
VOC	0.28(1)	0.76(2)	0.17(1)

(1) Statistically insignificant at the 10% significance level.

(2) Statistically significant at the 5% significance level.

Hypothesis 3. Different temporal emission patterns during weekends result in variations in O_3 concentrations. The diurnal profiles of ambient concentrations of NO_x and CO on weekends were very different from those on weekdays. In general, the diurnal profiles of NO_x and CO look very similar. Therefore, the 24-hour average concentrations of these two pollutants correlate well. In addition to the predawn concentrations investigated in Hypothesis 2, a notable weekend-weekday difference was the lower morning rush hour peak concentrations, as shown in Table E-4. We investigated how the reduced morning precursor concentrations affected O_3 as a function of the day of the week. In Atlanta, O_3 was not sensitive at all to the morning concentrations of CO, and the correlation with NO_x was positive but statistically insignificant. These observations were consistent with NO_x sensitivity and the importance of carry-over. In Philadelphia and Chicago, O_3 anticorrelated very strongly with both CO and NO_x. The anticorrelation of NO_x and O_3 could be explained by the direct effect of NO titration of morning O_3 on the afternoon O_3 peak or the formation of HNO_3 as a removal process for OH to reduce O_3 formation. The anticorrelation with CO was probably due to the significant correlation between NO_x and CO (correlation coefficients of 0.98 to 0.99 in Chicago and Philadelphia) rather than a direct effect of CO concentrations on O_3.

Table E-4. Summary of Hypothesis 3.

	Atlanta, GA		Chicago, IL		Philadelphia, PA	
	CO	NO_x	CO	NO_x	CO	NO_x
Morning (5-8 a.m. average) concentrations (ppb)						
Weekdays	1250 – 1290	40 – 51	1010 – 1120	61 – 75	1010 – 1050	64 – 52
Weekends	810 – 900	25 – 34	710 – 850	31 – 45	690 – 820	25 – 32
Correlation coefficients between maximum one-hour average O_3 and morning concentrations	0.01[(1)]	0.29[(1)]	- 0.94[(2)]	- 0.91[(2)]	-0.75[(2)]	- 0.81[(2)]

(1) Statistically insignificant at the 10% significance level.

(2) Statistically significant at the 5% significance level.

Hypothesis 4. Different spatial patterns of emissions on weekends result in variations in O_3 concentrations. The spatial distributions of 24-hour average CO and NO_x were analyzed to detect changes in the spatial traffic emission patterns on weekends vs. weekdays. Such an analysis was limited by the availability of monitors and the spatial representativeness of available monitors. Some shifts in the traffic patterns were evident from the changes in the ranking of a site by the concentrations on weekdays and weekends. In Atlanta, the NO_x monitor in Decatur, a suburb, recorded higher concentrations than a downtown monitoring site on weekdays, but lower concentrations on weekends. In Chicago, a site located on route to the south shore of Lake Michigan ranked higher in CO on weekends relative to weekdays. Two NO_x sites located near a baseball park also showed increased traffic on weekends. No change in rankings was observed in Philadelphia. We could not correlate changes in spatial patterns to the weekly O_3 behavior. When O_3 correlated strongly with the spatially averaged concentrations of NO_x and CO, the change in total emissions from weekdays to weekends had a much stronger effect than the change in spatial distribution. When O_3 did not correlate strongly with spatially averaged emissions, it also did not correlate to any significant extent to concentrations at individual sites.

Hypothesis 5. Emissions from sources other than on-road mobile sources vary from weekday to weekend. The composition of particles at an IMPROVE monitoring site in Washington D.C. was analyzed to illustrate any weekday-weekend changes that might be detectable in other urban emissions. A decrease in crustal minerals, silicon and calcium, was observed on weekends. In an urban area, road dust resuspended by traffic is an important source of crustal minerals in particles. Therefore, reduced road dust was consistent with reduced traffic on weekends. A decrease in elemental carbon (EC) was also observed. When the ratio of organic carbon (OC) and EC was tested, a statistically significant increase was observed, which provides some evidence of reduced truck traffic relative to light-duty vehicle traffic.

Hypothesis 6. A decrease in fine PM concentrations reduces light extinction and increases photochemistry and vice versa. The possible relationship between O_3 and PM inferred in this hypothesis was not proven due to the lack of specific changes in $PM_{2.5}$ during weekends. The relationships between solar radiation and O_3 and PM are summarized in Table E-5. The only significant correlation was found between solar radiation and $PM_{2.5}$ in Philadelphia. The positive correlation may indicate that instead of PM reducing the radiation reaching the surface, increasing radiation increases the production of secondary PM. UV radiation data were also tested. A weak correlation was observed between O_3 and UV in Chicago. The correlation was insignificant in Atlanta.

Table E-5. Summary of Hypothesis 6.

Correlation coefficients	Atlanta, GA	Chicago, IL	Philadelphia, PA
Maximum one-hour average O_3 and 24-hour average solar radiation	0.42(1)	0.63(1)	0.4(1)
Maximum one-hour average O_3 and 24-hour average UV radiation	-0.09(1)	0.69(3)	--
24-hour average $PM_{2.5}$ and 24-hour average solar radiation	0.59(1)	0.61(1)	0.81(2)
24-hour average $PM_{2.5}$ and 24-hour average UV radiation	-0.37(1)	0.60(1)	--

(1) Statistically insignificant at the 10% significance level.

(2) Statistically significant at the 5% significance level.

(3) Statistically significant at the 10% significance level.

Weekly behavior of O_3: 1986 - 90 vs. 1995 - 99

In Atlanta, smaller day-of-the-week differences were observed at four sites in the 1986 - 90 period than in the 1995 - 99 period. Diurnal profiles on different days of the week were very similar at three out of four sites. When the daily maximum one-hour average O_3 concentrations were tested, insignificant differences were found at those three sites. The remaining site showed high concentrations on Sundays and low concentrations on Tuesdays. The difference in the weekly behavior of O_3 between 1986 – 1990 and 1995 – 1999 may be due to the growth of the Atlanta metropolitan area. The lack of a weekly cycle at a majority of sites during 1986 to 1990 is postulated to be due to regionally distributed O_3, whose production was driven by biogenic emissions rather than anthropogenic emissions.

The weekend increase in O_3 observed in 1995 to 1999 in Chicago was also evident in the 1986 to 1990 data set. Weekday diurnal profiles were very similar. O_3 accumulation started earlier on Sundays than on Saturdays. At almost half the sites, O_3 accumulated faster on Saturday mornings and approached or exceeded the Sunday peak concentrations. The maximum one-hour average concentrations were highest on Saturdays at half the sites, compared to predominantly Sundays in the late 1990 sampling period. Low concentrations tended to be recorded on Fridays, rather than mid-week in the later period.

Philadelphia also showed weekend increases in O_3 in 1986 to 1990. The weekday profiles showed a decrease in morning O_3 concentrations that was not prominent on weekends. Sundays consistently showed higher O_3 in the mornings than Saturdays. With similar rates of O_3 accumulation, the high morning concentrations on Sundays translated into the highest peak concentrations in the afternoon relative to the weekdays. Saturday afternoon concentrations tended to peak later than those on Sundays. The mean value of the daily maximum one-hour average O_3 concentrations were highest on Sundays and Saturdays at three sites each. Lowest concentrations occurred on Thursdays or Wednesdays. The weekday-weekend differences were greater in this earlier period, as were the observed O_3 concentrations.

Recommendations

Our recommendations for future work include the following:

1. Investigate the reasons for the long-term changes in the weekly behavior of O_3.
2. Reanalyze the weekly behavior of $PM_{2.5}$ when more data are available.
3. Analyze weekday/weekend differences in VOC and PM composition when better data are available.
4. Reanalyze NO_y when more data are available.
5. Incorporate meteorological considerations to analyze the spatial difference in the day-of-the-week behavior of O_3.
6. Conduct airshed modeling of the weekday/weekend O_3 differences in the Atlanta metropolitan area to elucidate the governing processes.

1. INTRODUCTION

Weekday/weekend differences in ambient concentrations of ozone (O_3), particulate matter (PM), and other pollutants have been a topic of research interest since the 1970's (e.g., Cleveland et al., 1974; Levitt and Chock, 1976). Although weekly changes in the emissions due to human activities affect the weekly cycle of pollutant concentrations, details about this emission-concentration relationship are not well elucidated. Two areas of particular interest have been identified in the weekly behavior of ambient O_3 and PM. Significant geographical differences are observed in both the direction and magnitude of the weekly change. At a given location, the weekly behavior has changed over the years as emissions changed.

Several recent studies conducted for California airsheds (Altshuler et al., 1995; Blier and Winer, 1996; CARB, 2000) indicate that higher O_3 concentrations are typically observed on weekends than on weekdays in coastal airsheds such as the Los Angeles basin and the San Francisco Bay Area. The weekend increase is less apparent in the San Joaquin Valley. In the Sacramento Valley, O_3 increases from Fridays to Sundays, and continues to increase from Sundays to Mondays before returning to lower weekday concentrations. In the eastern part of the United States, Husar (1998) found that O_3 exceedances are less frequent on weekends than on weekdays.

Trend analyses suggest that the weekly behavior of O_3 has changed over the years, probably as a result of changes in emission patterns (e.g., urban growth) and controls (e.g., changes in reactivity or contribution of particular sources). For example, in the Los Angeles basin where O_3 has decreased from 1980 to 1998, the weekend effect has increased in magnitude at some sites (CARB, 2000).

A comprehensive research program, sponsored by California Air Resources Board (CARB), National Renewable Energy Laboratory (NREL), and Coordinating Research Council (CRC), is in progress to study the cause of the weekend effect in the Los Angeles Basin (http://www.arb.ca.gov/aqd/weekendeffect/weekendeffect.htm). With components that include data analysis, modeling, and field study, this program will characterize the day-of-the-week behavior in detail and provide information on the emissions and ambient concentrations that can be used to address the causes of the weekend effect in the Los Angeles Basin.

The project described here focuses on areas outside of California. Available data on O_3 and other pollutants are analyzed for three metropolitan areas: Atlanta, GA; Chicago, IL; and Philadelphia, PA. The goals of the project are to:

- Study the day-of-the-week behavior of hourly O_3 profiles, daily maximum one-hour and 8-hour O_3 concentrations, and PM concentrations
- Test various hypotheses for the weekly behavior of O_3.
- Identify changes in the weekday/weekend differences over the long term

This report is organized as follows. Section 2 describes the data obtained and analyzed in this work. The analysis procedures are outlined in Section 3. Results on the day-of-the-week behavior of O_3 and PM in Atlanta, GA; Chicago, IL; and Philadelphia, PA during 1995 to 1999 are provided in Section 4. In Section 5, we present our analysis regarding the possible causes of the weekday-weekend differences in O_3. Section 6 contains the day-of-the-week results of O_3 from an earlier time period, analyzed to identify any long-term changes in the day-of-the-week behavior. We present our conclusions and recommendations for future work in Section 7.

2. AMBIENT DATA

2.1 Data Record Length

The day-to-day meteorological variability of the data requires some temporal averaging before the data can be used in a meaningful way to elucidate day-of-the-week differences due to emissions and chemistry. Figure 2-1 illustrates the significant day-to-day variability of the one-hour average O_3 concentrations for Site 1324700014 in Atlanta for each day of the week during 1995. This site operated from March to November in 1995, and the plot of each day contains data from about 39 weeks (i.e., 39 data points for each hour of each day of the week).

Figure 2-2 illustrates the year-to-year variability using data from Site 1313500024 in Atlanta. Even though each profile plotted is an average of more than 30 days (except for 1999), year-to-year variability is still apparent in Figure 2-2. For example, in the mid afternoon, maximum O_3 was observed on Fridays in 1996-99 but on Saturdays in 1995. Mid-afternoon O_3 concentrations were lowest on Mondays, Wednesdays, or Sundays depending on the year.

In order to reach a more stable behavior in the weekly profiles of O_3 and other photochemical pollutants, we temporally averaged data from several years at each site. We considered data records from 1995 to 1999, because a data record length of five years was needed to obtain stable weekly behavior in Atlanta. Combining earlier records was not necessary, and probably not advisable because reformulated gasoline was introduced in 1995 in at least several metropolitan areas, resulting in changes in the reactivity of atmospheric organic compounds. Since a consistent pattern emerged after temporal averaging, spatial averaging was not performed in the characterization of weekly behavior.

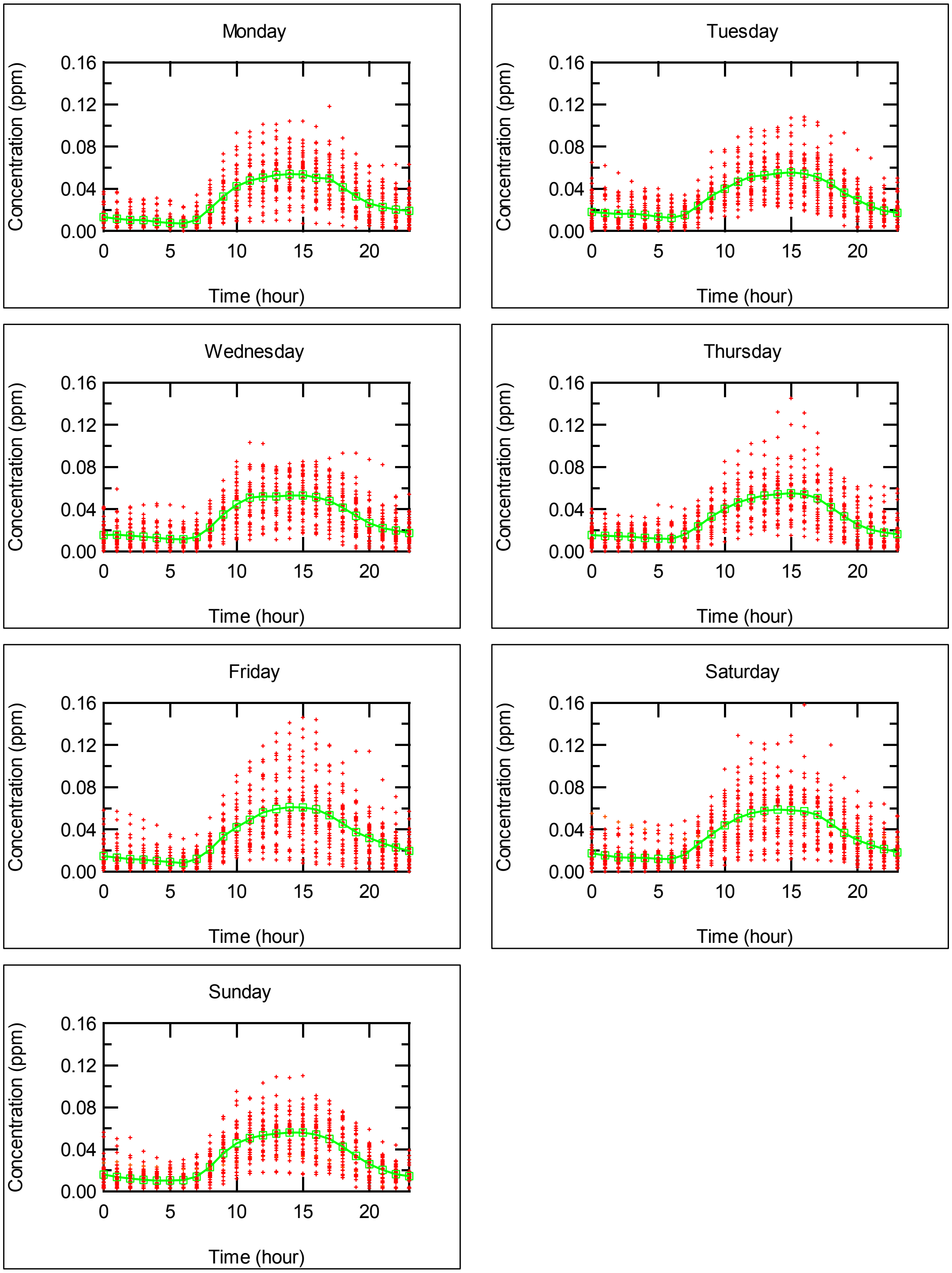


Figure 2-1. Day-to-day variability of O_3 concentrations at Site 1324700014 in Atlanta, GA during 1995 (line with square markers represent averaged concentrations, pluses represent raw data).

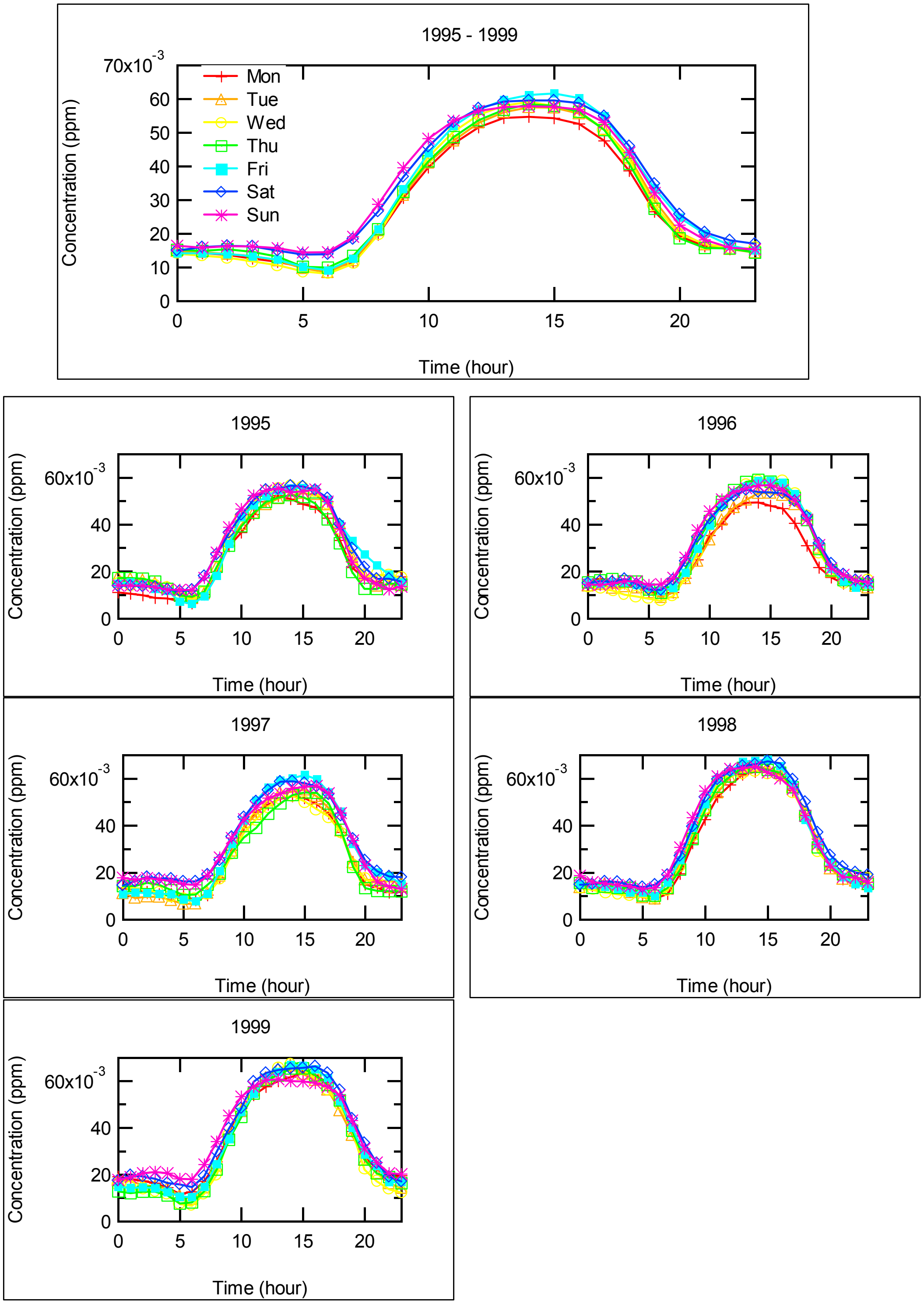


Figure 2-2. Year-to-year variability of O_3 concentrations at Site 1313500024 in Atlanta, GA.

2.2 Ozone Data

2.2.1 Atlanta, GA, 1995 - 99

There are 11 O_3 monitors in the Atlanta metropolitan area that were operational between 1995 and 1999. These sites and their data sets are listed in Table 2-1. Five of the 11 sites have been in continuous operation for all five years between 1995 and 1999. One started monitoring in 1997 and one in 1998. One-year O_3 records were obtained from the other three. O_3 is not monitored throughout the year in Atlanta; monitoring starts in March or April, and ends in the fall (October or November). The monitoring schedule corresponds roughly to the O_3 season in Atlanta, which is defined as March 1 to October 31 (S. Zimmer-Dauphnee, GA Department of Natural Resources, personal communication, 2001). At the time the data were downloaded, August was the last month for which data were available for 1999.

2.2.2 Chicago, IL, 1995 - 99

There are 26 O_3 monitors in the Chicago metropolitan area during the period of 1995 - 1999. These sites, together with the availability of data, are listed in Table 2-2. Twenty-one sites have been in continuous operation since 1995. Data records from the other 5 sites are either 2 or 3 years in length. During the 1995 to 1999 period, several sites were in operation around the year, while others were operational between spring (March/April) and fall (typically November). The O_3 season is defined as April 1 to October 31 in Illinois (D. Kenski, LADCO, personal communication, 2001). Several of the sites in the Chicago metropolitan area are located in Indiana, where the O_3 season excludes October.

2.2.3 Philadelphia, PA, 1995 - 99

There are six O_3 monitoring stations in the Philadelphia metropolitan area between 1995 and 1999, as listed in Table 2-3. Five-year data records were obtained for each of the six sites, although significant data gaps occurred in summer 1999 at two sites (as noted in Table 2-3). Three of the sites (3400700034, 4210100044, and 4210100244) operated around the year from 1995 to 1999. Sites 4210100144 and 4210101364

Table 2-1. Ozone data set in the Atlanta, GA metropolitan area: monitoring sites and years of data analyzed.

Site ID	Location	Designation	Years	
1307700024	University of W. GA at Newnan	Suburban, commercial		99[(1)]
1308900024	Decatur, South DeKalb (on DeKalb Co. Schools Environmental Education property)	Suburban, residential	86 – 90	95 – 99
1308930014	Idlewild Road, Tucker	Rural, residential		95 – 99
1309700024	Sweetwater Creek State Park	Suburban, residential	87 – 90	95[(1)]
1309700044	W. Strickland St., Douglasville	Suburban, commercial		97 – 99[(1)]
1311300014	Fayetteville	Suburban, commercial		98 – 99[(1)]
1312100534	MLK MARTA Station, 240 Grant St., Atlanta	Urban and center city, commercial	87 – 90	
1312100554	Confederate Ave., Atlanta	Suburban, commercial		95 – 99
1313500024	Gwinnett Tech, 1250 Atkinson Rd, Lawrenceville	Suburban, commercial		95 – 99
1315100024	Henry County Extension Office	Rural, residential		99[(1)]
1322300034	Yorkville	Rural, agricultural		96 – 99[(1)]
1324700014	Conyers Monastery, 3780 GA Hwy 212	Rural, agricultural	86 – 90	95 – 99

(1) Sites with incomplete data in 1995 – 1999 are not included in the O_3 day-of-the-week analysis.

Table 2-2. Ozone data set in the Chicago, IL metropolitan area: monitoring sites and years of data analyzed.

Site ID	Location	Designation	Years	
1703100014	4500 W. 123rd St., Alsip	Suburban, residential	88 – 90	95 – 99
1703100324	3300 E. Cheltenham, So. Water Filtration Plant, Chicago	Urban and center city, industrial	87 – 90	95 – 99
1703100374	Edgewater 5358 N. Ashland Ave., Chicago	Urban and center city, residential	86 – 90	95 – 96
1703100454	Lincoln Park Zoo, Chicago	Urban and center city, commercial	86	
1703100504	SE Police Sta., 103rd And Luella, Chicago	Suburban, industrial		95 – 99
1703100624	Harrison Crib, Chicago	Suburban, agricultural	89	
1703100634	CTA Building, 320 S. Franklin, Chicago	Urban and center city, mobile		95 – 99
1703100644	University of Chicago, 5720 S. Ellis Ave, Chicago	Suburban, residential	89 - 90	95 – 99
1703100724	Jardine Water Plant, 1000 E. Ohio, Chicago	Urban and center city, commercial		95 – 99
1703100754	Truman College,1145 W. Wilson, Chicago	Suburban, residential		98 – 99(1)
1703110024	15400 Marquette Ave, Calumet City	Suburban, residential	86 – 90	
1703110034	Taft H.S., 6545 W. Hurlbut St., Chicago	Urban and center city, mobile	86 – 90	95 – 99
1703116014	729 Houston, Lemont	Suburban, residential	86 – 90	95 – 99
1703140024	1830 S. 51st Ave., Cicero	Suburban, residential	86 – 90	95 – 99
1703140034	2nd Ave. & Thacker, Des Plaines	Suburban, residential	86 – 90	
1703140064	Forest Elem School, 1375 5th Ave., Des Plaines	Suburban, residential		95 – 99
1703142014	Northbrook Water Plant,750 Dundee Rd., Northbrook	Suburban, residential		97 – 99(1)
1703170024	531 E. Lincoln, Evanston	Suburban, residential	86 – 90	95 – 99
1703180034	1703 State St., Calumet City	Suburban, residential		95 – 99
1704360014	Morton Arboretum, Rt. 53, Lisle	Suburban, agricultural	86 – 90	95 – 99
1709700014	1321 Wilmot Rd. Woodland Park Elem. Sch., Deerfield	Suburban, residential	86 – 90	95 – 99
1709710024	Golf & Jackson Sts., Waukegan	Suburban, residential	86 – 90	95 – 99

Table 2-2. Ozone data set in the Chicago, IL metropolitan area: monitoring sites and years of data analyzed (continued).

Site ID	Location	Designation	Years	
1709710074	Camp Logan, Illinois Beach State Park	Rural, forest		95 – 99
1709710114	Com Ed Training Center, Rural Braidwood	Rural, agricultural		95 – 99
1709730014	1441 Lake Street, Libertyville	Suburban, residential	86 – 90	95 – 99
1808900224(2)	201 Mississippi St., Iitri Bunker, Gary	Urban and center, industrial		95 – 99
1808910164(2)	Federal Bldg. 6th Ave., Gary	Urban and center city, residential	86 – 90	95 – 96
1808920084(2)	1300 141 St Street, Hammond	Suburban, commercial	86 – 90	95 – 99
1812700204(2)	Indiana Dunes, N Lakeshore	Rural, industrial		98 – 99
1812700244(2)	Water Treatment Plant, Porter County	Suburban, residential	86 – 90	95 – 99

(1) Sites with incomplete data in 1995 – 1999 are not included in the O_3 day-of-the-week analysis.
(2) Monitoring season corresponds to the O_3 season in Indiana (April to September), which is shorter than that in Illinois (April to October); not included in the O_3 day-of-the-week analysis.

Table 2-3. Ozone data set in the Philadelphia, PA metropolitan area: monitoring sites and years of data analyzed.

Site ID	Location	Designation	Years	
3400500014	N. Bolling Blvd. & E.Castle Rd., McGuire AFB	Suburban, residential	86 - 90	
3400700034	Copewood-E. Davis Sts, Camden	Suburban, residential	86 – 90	95 - 99
4204500024	Front St & Norris St, Chester	Urban and center, industrial	86 – 90	95 - 99
4210100044	1501 E Lycoming Ave Ams Lab, Philadelphia	Urban and center, residential		95 – 99
4210100144	Roxy Water Pump Sta Eva-Dearnley, Philadelphia	Suburban, residential	86 – 90	95 – 99 (1)
4210100234	SE Sewage Plant Front-Packer Streets, Philadelphia	Urban and center, industrial	86 – 90	
4210100244	Grant-Ashton Roads Phila NE Airport, Philadelphia	Suburban, industrial	86 – 90	95 – 99 (2)
4210101364	6001 Elmwood St., Philadelphia	Urban and center, residential		95 - 99

(1) Data gap in July and August, 1999; not included in the O_3 day-of-the-week analysis.
(2) Data gap between June and August, 1999; not included in the O_3 day-of-the-week analysis.

operated from March to November during 1995, 96, and 97 and around the year from 1998 onwards. The remaining site, 4204500024, adhered to a monitoring schedule from April to October.

2.3 Ozone Data, 1986 – 1990

Ozone data from a previous time period were downloaded for the analysis of long-term changes in the weekly behavior. We selected the five-year period between 1986 and 1990 before reformulated gasoline was introduced in many areas. Generally, there were fewer monitoring stations in the eighties than in the nineties.

Hourly O_3 data were collected at only two stations in the Atlanta, GA area from 1986 to 1990 (see Table 2-1). Two other stations operated from 1987 to 1990. Three out of these four sites were also included in the data set from 1995 to 1999. These sites were operational from March to November.

Twenty O_3 monitoring sites in the Chicago, IL metropolitan area provided hourly data between 1986 and 1990. Sixteen of these sites also operated during the period from 1995 to 1999 (see Table 2-2). Three of these 16 started monitoring in either 1987 or 1988, one in 1990. Of the four remaining sites not in operation in the later period, two operated for only one year (1986 or 1990) and the other two operated for all five years. The available data were year-round for 6 sites and from March to November for the majority of the monitoring sites.

There were six O_3 monitoring sites in the Philadelphia, PA area from 1986 to 1990. Four overlapped with the sites from which O_3 data were downloaded for the years 1995 to 1999 (see Table 2-3). All 6 sites provided five years' worth of data. The monitoring schedules were either year round or from March/April to November.

2.4 PM Data

PM_{10} is measured continuously in all three urban areas using a tapered element oscillating microbalance (TEOM) or a beta attenuation monitor. $PM_{2.5}$ monitoring started in 1999. However, data from several sites were generally available for each region of interest. Some states reported 24-hour average values, while others reported hourly concentrations of $PM_{2.5}$.

2.4.1 Atlanta, GA

Hourly-averaged PM_{10} data were downloaded for one monitoring site (Site ID 1312100488) in an urban location in Atlanta near the Georgia Institute of Technology. Data were only available for the one-year period between July 1998 and June 1999.

Georgia established 8 $PM_{2.5}$ monitoring sites in 1999. These sites measure 24-hour average concentrations of $PM_{2.5}$. Three of the sites operated every day, the rest followed a one-in-three-day schedule. The 1999 data set contained about 100 valid data records (averaging about 14 per day of the week) from the sites operating every third day or about 280 valid data records (40 per day of the week) from the sites operating everyday. Both PM_{10} and $PM_{2.5}$ sites and their schedule of operation are listed in Table 2-4.

2.4.2 Chicago, IL

There are five sites that measure PM_{10} around the year (Table 2-5). One site has been in continuous operation from October 1995 to 1999. Data records from the other sites are either two or three years in length.

A network of 13 sites was established in 1999 to measure 24-hour average $PM_{2.5}$ concentrations. These monitors operated year-round and reported $PM_{2.5}$ concentrations every sixth day. Each station collected 50 to 60 data points for 24-hour average $PM_{2.5}$ in 1999 (7-9 per day of the week).

2.4.3 Philadelphia, PA

Two PM_{10} sites (Table 2-6) were located in the metropolitan Philadelphia area during 1995 to June 1998. These sites were operational year round and measured hourly PM_{10} concentrations.

Continuous measurements of $PM_{2.5}$ were taken at one site in 1999 in the Philadelphia area using a modified TEOM instrument. This site was located in Camden, NJ in a suburban residential area.

Table 2-4. PM monitoring sites in the Atlanta, GA metropolitan area, years of data analyzed, and data characteristics.

PM	Site ID	Years	Data Characteristics
PM_{10}	1312100488	July 98 – June 99	Hourly data
$PM_{2.5}$	1306300918	99	24-hour average data every third day
$PM_{2.5}$	1306700038	99	24-hour average data every third day
$PM_{2.5}$	1308900028	99	24-hour average data everyday
$PM_{2.5}$	1308920018	99	24-hour average data everyday
$PM_{2.5}$	1312100328	99	24-hour average data everyday
$PM_{2.5}$	1312100398	99	24-hour average data every third day
$PM_{2.5}$	1312110018	99	24-hour average data every third day
$PM_{2.5}$	1322300038	99	24-hour average data every third day

Table 2-5. PM monitoring sites in the Chicago, IL metropolitan area and years of data analyzed.

PM	Site ID	Years
PM_{10}	1703100598	96 – 97
PM_{10}	1703110168	95 – 97
PM_{10}	1703120018	96 – 97
PM_{10}	1808900228	97 – 99
PM_{10}	1812700238	95 – 99
$PM_{2.5}$	1703100148	99
$PM_{2.5}$	1703100228	99
$PM_{2.5}$	1703100508	99
$PM_{2.5}$	1703100528	99
$PM_{2.5}$	1703110168	99
$PM_{2.5}$	1703117018	99
$PM_{2.5}$	1703120018	99
$PM_{2.5}$	1703133018	99
$PM_{2.5}$	1703140068	99
$PM_{2.5}$	1703142018	99
$PM_{2.5}$	1704340028	99
$PM_{2.5}$	1719710028	99
$PM_{2.5}$	1719710118	99

Table 2-6. PM monitoring sites in the Philadelphia, PA metropolitan area and years of data analyzed.

PM	Site ID	Years of Operation
PM_{10}	4201700128	95 – 98
PM_{10}	4204500028	95 – 98
$PM_{2.5}$	3400700038	99

2.5 Other Data

Supplementary data were also obtained from the AIRS database for use in the hypotheses testing phase of the project. Such data included nitrogen oxides (NO_x, NO and NO_2), total oxidized nitrogen (NO_y), carbon monoxide (CO), volatile organic compounds (VOC) (VOC data were downloaded as TNMOC, total non-methane organic compounds), individual organic compounds, solar radiation, and ultra violet (UV) radiation. Of these concentrations and parameters, NO_x, NO_y, CO, and radiation were recorded in one-hour intervals. VOC data were available as one-hour averages, three-hour averages, or 24-hour averages. Individual organic compounds were measured at three-hour intervals. NO_x and CO monitors generally operated year round; while NMOC and NO_y monitors typically only operated during the summer ozone season. NO_y data tended to be more error-prone, resulting in a much smaller sample than the dates in the data file would indicate. Some monitors for speciated organic compounds may also be operational on a one-in-three day or one-in-six day schedule. Table 2-7 summarizes the supplementary data analyzed in this study for Atlanta, GA; Chicago, IL; and Philadelphia, PA. In addition, limited PM composition data were available from the only IMPROVE site in an urban area, Washington D.C. PM data from 1988 to 1997 were taken on Wednesdays and Saturdays.

Table 2-7. Supplementary data and number of sites in Atlanta, GA; Chicago, IL; and Philadelphia, PA.

Parameter	No. of Sites		
	Atlanta, GA	**Chicago, IL**	**Philadelphia, PA**
NO	5	14	2
NO_2	5	14	2
NO_x	5	14	2
NO_y	3	1	1
CO	2	11	6
VOC	5	5	1 (1)
Individual species	5	5	2
Solar Radiation	4	7	1
UV Radiation	4	3	--

(1) Site 421010004 has co-located measurements of 3-hour average and 24-hour average total non-methane organic compound measurements

3. PROCEDURE

3.1 Analysis

For each metropolitan area, Atlanta, GA; Chicago, IL; and Philadelphia, PA, we characterized the day-of-the-week behavior of ozone (O_3) by plotting the 24-hour profile of the one-hour average concentrations and by analyzing the daily one-hour maximum concentrations grouped by the day of the week. In Atlanta, GA, the O_3 season is defined as March 1 through October 31 (S. Zimmer-Dauphnee, GA Department of Natural Resources, Environmental Protection Division, personal communication, 2001). Since the O_3 monitors in Atlanta operated roughly during the O_3 season (most sites operate between March/April and October/November), all available data are included in the analyses. In Chicago, IL and Philadelphia, PA, the O_3 season is defined as April 1 to October 31. In both metropolitan areas, some monitoring sites were operational year round, while others operated between March/April and September/October/November. An initial analysis was carried out in Chicago and Philadelphia using all available data. At the request of CRC, we limited the analyses to data from the O_3 season for Chicago and Philadelphia.

We first processed and sorted the available data according to the day of the week. For each day of the week, an average concentration profile was generated by calculating the average concentration at each hour. Second, we determined the daily maximum one-hour average O_3 concentrations and grouped the data by the day of the week. To ensure the robustness of the conclusions regarding the day-of-the-week differences, we tested several characteristic values of the maximum one-hour concentrations. For each group of daily maximum concentrations, we calculated the mean, median, and 90th percentile. Day-of-the-week differences in these quantities were calculated and the statistical significance of any difference was determined using bootstrap sampling (discussed below). Third, we determined the number of days when the maximum one-hour average concentration exceeded the National Ambient Air Quality Standard (NAAQS) of 120 ppb for each day of the week. We identified the days of the week when exceedances were most likely to occur when the number of exceedances was large enough to provide a statistically meaningful sample.

The 8-hour average O_3 concentrations were determined at each monitoring site by calculating the running average of the hourly concentrations. Daily maximum 8-hour average concentrations were determined and grouped by the day of the week. The mean value of the maximum 8-hour average concentrations was determined for each group and the difference in those mean values was tested using bootstrap sampling.

We also investigated the day-of-the-week differences in PM concentrations. Average day-of-the-week profiles were determined for PM_{10} data obtained from routine monitoring. Data from each hour of the day were averaged, grouped by day of the week, to produce these profiles. 24-hour average concentrations of PM_{10} and $PM_{2.5}$ were also analyzed.

3.2 Bootstrap Resampling

A computer program was developed to perform bootstrap resampling (Noreen, 1989), a statistical technique that generates a large number of artificial samples from the observed data. Given a set of observations from a population, the non-parametric maximum likelihood estimate of the population (from which the sample is drawn) is the sample itself, if there is no other information available about the population. The basic premise of bootstrap resampling is that the observations can be sampled at random with replacement in the Monte Carlo sense to generate alternative samples consistent with the characteristics of the estimated population. The best estimate of a metric of the population can be determined as the mean value of that metric of the bootstrap samples.

A distribution of the metric of interest can also be determined from the bootstrap samples. This distribution can be used in several tests for determining if the observed value, treated as one random sample from the distribution, occurs by chance given a null hypothesis, much like the traditional student-t distribution is used in determining the statistical significance of a mean value. In this study, we applied bootstrap sampling to test the differences in the mean, median, and 90th percentile of O_3 concentrations, and the number of exceedances (e.g., of the O_3 standard) between different days of the week.

The main advantage of bootstrap sampling is its flexibility. Hypothesis testing can be accomplished without restricting assumptions about the population distribution from which the sample is drawn. This method is particularly useful for metrics (e.g., of the median, or the difference of the median in two samples) whose population distribution cannot be readily determined.

Hypothesis testing is conducted using one of two methods based on the bootstrap population: the shift method or the normal approximation method. For the analysis of the weekly behavior of O_3 and other pollutants, we tested the significance of the difference of some metric between two sets of data (e.g., weekday and weekend). Instead of sampling one set of data and determining if the selected metric is statistically different from an observed value of the same metric of a second set of data, we chose to sample both sets of data in the same test. In this way, we calculated the difference in the selected metric between weekday sample and the weekend sample and generated a distribution of the difference. Using the bootstrap distribution so determined, we then tested the observed difference against a null hypothesis that there was no difference.

This procedure can be demonstrated with a simple example to determine if the difference in the mean values of samples from two different days is statistically different from a null hypothesis value of 0.0. From Atlanta's Site 1313500024, we have a Friday maximum one-hour concentration data set and a Monday data set whose means are different by 5.2 ppb. We hypothesize that the population difference in the means is actually 0.0 ppb (null hypothesis). The question that we want to ask is: "is a difference of 5.2 statistically different from 0.0?"; or, "if the true difference in the mean is 0.0, what is the probability that a random sample drawn from the population has an observed mean of 5.2?" To answer this question, we resample our Friday and Monday data sets a large number of times, say 1000 times each. We calculate the difference in the mean values of each pair of Monday-Friday samples. Then we prepare a distribution of the difference with 1000 data points. Note that there is no restriction on the shape of the distribution. This distribution is the bootstrap distribution and it has a mean value slightly different from the observed difference. In this case, the bootstrap mean is 5.3 ppb. We also calculate the standard deviation of the bootstrap distribution to be 2.6 ppb.

In the shift method, we assume that the distribution of the statistic of interest has a fixed shape (see Figure 3-1). We can approximate the null distribution, which is the distribution of the statistic of interest under the null hypothesis, by the distribution shifted over by 5.3 ppb, which is the difference between the bootstrap mean of the distribution and the hypothesized mean. Then, the statistical significance of an observed difference of mean of 5.2 ppb as opposed to a guessed difference of 0.0 can be estimated by the probability that the difference in the Friday-Monday sample means is above 5.2 ppb in this approximated null distribution. The probability can be calculated as the actual number of bootstrap samples whose shifted differences are above 5.2. In this case, only 2% of the samples have a shifted statistic above 5.2 ppb, so the difference is statistically significant at the 2% level. The higher the probability that bootstrap samples have a mean of greater than 5.2 in this distribution with a mean of 0.0, the lower the confidence that the mean of 5.2 is different from a mean of 0.0.

An alternative assumption in hypothesis testing is to assume the null population distribution of the statistic (the difference of means) has the same standard deviation as the collection of bootstrap samples, which is 2.6 ppb. Using the normal approximation method, we can follow the procedure of the student-t test and define z_0 = (observed statistic – hypothesized statistic)/standard deviation, which in this example is (5.2 – 0.0) / 2.6 = 2.0. The central limit theorem suggests that for many test statistics, if the sample is sufficiently large, the random variable z_0 is approximately a standard normal variable. The statistical significance is the area under a standard normal distribution beyond the absolute value of 2 on the right, which can be looked up in statistical tables. The probability that z_0 is greater than 2 is given by the complementary error function. The probability is 0.02, which agrees with the result from the shift method.

The day-of-the-week differences in O_3 and PM, presented in Sections 4 and 6, are tested using the bootstrap resampling technique. The statistical significance of the results is reported as one of three categories: (1) statistically significant at the 5% level, (2) statistically significant at the 10% level, and (3) statistically insignificant at the 10% level.

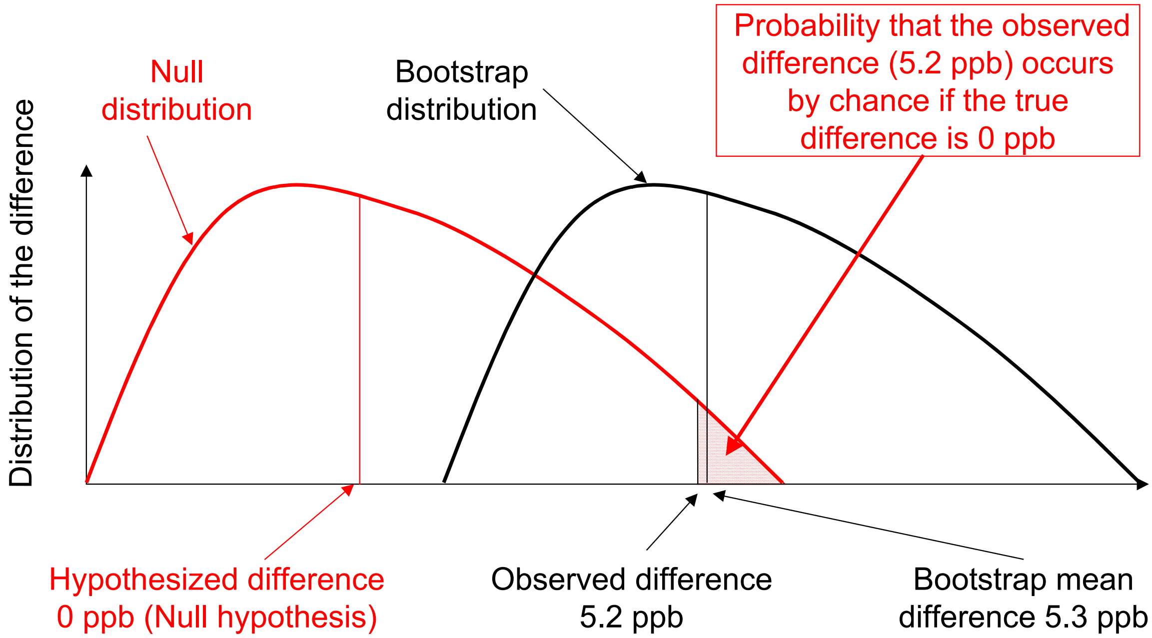


Figure 3-1. Hypothesis testing using bootstrap resampling and the shift method.

3.3 Regression Analysis

Regression analyses were performed to test several hypotheses, discussed further in Section 5. We explain here the statistical procedures used to generate data sets that were correlated to one another.

The metric of interest in these day-of-the-week analyses was the maximum one-hour average concentration of O_3. For each monitoring site, the daily one-hour maximum concentration was first calculated for every day in 1995 to 1999, generating an array of about 1830 data points in chronological order. Zeros were used to indicate invalid data, which were excluded from the regression analyses.

For primary pollutants, we were interested in other metrics that described their weekly behavior. For example, an averaged predawn (midnight to 4 a.m.) concentration could be used as an indication of nighttime emissions carried over to the next day, a morning average concentration (5 a.m. to 8 a.m.) could be used to indicate the morning commute, and a 24-hour average concentration could be used as a general indicator of daily emissions.

For correlating O_3 with concentrations of other pollutants or parameters, some spatial aggregation was desirable. There were generally more O_3 sites than sites that measure other pollutants and parameters. Since only a fraction of the O_3 data were taken at sites with co-located monitors of other parameters, using only data from co-located monitors will reduce the representativeness of the O_3 data set. Furthermore, the concentrations of primary pollutants, such as NO_x and CO, would be affected by local sources. Spatial aggregation would reduce the spatial variability of these data. Two approaches of spatial aggregation were considered for O_3 on any given day: (1) spatial average of all available measurements or (2) the peak concentration amongst all the available measurements. The spatial average of the maximum one-hour concentrations at all the sites was chosen because it was expected to be less sensitive to outliers and missing data (e.g., from a site that recorded high concentrations). Therefore, by selecting one metric per site per day and spatially averaging all available information, we distilled the daily behavior of O_3 and other parameters into a series of 1830 numbers for the five-year period from 1995 to 1999.

Ratios of pollutants (e.g., VOC/NO_x) were calculated in several steps. First, a metric (e.g., 24-hour average) was calculated for each site on each day for both pollutants involved in the ratio. Second, a spatial average of the metric was calculated for each pollutant, resulting in a 5-year data record of the spatial average of the metric. Finally, a ratio was calculated for each day in the 5-year record where matching concentrations existed for both pollutants.

Meteorology caused significant scatter in the concentration data, obscuring the effects of emissions and chemistry, which in all likelihood drive the weekly behavior in O_3. As shown in Section 2.1, the weekly behavior in O_3 was observed clearly after temporally averaging the five-year data record. In the correlation analysis, the same approach was used. We grouped the data (e.g., spatial average of the maximum one-hour O_3 concentration on each day) by the day of the week into 7 groups. All correlations were performed using the average values of these 7 groups of data. In the correlation analyses in Section 5, we report the correlation coefficient (R) and the coefficient of determination (R^2). The correlation coefficient ranges from –1 (perfectly anticorrelated) to 1 (perfectly correlated). For a data set of 7 points (i.e., 5 degrees of freedom), a correlation coefficient with an absolute value above 0.75 is significant at the 5% level, and a value of 0.67 is significant at the 10% level. The coefficient of determination can be interpreted as the percentage of the variance in one variable that can be explained by the second variable.

4. WEEKLY BEHAVIOR OF OZONE AND PM, 1995 – 99

As shown in Section 2.1, a five-year data record from 1995 to 1999 provides stable estimates of the weekly behavior of O_3 in the O_3 season. During this period, there are 5, 18, and 4 monitoring stations in Atlanta, Chicago, and Philadelphia, respectively, with complete data records (see Table 2-1 through 2-3). We focus on these stations in the analysis of the weekly behavior of O_3. PM data are relatively limited in all areas compared to O_3 data; therefore, all available data are used in the PM analysis.

4.1 One-Hour Average Ozone Concentrations

4.1.1 Atlanta

24-hour profiles of each day of the week. The averaged temporal profiles of Site 1313500024 are shown in Figure 4-1 as a representative example of the 24-hour profiles observed in Atlanta. The plot contains 7 profiles, one for each day of the week averaged over five years. Appendix A1 contains similar plots for all sites in the Atlanta area that operated for the entire period of interest. Peak O_3 was observed daily in the late afternoon, most frequently at 4 p.m. At several sites, O_3 peaked earlier (e.g., 2 or 3 p.m.) on Mondays than on other weekdays. All five sites showed consistent day-of-the-week trends. Afternoon O_3 concentrations were highest on Fridays, and lowest on Mondays. The second highest afternoon O_3 concentrations occurred on Saturdays.

A noticeable difference between the O_3 profiles during the week and during the weekend was the morning concentrations. During the week, minimum O_3 was observed during morning rush hour. At about half of the monitoring sites (including Site 1313500024 shown in Figure 4-1), the decrease in O_3 concentrations between 5 and 7 a.m. was not as significant on the weekends as on weekdays and O_3 started building up earlier on Saturdays and Sundays. These observations seem to be consistent with decreased NO_x emissions from early morning traffic on weekends and the reduction in titration of O_3 by NO. One parameter that characterizes the NO titration effect is the "NO-O_3 cross-over time" (Fujita et al., 2000), which is the time during the morning commute when the concentration of O_3 equals that of NO. From that point on, O_3 starts

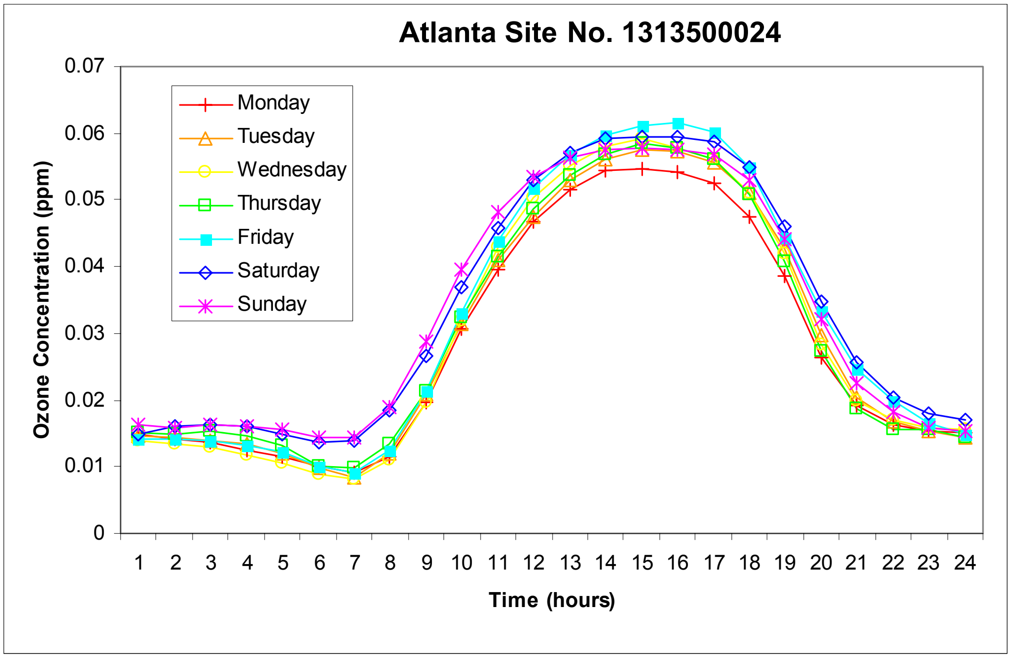


Figure 4-1. Average daily ozone profiles at Site 1313500024 in Atlanta, GA from 1995 to 1999.

building up and NO remains at relatively low concentrations throughout the day until late afternoon. At Site 1308900024, which measured both O_3 and NO concentrations, the cross-over time was on average 0.5 and 1 hour earlier on Saturdays and Sundays, respectively, than on weekdays. (The other 3 sites in the Atlanta area with both NO and O_3 monitors were all rural sites and measured higher O_3 than NO at all hours.) The rate of O_3 increase in the morning on weekends, especially on Sundays, was comparable to or greater than that on weekdays, so that the mid morning (e.g., 9 a.m.) concentrations of O_3 were typically higher on weekends than on weekdays. By early afternoon, O_3 production slowed down and a broad O_3 peak can be observed from 2 to 5 p.m. on Sundays. However, O_3 production continued into the early afternoon on Fridays at some sites and Friday's O_3 overtook that on other days during the early afternoon hours.

Maximum one-hour average concentration. The maximum one-hour average concentration was determined for each 24-hour record at each site. The mean of the maximum concentrations was determined for each day of the week grouped by site. Appendix A2 contains the graphs of the mean daily maximum concentrations, together with the standard deviation of each group of maximum concentrations. These data are summarized in Table 4-1. The day-of-the-week behavior of the mean daily maximum concentrations was consistent with the daily profile. The maximum one-hour concentrations on Fridays were higher than on the other days at all five sites in the Atlanta area. The daily maximum concentrations were lowest on Mondays. (Sites with data records of 1 to 3 years, not listed in Table 4-1, showed statistically significant differences in highest concentrations on Fridays and Saturdays and lowest daily maximum concentrations on Mondays and Sundays.)

Between different days of the week, the difference in the mean values of the maximum daily concentrations was 5 to 6 ppb. Due to atmospheric variability, the standard deviations associated with the daily maximum concentrations were quite significant at all sites. The coefficients of variation (the ratio of the standard deviation to the mean) were 30% to 50% in the O_3 data. The large sample size (5 years) helped minimize the error associated with the mean estimate of the maximum one-hour concentration for each day of the week, since the standard error of the mean scales with

Table 4-1. Statistics of mean daily maximum one-hour average ozone concentrations (ppm) by day of the week in Atlanta, GA.

Site	Maximum (ppm)	Day of maximum	Minimum (ppm)	Day of minimum	Maximum minus minimum (ppm)	Statistical significance of the difference
1308900024	0.0650	Friday	0.0598	Monday	0.0052	10%
1308930014	0.0643	Friday	0.0593	Monday	0.0051	5%
1312100554	0.0692	Friday	0.0647	Monday	0.0046	5%
1313500024	0.0654	Friday	0.0601	Monday	0.0052	10%
1324700014	0.0702	Friday	0.0642	Monday	0.0060	5%

$n^{-1/2}$, where n is the sample size. However, it was important to test the statistical significance of the relatively small day-of-the-week difference.

The testing was performed using bootstrap sampling with 999 bootstrap samples. All five sites with five-year data records showed statistically significant differences between the highest mean concentrations on Fridays and the lowest on Mondays at the 5% or 10% significance level. A sixth site operational between 1998 and 1999 also showed a statistically significant Friday-Monday difference. Note that the magnitude of the difference is a poor measure of statistical significance. For example, a large difference of 13 ppb was observed at Site 1315100024 between high concentrations on Thursdays and low concentrations on Mondays. This difference was statistically insignificant due to a small data set (13 data points for each day of the week, since this site started operation in June of 1999).

Since the highest and lowest mean concentrations were recorded on Fridays and Mondays, respectively, we investigated the weekday-weekend differences in O_3 by grouping the maximum one-hour concentrations during midweek (Tuesdays, Wednesdays, and Thursdays) and during weekends (Saturdays and Sundays). The mean value of the midweek maximum one-hour average concentrations was slightly higher than the mean value on weekends. With differences of only 1 to 2 ppb at all sites, no statistically significant difference between weekend and midweek O_3 was detected, despite significant weekday-weekend changes in the emissions of NO_x and VOC, as shown in Section 5. The decoupling of the weekly cycle of O_3 and the weekly cycle of emissions will be investigated in Section 5.

The median values of the daily maximum concentrations were calculated for each day of the week. The results are listed in Table 4-2. The trends in the median values were not as clear as those in the mean values. The maximum median values occurred most frequently on Fridays, consistent with the observed high mean concentrations on Fridays (Table 4-1). Three sites also showed high median concentrations on Wednesdays (1 site) and Saturdays (2 sites). The lowest median concentrations were observed on Sundays, Mondays, or Tuesdays, with Tuesdays recording the most low median concentrations. When tested with bootstrap sampling, the differences were found to be statistically insignificant for the pairs of high-low median concentrations listed in Table 4-2

Table 4-2. Statistics of median daily maximum one-hour average ozone concentrations (ppm) by day of the week in Atlanta, GA.

Site	Maximum (ppm)	Day of maximum	Minimum (ppm)	Day of minimum	Maximum minus minimum (ppm)	Statistical significance of the difference
1308900024	0.061	Friday/ Wednesday	0.057	Tuesday	0.004	insignificant
1308930014	0.063	Friday	0.057	Monday/ Tuesday	0.006	5%
1312100554	0.066	Friday/ Saturday	0.062	Tuesday/ Sunday Tuesday/ Sunday	0.004	10% insignificant
1313500024	0.065	Friday/ Saturday	0.059	Monday	0.006	5% insignificant
1324700014	0.067	Friday	0.061	Sunday/ Tuesday	0.006	5%

involving high concentrations on Wednesdays and Saturdays. The maximum concentration on Fridays was statistically significant at four sites. The Monday-Friday difference was significant at three of the five sites listed in Table 4-2, whether or not they represented the extreme values. These results support a conclusion that O_3 accumulated throughout the work week to a maximum on Fridays; lower concentrations were typically observed on Sundays, Mondays, and Tuesdays.

Like the median values, the 90th percentile values of the daily maximum concentrations showed that concentrations tended to be high on Fridays. High 90th percentile concentrations that were statistically significant were also observed on Saturdays. That Fridays and Saturdays showed the maximum concentrations in the week is consistent in the analysis of both the profiles and the maximum one-hour average concentrations (mean, median, and 90th percentile values).

Most of the low 90th percentile concentrations were on Mondays. Low 90th percentile values were observed at three sites on Mondays, compared to only two showing low median values on Mondays, although the trend was not as clear as with the mean values. However, Tuesdays, Wednesdays, and Thursdays were among the days when the lowest 90th percentile daily maximum O_3 concentrations were observed. The day-of-the-week differences in the 90th percentile concentrations were 9 to 16 ppb, which were statistically significant at all five sites (Table 4-3). The differences in 90th percentile concentrations between Mondays and Fridays were significant at four sites, as were the differences between Mondays and Saturdays.

Exceedances of the one-hour standard of 120 ppb. The number of days when the one-hour average NAAQS of 120 ppb was exceeded at each site is shown in Table 4-4. At the five sites with complete data records between 1995 and 1999, the highest number of the exceedances was observed on Fridays, with 38 out of 167 exceedances. Thursdays and Saturdays have the next highest numbers of exceedances. Including other sites with high numbers of exceedances over shorter data records did not change the conclusion on Friday exceedances. Sundays and Mondays were the days with the fewest exceedances. The statistical significance of the high-low pairs was tested using bootstrap resampling. The differences in the number of exceedance days were found to be significant at the 5% level for all sites with two exceptions. Site 1308900024 had a difference that was

Table 4-3. Statistics of 90th percentile daily maximum one-hour average ozone concentrations (ppm) by day of the week in Atlanta, GA.

Site	Maximum (ppm)	Day of maximum	Minimum (ppm)	Day of minimum	Maximum minus minimum (ppm)	Statistical significance of the difference
1308900024	0.102	Friday/ Saturday	0.092	Tuesday/ Wednesday	0.01	10%
1308930014	0.099	Friday	0.086	Thursday	0.013	10%
1312100554	0.109	Saturday	0.1	Monday	0.009	10%
1313500024	0.098	Friday	0.084	Monday	0.014	5%
1324700014	0.113	Friday	0.097	Monday	0.016	5%

Table 4-4. The number of days on which the one-hour average ozone NAAQS was exceeded in Atlanta, GA.

	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday	Total
Sites in operation from 1995 to 1999								
1308900024	4	3	5	5	8	5	3	**33**
1308930014	2	1	1	6	6	3	1	**20**
1312100554	3	7	6	7	10	9	8	**50**
1313500024	2	3	0	4	1	2	2	**14**
1324700014	5	7	6	7	13	8	4	**50**
Subtotal	**16**	**21**	**18**	**29**	**38**	**27**	**18**	**167**
Other sites with 10 or more exceedances (years in operation)								
1309700044 (3)	2	3	2	2	1	2	0	**12**
1311300014 (2)	0	2	4	6	4	1	0	**17**
1315100024 (1)	1	3	1	3	2	1	1	**12**
Total (all sites with 10 or more exceedances)	**19**	**29**	**25**	**40**	**45**	**31**	**19**	**208**

significant at the 10% level. Site 1313500024 averaged less than three exceedances per year and the day-of-the-week difference in exceedances was insignificant. These observations were consistent with the previous analyses of the mean, the median, and the 90th percentile of the maximum O_3 concentrations.

Summary. From the above analysis, we can summarize the weekly cycle of O_3 concentrations in the Atlanta area as follows:

(1) On weekdays, morning O_3 concentrations (e.g., 7 a.m.) were low, possibly due to titration of O_3 by NO emitted by traffic. On weekends, morning O_3 tended to be higher, consistent with reduced titration.

(2) O_3 concentrations increased over the work week, and decreased over the weekend. Hour-by-hour comparisons indicate that Mondays tended to have the lowest concentrations, Fridays the highest.

(3) Mean daily maximum one-hour average O_3 concentrations were highest most frequently on Fridays. Low mean O_3 concentrations were observed on Mondays.

(4) Median and 90th percentile concentrations did not show as clear a day-of-the-week trend as the mean statistic. Higher concentrations were observed on Fridays and Saturdays, and lower concentrations primarily on Mondays. Lower median concentrations were recorded on Sundays and Tuesdays at more than one monitor.

(5) Sites with the most exceedances showed the highest number of exceedances on Fridays. Thursdays and Saturdays showed the next highest number of exceedances. The lowest numbers of exceedances were observed on Sundays and Mondays.

4.1.2 Chicago

24-hour profiles of each day of the week. An example of the diurnal profiles by day-of-the-week in Chicago is presented in Figure 4-2 for Site 1703110034 (see Appendix B1 for other sites). Each profile represents an average over the five-year monitoring period for the specific day of the week at each site. At all 18 sites, weekend O_3 concentrations were higher than weekday values at virtually every hour. The

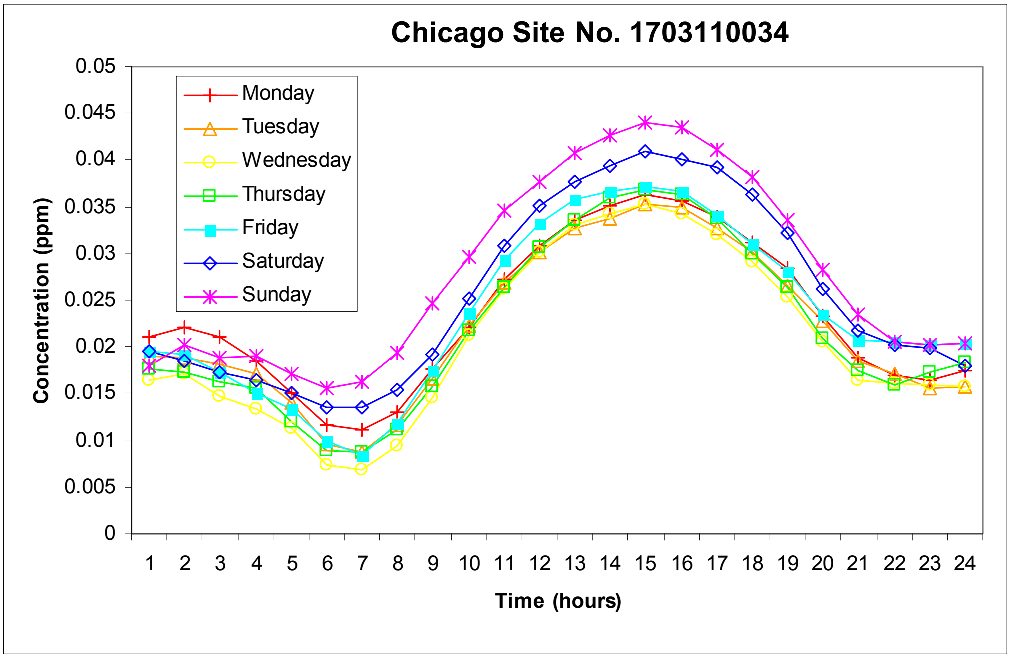


Figure 4-2. Average daily ozone profiles at Site 1703110034 in Chicago, IL from 1995 to 1999.

afternoon concentrations on Sundays were the highest. At Site 1703100724, peak afternoon concentrations on Saturdays and Sundays were similar. O_3 concentrations in the morning (e.g., 7 a.m.) were highest on Sundays, and second-highest on Saturdays. Of the weekdays, morning O_3 concentrations tended to be highest on Mondays and lowest on Wednesdays at a majority of sites. The high "initial condition" on weekends was probably a result of reduced NO titration. The time of NO-O_3 cross-over was accelerated by one to two hours on Saturdays and sometimes even more on Sundays relative to weekdays at a majority of sites that monitor both pollutants. The rate of O_3 increase on weekday mornings was quite similar to that on weekends. The earlier start for O_3 accumulation with no significant change in the rate of increase resulted in higher O_3 concentrations throughout the morning and afternoon on the weekend days. At more than half the sites, the afternoon average O_3 concentrations were lowest on Tuesdays or Wednesdays.

Maximum one-hour average concentration. The maximum one-hour average concentration was determined for each 24-hour period, and grouped according to the day of the week. Appendix B2 shows the mean daily maximum values for each day of the week at each site. The error bars denote the standard deviation associated with the maximum observations. The results are summarized in Table 4-5. The difference ranged from 5 ppb to 11 ppb between the day with the highest O_3 concentration and the day with the lowest. At all 18 sites, the mean value of the daily maximum concentration was highest on Sundays. The minimum values of the daily maximum were observed on Tuesdays or Wednesdays. The observations with the mean values of the maximum one-hour average concentrations were consistent with those for the average diurnal profiles, showing a weekend increase in O_3 relative to weekdays.

The statistical significance of the day-of-the-week difference was tested using bootstrap sampling. Albeit small, all of these differences were found to be statistically significant at the 5% level. In fact, many of the sites showed day-of-the-week differences that were significant at the 1% level. Five-year data records increased the statistical confidence of the differences in mean values, since the standard errors associated with the mean values scale as $n^{-1/2}$.

Table 4-5. Statistics of mean daily maximum one-hour average ozone concentrations (ppm) by day of the week in Chicago, IL.

Site ID	Maximum (ppm)	Day of maximum	Minimum (ppm)	Day of minimum	Maximum minus minimum (ppm)	Statistical significance of the difference
1703100014	0.0508	Sunday	0.0419	Wednesday	0.0088	5%
1703100324	0.0552	Sunday	0.0483	Wednesday	0.0069	5%
1703100504	0.0499	Sunday	0.0424	Tuesday	0.0075	5%
1703100634	0.0432	Sunday	0.0326	Tuesday	0.0106	5%
1703100644	0.0502	Sunday	0.0423	Wednesday	0.0079	5%
1703100724	0.0553	Sunday	0.0499	Wednesday	0.0054	5%
1703110034	0.0487	Sunday	0.0396	Wednesday	0.0090	5%
1703116014	0.0491	Sunday	0.0437	Tuesday	0.0053	5%
1703140024	0.0482	Sunday	0.0391	Tuesday	0.0091	5%
1703140064	0.0517	Sunday	0.0434	Tuesday	0.0083	5%
1703170024	0.0559	Sunday	0.0496	Tuesday	0.0063	5%
1703180034	0.0464	Sunday	0.0390	Wednesday	0.0074	5%
1704360014	0.0504	Sunday	0.0424	Wednesday	0.0080	5%
1709700014	0.0500	Sunday	0.0437	Wednesday	0.0063	5%
1709710024	0.0530	Sunday	0.0471	Tuesday	0.0059	5%
1709710074	0.0549	Sunday	0.0500	Tuesday	0.0049	5%
1709730014	0.0495	Sunday	0.0433	Tuesday	0.0062	5%
1719710114	0.0547	Sunday	0.0509	Tuesday	0.0038	5%

We analyzed the median values of the daily maximum concentrations by day of the week. The data are summarized in Table 4-6. High median concentrations were observed on Sundays at all sites. However, a less consistent trend was observed for days with low median concentrations. Low median concentrations were observed mostly on Tuesdays, Wednesdays, and Thursdays, but occasionally on Mondays and Fridays. Since most of the day-of-the-week differences in the median values were statistically significant, the results were consistent with the conclusions drawn from the analysis of the mean daily maximum value, that weekend, especially Sunday, concentrations were in general higher than the mid-week concentrations.

The 90th percentile of the daily maximum one-hour average O_3 concentrations (Table 4-7) showed a slightly different trend from those of the median and mean values. O_3 still seemed highest during the weekend. However, at three quarters of the sites (14 sites), the 90th percentile values of the daily maximum concentrations were highest on Saturdays rather than on Sundays (3 sites). At one site, the 90th percentile concentrations on Sundays and Saturdays were the same. (Sundays typically showed higher median and mean concentrations.) High 90th percentile concentrations were also observed on Fridays at two sites.

Lower 90th percentile values were observed during the early work week, about equally frequently on Mondays and Tuesdays (about 10 sites) and on Wednesdays at five sites. Note that the high O_3 days and the low O_3 days were mutually exclusive, since the maximum values occurred on Fridays, Saturdays, or Sundays and the minimum values occurred on Mondays through Wednesdays. These observations were also consistent with higher weekend O_3 concentrations.

The difference between the highest and lowest 90th percentile concentrations can be as high as 19 ppb. Except for Site 1709710014, the day-of-the-week difference between the extreme values was significant at the 5% or 10% level.

Exceedances of the one-hour standard of 120 ppb. The number of days when the one-hour average NAAQS was exceeded is listed in Table 4-8. The data showed that the Chicago metropolitan area exceeded the NAAQS on average five times a year during 1995–99. Therefore, the statistical significance of the exceedance numbers was weak. The majority of the exceedances were observed on Sundays, consistent with the

Table 4-6. Statistics of median daily maximum one-hour average ozone concentrations (ppm) by day of the week in Chicago, IL.

Site ID	Maximum (ppm)	Day of maximum	Minimum (ppm)	Day of minimum	Maximum minus minimum (ppm)	Statistical significance of the difference
1703100014	0.0480	Sunday	0.0410	Wednesday	0.0070	5%
1703100324	0.0530	Sunday	0.0460	Thursday	0.0070	5%
1703100504	0.0460	Sunday	0.0410	Tuesday/ Wednesday/ Thursday	0.0050	10% 5% 5%
1703100634	0.0400	Sunday	0.0290	Thursday	0.0110	5%
1703100644	0.0470	Sunday	0.0400	Wednesday	0.0070	5%
1703100724	0.0520	Sunday	0.0470	Tuesday/ Thursday	0.0050	5% 5%
1703110034	0.0470	Sunday	0.0380	Tuesday	0.0090	5%
1703116014	0.0480	Sunday	0.0420	Thursday	0.0060	5%
1703140024	0.0450	Sunday	0.0360	Wednesday	0.0090	5%
1703140064	0.0470	Sunday	0.0410	Tuesday/ Thursday	0.0060	5% 5%
1703170024	0.0520	Sunday	0.0470	Monday/ Tuesday/ Thursday/ Friday	0.0050	5% 5% 5% 5%
1703180034	0.0450	Sunday	0.0370	Tuesday/ Wednesday	0.0080	5% 5%
1704360014	0.0500	Sunday	0.0400	Thursday	0.0100	5%
1709700014	0.0480	Sunday	0.0410	Tuesday	0.0070	5%
1709710024	0.0490	Sunday	0.0450	Monday/ Tuesday/ Thursday/ Friday	0.0040	10% 10% 10% 10%
1709710074	0.0510	Sunday	0.0470	Monday/ Tuesday	0.0040	5% 10%
1709730014	0.0480	Sunday	0.0400	Wednesday	0.0080	5%
1709710114	0.0540	Sunday	0.0510	Tuesday/ Wednesday/ Thursday	0.0030	10% 10% insignificant

Table 4-7. Statistics of 90th percentile daily maximum one-hour average ozone concentrations (ppm) by day of the week in Chicago, IL.

Site ID	Maximum (ppm)	Day of maximum	Minimum (ppm)	Day of minimum	Maximum minus minimum (ppm)	Statistical significance of the difference
1703100014	0.0810	Saturday	0.0650	Monday/ Wednesday	0.0160	5%
1703100324	0.0850	Saturday	0.0710	Monday/ Tuesday/ Wednesday	0.0140	5%
1703100504	0.0810	Saturday	0.0630	Monday/ Tuesday	0.0180	5%
1703100634	0.0680	Saturday	0.0490	Monday	0.0190	5%
1703100644	0.0780	Saturday	0.0640	Monday/ Wednesday	0.0140	5%
1703100724	0.0840	Saturday	0.0700	Wednesday	0.0140	5%
1703110034	0.0740	Saturday/ Sunday	0.0610	Monday/ Tuesday	0.0130	5%
1703116014	0.0750	Friday	0.0650	Tuesday	0.0100	5%
1703140024	0.0740	Saturday	0.0590	Tuesday	0.0150	5%
1703140064	0.0790	Sunday	0.0650	Monday	0.0140	5%
1703170024	0.0840	Saturday	0.0700	Wednesday	0.0140	5%
1703180034	0.0730	Saturday	0.0580	Tuesday	0.0150	5%
1704360014	0.0720	Saturday	0.0600	Monday/ Tuesday	0.0120	5%
1709700014	0.0720	Saturday	0.0640	Monday	0.0080	insignificant
1709710024	0.0850	Saturday	0.0660	Tuesday	0.0190	5%
1709710074	0.0790	Sunday	0.0710	Monday/ Tuesday	0.0080	5%
1709730014	0.0720	Saturday	0.0610	Tuesday	0.0110	5%
1709710114	0.0780	Friday	0.0680	Tuesday	0.0100	5%

Table 4-8. The number of days on which the one-hour ozone NAAQS was exceeded in Chicago, IL.

Site	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday	Total
1703100014	0	0	0	1	0	0	0	1
1703100324	0	0	0	2	0	2	0	4
1703100504	0	0	0	1	0	1	0	2
1703100634	0	0	0	0	0	0	0	0
1703100644	0	0	0	1	0	1	0	2
1703100724	0	0	0	0	0	2	0	2
1703110034	0	0	0	0	0	1	0	1
1703116014	0	0	0	0	0	0	0	0
1703140024	0	0	0	0	0	0	0	0
1703140064	0	0	1	1	0	1	0	3
1703170024	0	0	0	1	0	2	1	4
1703180034	0	0	0	0	0	1	0	1
1704360014	0	0	0	0	0	0	0	0
1709700014	0	0	0	0	0	0	0	0
1709710024	0	1	0	0	0	0	1	2
1709710074	0	1	0	1	0	1	1	4
1709730014	0	0	0	0	0	0	0	0
1719710114	0	0	0	0	0	0	0	0
Total	**0**	**2**	**1**	**8**	**0**	**12**	**3**	**26**

observations drawn from the 90th percentile daily maximum O_3 concentrations. However, the second-highest number of exceedances on Thursdays was not consistent with the analysis so far, and could be a symptom of the lack of statistical power of the exceedance analysis.

Summary. Chicago seemed to exhibit a weekend increase in O_3. The average profile and the mean and median daily maximum one-hour concentrations all showed relatively high O_3 on Sundays. Low mean O_3 occurred on Tuesdays and Wednesdays. Low median concentrations were primarily observed between Tuesdays and Thursdays. The O_3 profiles further showed an increase in morning O_3 on the weekends (possibly due to limited titration by traffic NO_x) as a prelude to the higher concentrations observed in the afternoon. On the other hand, the 90th percentile of the daily maximum O_3 concentrations indicated highest O_3 on Saturdays at a majority of the sites (highest O_3 was observed on Sundays at 3 sites), and lower O_3 early in the work week (Monday through Wednesday). O_3 exceeded the one-hour NAAQS of 120 ppb most frequently on Saturdays between 1995 and 1999, consistent with the observations from the 90th percentile analysis.

4.1.3 Philadelphia

24-hour profiles of each day of the week. The average O_3 profile of each day of the week is shown in Figure 4-3 for Philadelphia area Site 4210101364. Appendix C1 contains plots of the diurnal O_3 concentration profiles. As in Chicago, afternoon O_3 concentrations in Philadelphia were typically higher during weekends than weekdays. The highest concentrations in the average profiles were observed on Saturdays at three sites and Sundays at the remaining site. Minimum afternoon concentrations tended to occur late in the week, e.g., Thursdays or Fridays. The days with higher and lower afternoon concentrations seemed to differ between Chicago and Philadelphia, even though both cities showed an increase in O_3 during the weekend. High afternoon concentrations during weekends were preceded by higher concentrations in the morning. For example, at 7 a.m., O_3 was consistently highest on Sundays, and second-highest on Saturdays. The O_3-NO cross-over time shifted earlier on Saturdays and Sundays by 1.5 and 2.5 hours, respectively, at two sites with co-located measurements of O_3 and NO.

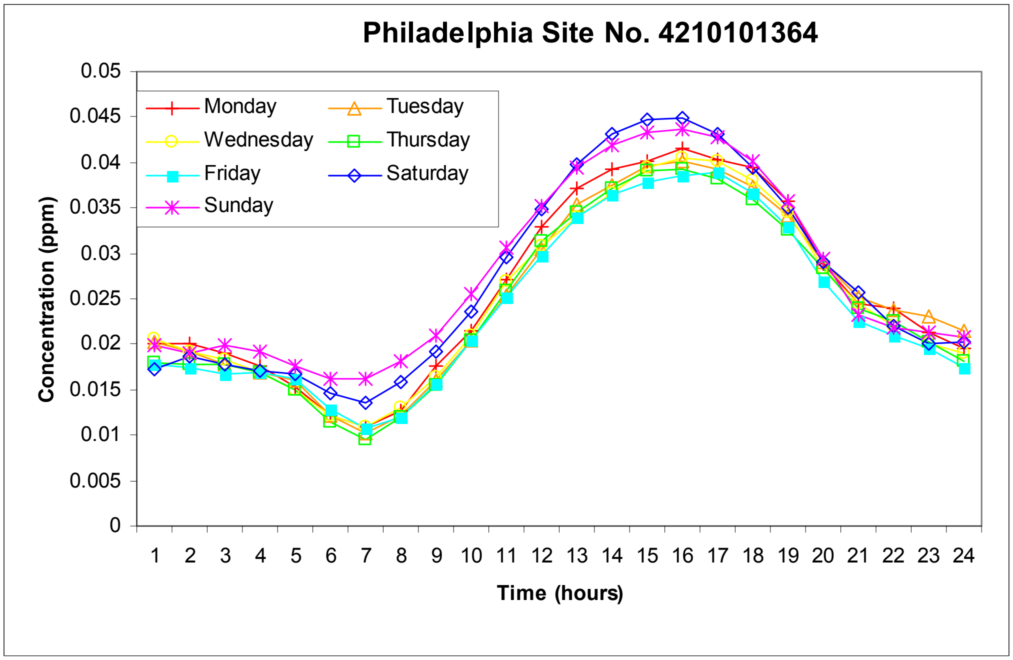


Figure 4-3. Average daily ozone profiles at Site 4210101364 in Philadelphia, PA from 1995 to 1999.

The high initial conditions (morning concentrations) probably contributed to the observed afternoon peak value. Peak concentrations in the afternoon were higher on Saturdays than on Sundays, despite the reverse in morning concentrations, indicating that the rate of O_3 accumulation also varied by the day of the week.

Maximum one-hour average concentrations. The mean daily maximum one-hour average concentrations of each day of the week (Appendix C2) showed a trend that was consistent with the averaged diurnal profiles in terms of high concentration observations. The highest maximum one-hour concentrations were observed on Saturdays, as shown in Table 4-9. The lowest maximum one-hour concentrations were observed on Fridays (3 sites) and Thursdays (1 site). Although the differences between the maximum and the minimum of the mean daily maximum O_3 were small (5 to 7 ppb), they were found to be statistically significant, supported by long data records. As shown in Appendix C2, the coefficients of variation (ratio of the standard deviation to the mean) of the maximum one-hour average O_3 concentrations can be as much as 50%.

The median values of the daily maximum O_3 concentrations, tabulated in Table 4-10, were highest on Saturdays or Sundays. The lowest median concentrations were observed on Fridays. At two sites, the median concentrations on Fridays were the same as those on other days of the work week. The maximum weekly difference in the median values of the daily maximum concentrations were 4 to 8 ppb. These differences were found to be statistically significant at the 5% or 10% level.

As in the cases of Chicago and Atlanta, the day-of-the-week difference in the 90^{th} percentile daily maximum concentrations (10 to 15 ppb) was much amplified relative to the median and the mean values. As shown in Table 4-11, the 90^{th} percentile daily maximum concentrations were highest on Saturdays. At Site 4210100044, Saturday's 90^{th} percentile concentration tied with Monday's, at 80 ppb. The minimum 90^{th} percentile values were observed on Fridays at three out of four sites. All differences between the maximum-minimum pairs were statistically significant. The maximum and minimum were consistent with the weekend O_3 increase concluded from the analysis of the mean and median.

Exceedances of the one-hour standard of 120 ppb. The one-hour O_3 NAAQS was exceeded on average at least twice a year at two out of four sites in the Philadelphia area

Table 4-9. Statistics of mean daily maximum one-hour average ozone concentrations (ppm) by day of the week in Philadelphia, PA.

Site ID	Maximum (ppm)	Day of maximum	Minimum (ppm)	Day of minimum	Maximum minus minimum (ppm)	Statistical significance of the difference
3400700034	0.0588	Saturday	0.0533	Thursday	0.0054	5%
4204500024	0.0630	Saturday	0.0583	Friday	0.0046	5%
4210100044	0.0493	Saturday	0.0421	Friday	0.0072	5%
4210101364	0.0485	Saturday	0.0435	Friday	0.0050	5%

Table 4-10. Statistics of median daily maximum one-hour average ozone concentrations (ppm) by day of the week in Philadelphia, PA.

Site ID	Maximum (ppm)	Day of maximum	Minimum (ppm)	Day of minimum	Maximum minus minimum (ppm)	Statistical significance of the difference
3400700034	0.0550	Saturday	0.0490	Friday	0.0060	5%
4204500024	0.0590	Saturday	0.0550	Friday	0.0040	10%
4210100044	0.0470	Sunday	0.0400	Monday/ Wednesday/ Thursday/ Friday	0.0070	5% 5% 5% 5%
4210101364	0.0480	Sunday	0.0400	Monday/ Tuesday/ Wednesday/ Friday	0.0080	5% 5% 5% 5%

Table 4-11. Statistics of 90th percentile daily maximum one-hour average ozone concentrations (ppm) by day of the week in Philadelphia, PA.

Site ID	Maximum (ppm)	Day of maximum	Minimum (ppm)	Day of minimum	Maximum minus minimum (ppm)	Statistical significance of the difference
3400700034	0.0960	Saturday	0.0840	Monday/ Tuesday	0.0120	5% 5%
4204500024	0.1010	Saturday	0.0860	Friday	0.0150	5%
4210100044	0.0800	Monday/ Saturday	0.0700	Tuesday/ Wednesday/ Thursday/ Friday	0.0100	Mo-Fr 10% Sa-Tu 10% Sa-Fr 10% Other pairs 5%
4210101364	0.0800	Saturday	0.0690	Friday	0.0110	5%

with complete data during the period of 1995 – 1999. As shown in Table 4-12, the highest number of exceedances occurred on Mondays and Saturdays, consistent with the high 90th percentile values on Mondays and Saturdays at most sites. However, high Monday concentrations were not observed in the analyses of the mean and median daily maximum one-hour concentrations. No exceedance was observed on Wednesdays or Thursdays.

Summary. Philadelphia showed a weekend increase in O_3.

- Averaged profiles showed maximum afternoon concentrations on Saturdays and Sundays, possibly resulting from increased initial conditions (due to less NO titration), and low concentrations late during the week (Wednesday, Thursday, or Friday).
- Mean values of daily maximum one-hour average concentrations showed higher values on Saturdays. Mean values were low primarily on Fridays.
- Median values were high on Saturdays and Sundays, and low on Fridays. Low median concentrations on other weekdays tied with Fridays at half the sites.
- 90th percentile values were highest on Saturdays (and Mondays at one site) and lowest on weekdays.
- Exceedances were observed primarily on Mondays and Saturdays.

4.2 Maximum Eight-Hour Average Ozone Concentrations

The weekly behavior of O_3 was quite consistent between different metrics (mean, median, 90th percentile) in the analyses of the daily maximum one-hour average concentrations discussed in Section 4.1. In this section, a streamlined analysis is performed for the daily maximum 8-hour average concentrations by considering the mean values for each day of the week.

Table 4-12. The number of days on which the one-hour ozone NAAQS was exceeded in Philadelphia, PA.

Site ID	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday	Total
3400700034	2	2	0	0	2	4	2	**12**
4204500024	5	2	0	0	1	2	2	**12**
4210100044	0	1	0	0	0	1	0	**2**
4210101364	1	0	0	0	0	1	0	**2**
Total	**8**	**5**	**0**	**0**	**3**	**8**	**4**	**28**

4.2.1 Atlanta

The maximum eight-hour average concentrations in Atlanta, GA are characterized by the mean and standard deviation presented in Appendix A3. On average, the maximum 8-hour average O_3 concentration was about 7 to 10 ppb below the one-hour daily maximum O_3. The weekly trends in the one-hour maximum values and profiles were slightly different from those observed in the 8-hour maximum values. Table 4-13 shows some of the key statistics of the 8-hour average O_3 concentrations.

The weekly difference in the 8-hour O_3 concentrations, 4 or 5 ppb, was smaller than the one-hour difference at all sites. The statistically significant weekly differences at five sites with complete data records between 1995 and 1999 split between having Saturday and Friday maximum concentrations. Note that in Table 4-1, all sites showed maximum one-hour concentrations on Fridays. Monday was consistently the day with the lowest 8-hour O_3 concentrations, an observation consistent with the one-hour average concentrations. The maximum 8-hour average concentration increased throughout the work week, as did the maximum one-hour concentration, but the recovery to lower O_3 values seemed to occur primarily on Sundays rather than over the weekend as the mean value of the maximum one-hour average concentration did.

4.2.2 Chicago

In Chicago, the daily maximum one-hour concentrations and 8-hour concentrations differed by 4 ppb to 7 ppb. The percentage difference ranged from 8 to 16% at most Chicago sites. Higher percentage differences between one-hour and 8-hour O_3 were observed during mid to late work week (compared to weekends and Mondays) when the O_3 concentrations tended to be lower. For Site 1703100634, the difference between one-hour and 8-hour average concentrations was as much as 20% on weekdays. We included in Appendix B3 the mean value of the daily maximum 8-hour concentrations at each of the sites, grouped by the day of the week. At a few sites, the differences between one-hour and 8-hour averages seemed smallest on Mondays.

The mean values for the 8-hour average O_3 concentrations on different days of the week are summarized in Table 4-14, which may be compared to Table 4-5, the

Table 4-13. Statistics of mean daily maximum 8-hour average ozone concentrations (ppm) by day of the week in Atlanta, GA.

Site ID	Maximum (ppm)	Day of maximum	Minimum (ppm)	Day of minimum	Maximum minus minimum (ppm)	Statistical significance of the difference
1308900024	0.0554	Saturday	0.0508	Monday	0.0047	5%
1308930014	0.0558	Friday	0.0511	Monday	0.0047	5%
1312100554	0.0601	Saturday	0.0560	Monday	0.0041	10%
1313500024	0.0571	Saturday	0.0521	Monday	0.0050	5%
1324700014	0.0608	Friday	0.0569	Monday	0.0039	10%

Table 4-14. Statistics of mean daily maximum 8-hour average ozone concentrations (ppm) by day of the week in Chicago, IL.

Site ID	Maximum (ppm)	Day of maximum	Minimum (ppm)	Day of minimum	Maximum minus minimum (ppm)	Statistical significance of the difference
1703100014	0.0442	Sunday	0.0360	Wednesday	0.0082	5%
1703100324	0.0492	Sunday	0.0429	Wednesday	0.0063	5%
1703100504	0.0430	Sunday	0.0359	Tuesday	0.0071	5%
1703100634	0.0366	Sunday	0.0255	Wednesday	0.0111	5%
1703100644	0.0441	Sunday	0.0370	Wednesday	0.0072	5%
1703100724	0.0487	Sunday	0.0442	Wednesday	0.0045	5%
1703110034	0.0419	Sunday	0.0341	Wednesday	0.0078	5%
1703116014	0.0428	Sunday	0.0379	Tuesday	0.0049	5%
1703140024	0.0409	Sunday	0.0328	Tuesday	0.0082	5%
1703140064	0.0458	Sunday	0.0374	Tuesday	0.0085	5%
1703170024	0.0506	Sunday	0.0441	Friday	0.0065	5%
1703180034	0.0399	Sunday	0.0330	Tuesday	0.0069	5%
1704360014	0.0440	Sunday	0.0358	Wednesday	0.0082	5%
1709700014	0.0447	Sunday	0.0380	Wednesday	0.0067	5%
1709710024	0.0483	Sunday	0.0422	Tuesday	0.0061	5%
1709710074	0.0505	Sunday	0.0453	Wednesday	0.0052	5%
1709730014	0.0446	Sunday	0.0384	Wednesday	0.0063	5%
1719710114	0.0493	Sunday	0.0462	Tuesday	0.0031	5%

corresponding table for the maximum one-hour concentration results. On average, the difference in the one-hour concentrations was slightly higher than the difference in the 8-hour concentrations. At individual sites, the difference between the highest and lowest 8-hour concentrations may be higher or lower than the corresponding observation in the one-hour concentrations.

Maximum 8-hour O_3 concentrations occurred on Sundays while minimum concentrations occurred primarily in the middle of the week. All weekly differences were statistically significant. On average, the differences in weekend 8-hour maximum O_3 and weekday 8-hour maximum O_3 concentrations ranged from 2 to 9 ppb. The day-of-the-week behavior of the 8-hour O_3 concentrations was quite similar to that of the maximum one-hour average O_3 concentrations.

4.2.3 Philadelphia

The day-of-the-week behavior of the 8-hour average maximum O_3 value seemed to be similar to the one-hour average concentrations. The mean and standard deviation of the 8-hour concentrations are listed in Appendix C3 for each day of the week. The highest means of the 8-hour O_3 concentrations were observed on Saturdays (and Sundays at one site), while the lowest 8-hour O_3 concentrations were observed on Fridays. Comparing Table 4-15 and Table 4-9, the weekly difference in the maximum values of 8-hour concentrations was slightly lower than that in the one-hour concentration at each monitoring site. The differences between the maximum and minimum 8-hour concentrations were statistically significant at all sites.

4.3 PM_{10} Concentration Results

4.3.1 Atlanta

Average diurnal profiles of PM_{10} calculated from the single station in Atlanta (Site 1312100488) are shown in Figure 4-4. Each profile was an average of about 50 days since the station was operated for only about a year between 1998 and 1999. The profiles were very jagged, possibly due to a short data record. This site is located near the Georgia Institute of Technology and classified as an urban/center city site. The

Table 4-15. Statistics of mean daily maximum 8-hour average ozone concentrations (ppm) by day of the week in Philadelphia, PA.

Site ID	Maximum (ppm)	Day of maximum	Minimum (ppm)	Day of minimum	Maximum minus minimum (ppm)	Statistical significance of the difference
3400700034	0.0511	Saturday	0.0460	Friday	0.0051	5%
4204500024	0.0553	Saturday	0.0515	Friday	0.0038	5%
4210100044	0.0419	Sunday	0.0362	Friday	0.0057	5%
4210101364	0.0415	Saturday	0.0379	Friday	0.0036	5%

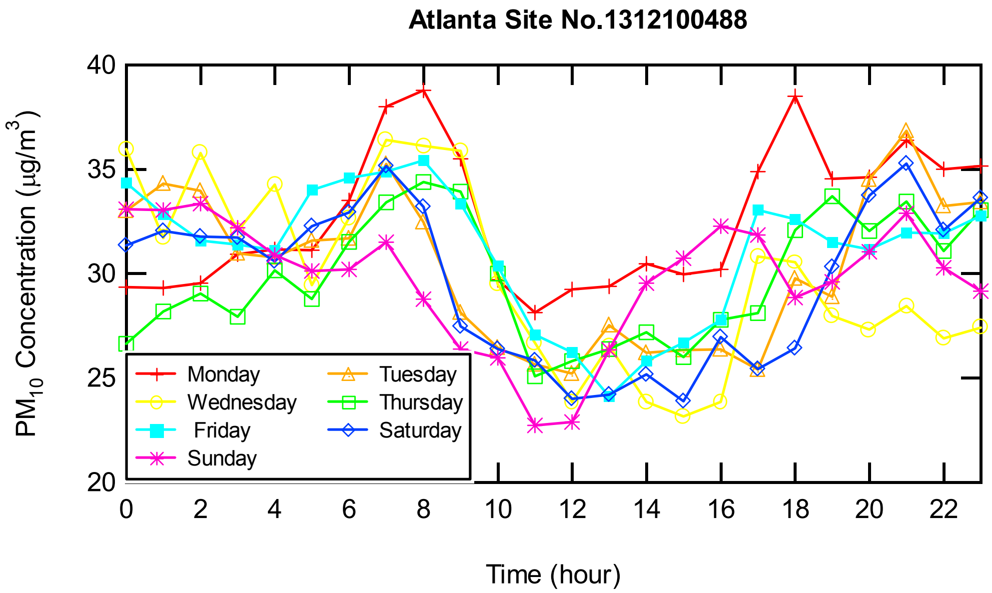


Figure 4-4. Average daily PM_{10} profiles at Site 1312100488 in Atlanta, GA from 1998 to 1999

proximity of this site to emission sources may also explain the variability in the concentration data. No conclusions could be reached regarding the day-of-the-week behavior.

Twenty-four hour average concentrations of PM_{10} are presented in Figure 4-5 for each day of the week. PM_{10} concentrations were highest on Tuesdays and lowest on Sundays. Despite large standard deviations (coefficients of variation were almost 50%), the Tuesday-Sunday difference of 3.7 μg m^{-3} was statistically significant at the 10% level.

Summary. 24-hour average PM_{10} concentrations in Atlanta showed weak evidence for high concentrations on Tuesdays and low concentrations on Sundays. Diurnal profiles were jagged and no conclusion could be reached regarding the changes in diurnal profiles of PM_{10} from weekdays to weekends.

4.3.2 Chicago

The averaged daily PM_{10} profiles are collected in Appendix B4. There are five sites for PM_{10}, fewer than for O_3, with relatively shorter data records. A few sites might have data capture problems (e.g., Site 1808900228, 1998) or might be affected by local sources (e.g., readings of over 1000 μg/m^3 were recorded at Site 1812700238 in 1996). Therefore, smooth profiles like those for O_3 were not observed in the case of PM_{10} temporal profiles. Despite the "jaggedness" of these profiles, Sundays' and Saturdays' profiles were consistently below those of weekdays. Of the weekdays, Mondays' profiles were typically lower compared to those of the other days. An example is shown in Figure 4-6.

Clearer trends were observed when we analyzed 24-hour average PM_{10} concentrations (neglecting 24-hour concentrations above 200 μg/m^3). These results are shown in Table 4-16. Lowest PM_{10} concentrations were observed on Sundays at all 5 sites. The highest concentrations were observed on Fridays at 3 sites and Tuesdays at 2 sites. The maximum differences were statistically significant at the 5% level, as shown in Table 4-16.

Summary. PM_{10} in Chicago seemed to exhibit a weekly cycle where the concentrations were highest on weekdays (Fridays and Tuesdays) and lowest on

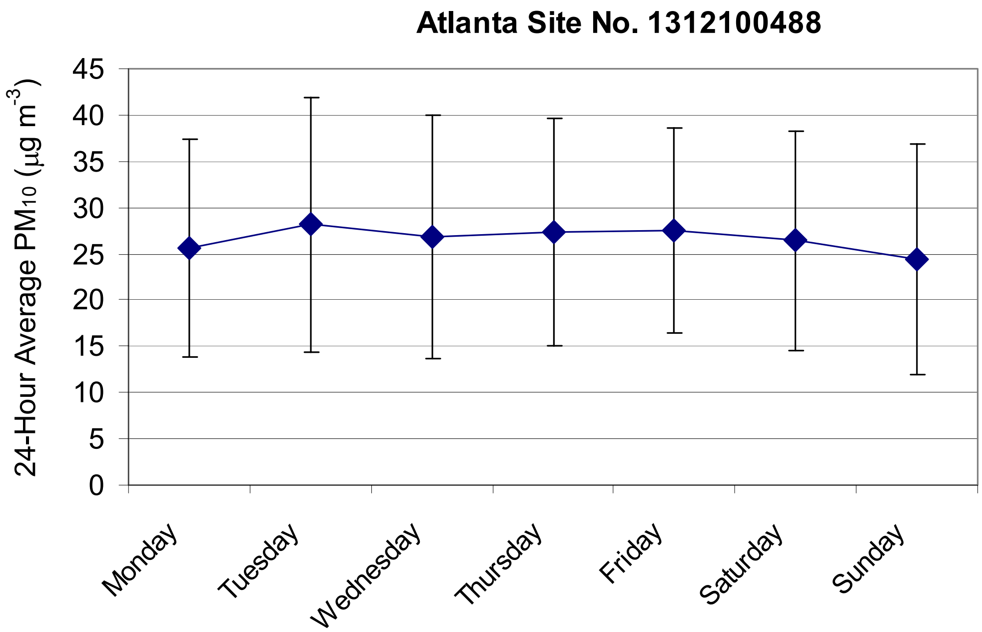


Figure 4-5. Mean 24-hour average PM_{10} concentrations by day of the week at Site 1312100488 in Atlanta, GA. (Error bars represent the standard deviations in the 24-hour average PM_{10} data.)

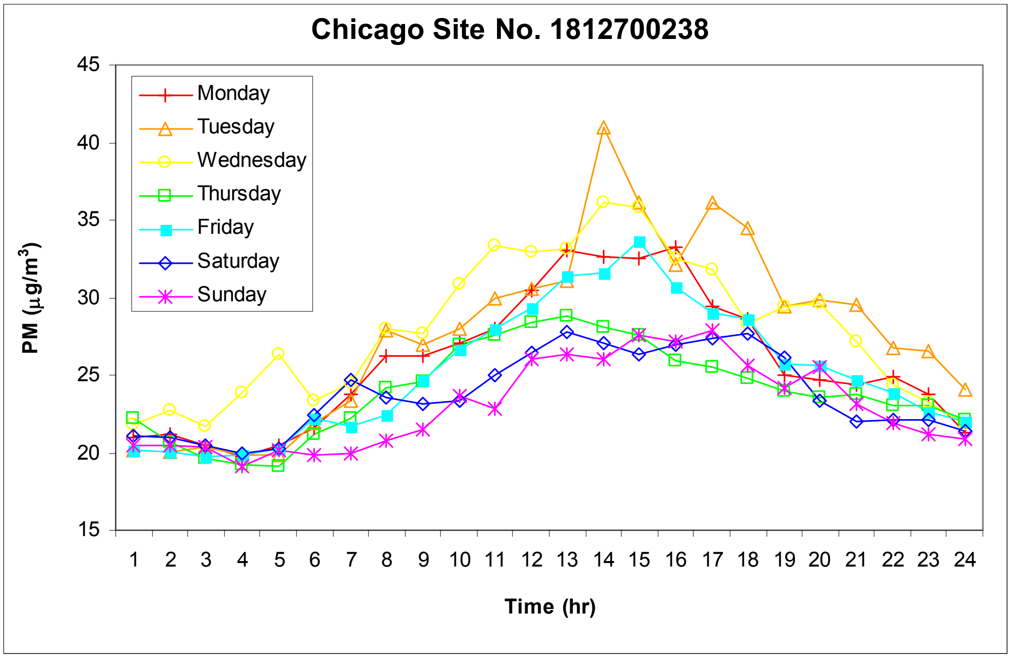


Figure 4-6. Average daily PM_{10} profiles at Site 1812700238 in Chicago, IL from 1995 to 1999.

Table 4-16. Statistics of mean 24-hour average PM_{10} concentrations ($\mu g/m^3$) by day of the week in Chicago, IL.

Site ID	Maximum ($\mu g/m^3$)	Day of maximum	Minimum ($\mu g/m^3$)	Day of minimum	Maximum minus minimum ($\mu g/m^3$)	Statistical significance of the difference
1703100598	30.9	Friday	26.8	Sunday	4.1	5%
1703110168	40.0	Friday	28.3	Sunday	11.7	5%
1703120018	27.6	Friday	24.2	Sunday	3.4	5%
1808900228	36.5	Tuesday	30.6	Sunday	5.9	5%
1812700238	26.9	Tuesday	23.7	Sunday	3.3	5%

weekends. Hourly profiles tended to be jagged so the differences in the one-hour average PM_{10} temporal distributions were not elucidated.

4.3.3 Philadelphia

Compared to the other two cities, the diurnal profiles of PM_{10} in Philadelphia show much clearer day-of-the-week behavior. Figure 4-7 shows the average diurnal profiles at both Philadelphia area sites, generated from four-year data records. On weekdays, PM_{10} showed the characteristic morning rush hour peak of a primary pollutant emitted by traffic. Weekend PM_{10} concentrations were lower throughout most of the day, especially between 5 a.m. and 8 a.m. Highest concentrations were observed at night rather than during the morning traffic hours.

The 24-hour average PM_{10} concentrations were fairly similar during the work week at both sites. Maximum concentrations were observed on Wednesdays and Thursdays, with the second highest concentration on Tuesdays at both sites. Lowest mean 24-hour average concentrations occurred on Sundays, second lowest on Saturdays. As shown in Figure 4-8, the 24-hour average PM_{10} concentrations were highly variable, with standard deviations sometimes exceeding 50% of the mean values. The difference between the maximum and minimum were 4.1 and 6.4 µg m^{-3} at Site 4201700128 and Site 4204500028, respectively. These differences were significant at the 5% level when tested using bootstrap sampling. In fact, the differences between all weekday-weekend pairs were significant at that level.

Summary. On weekdays, diurnal profiles of PM_{10} showed characteristics of primary emissions. Concentrations on weekends were lower at all hours than concentrations on weekdays, but especially during the morning rush hour. PM_{10} concentrations in Philadelphia were high during the week and low on Sundays, followed by Saturdays. Statistically significant differences were observed between weekend and weekday 24-hour average PM_{10} concentrations.

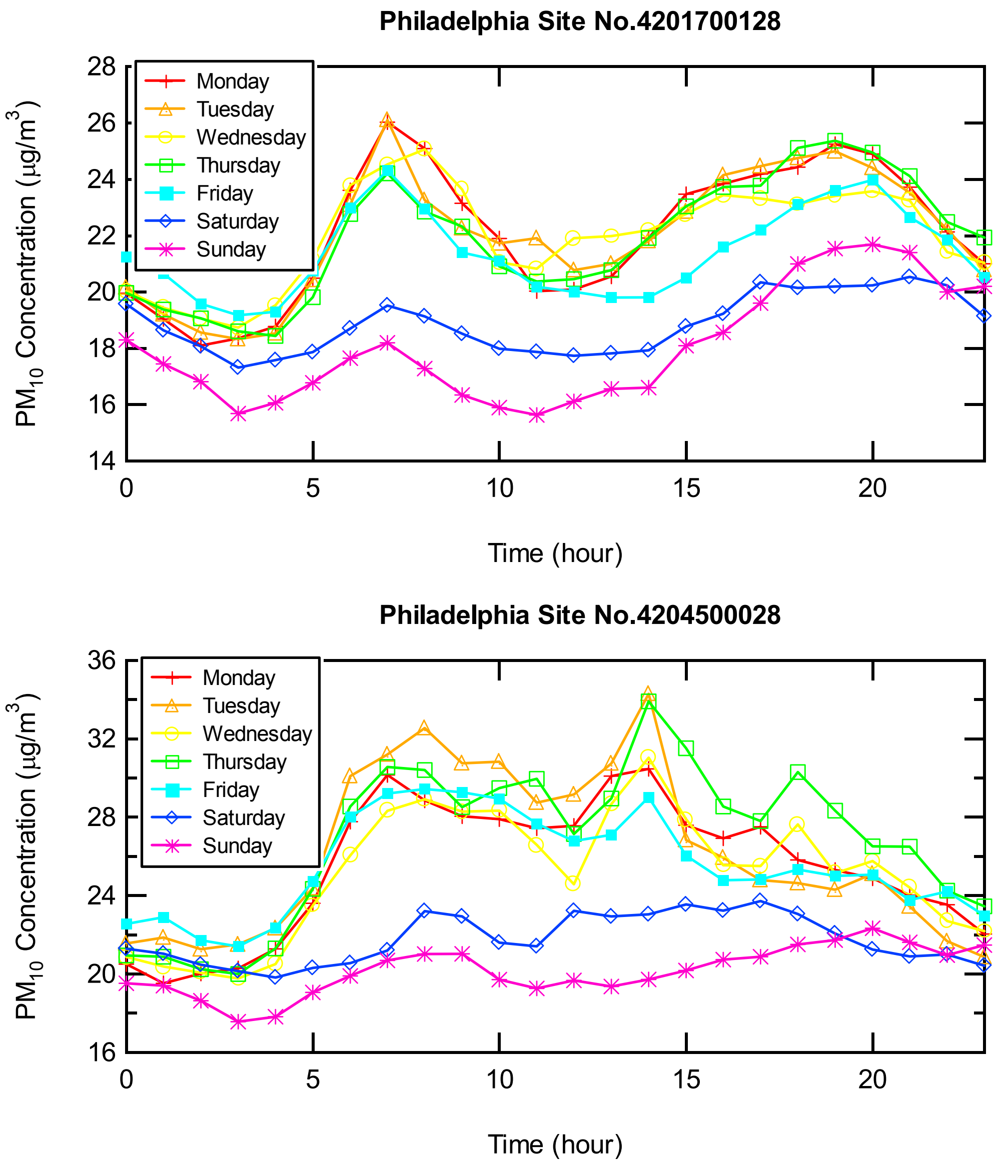
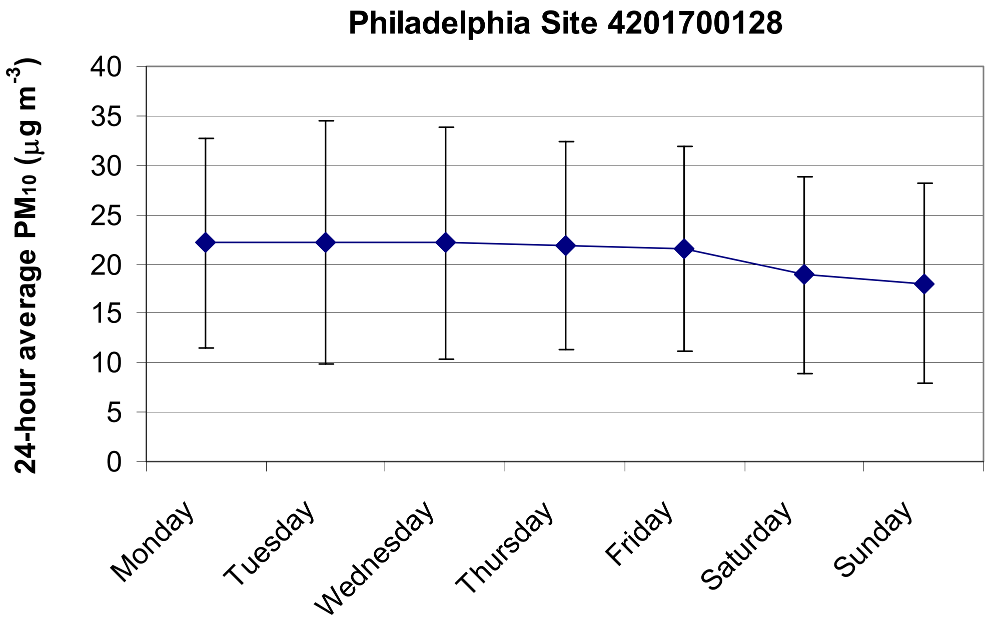


Figure 4-7. Average daily PM_{10} profiles at Sites No. 4201700128 and No. 4204500028 in Philadelphia, PA from 1995 to 1999.



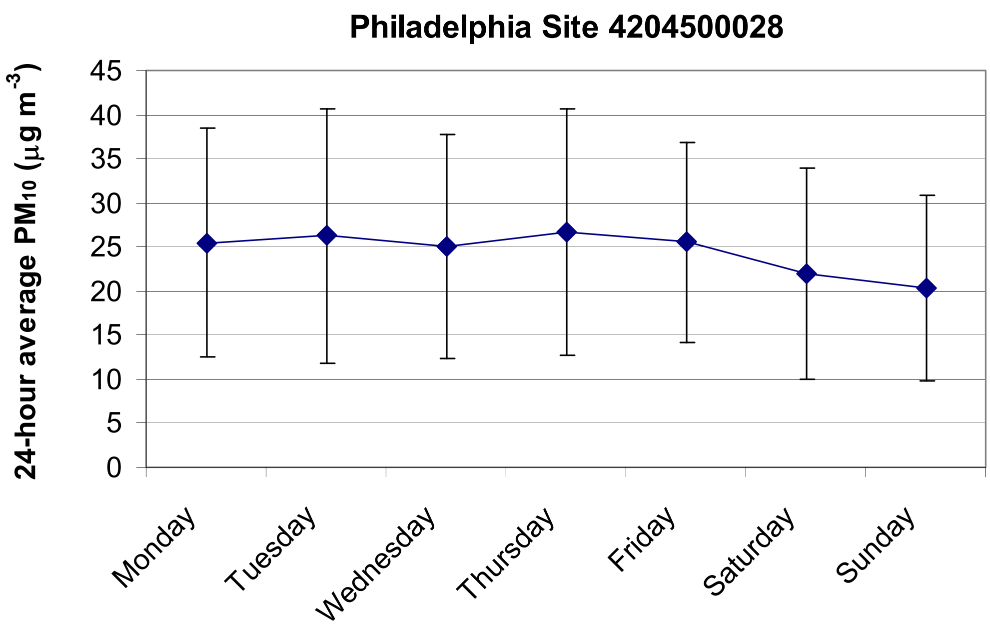


Figure 4-8. Mean 24-hour average PM_{10} concentrations by day of the week at Sites No. 4201700128 and No. 4204500028 in Philadelphia, PA. (Error bars represent the standard deviations in the 24-hour average PM_{10} data.)

4.4 $PM_{2.5}$ Concentration Results

4.4.1 Atlanta

24-hour average $PM_{2.5}$ concentrations were available in 1999 from 8 sites in the Atlanta metropolitan area. The mean of the 24-hour average concentrations was calculated for each day of the week at each site and these statistics are summarized in Table 4-17. Highest concentrations of $PM_{2.5}$ were observed late in the work week (Fridays at 2 sites, Thursdays at 3 sites, and Wednesdays at 1 site) and on Saturdays (2 sites). Lowest concentrations of PM were observed on Sundays (3 sites), Mondays (4 sites), and Tuesdays (1 site). Four out of 8 sites showed statistically significant differences between the maximum and minimum concentrations at the 5% level, and the difference at one other site was significant at the 10% level.

4.4.2 Chicago

Thirteen sites were set up in the Chicago, IL metropolitan area to measure 24-hour average concentrations of $PM_{2.5}$ in 1999. The mean value of $PM_{2.5}$ concentrations was calculated for each day of the week and presented in Table 4-18. These data showed an odd trend. $PM_{2.5}$ seemed high on Saturdays, Wednesdays, and Fridays. Low concentrations were observed on Tuesdays and Thursdays. Although the statistical significance was high as calculated by bootstrap sampling, we caution that the sample size was very small, 7 to 9 samples for each day of the week, due to the monitoring schedule. Since all sites measure $PM_{2.5}$ on the same days in the year, we could not evaluate the representativeness of the sample. The significant differences between different days of the week, e.g., a Saturday and a Tuesday, could have been driven by a larger number of "clean" days in the Tuesday samples compared to the Saturday samples.

4.4.3 Philadelphia

Philadelphia was the only city that measured hourly $PM_{2.5}$ concentrations. There was only one station operational in 1999. The average diurnal profiles for different days of the week are shown in Figure 4-9. $PM_{2.5}$ concentrations showed a small peak in the

Table 4-17. Statistics of mean 24-hour average $PM_{2.5}$ concentrations ($\mu g\ m^{-3}$) by day of the week in Atlanta, GA

Site ID	Maximum ($\mu g\ m^{-3}$)	Day of maximum	Minimum ($\mu g\ m^{-3}$)	Day of minimum	Maximum minus minimum ($\mu g\ m^{-3}$)	Statistical significance of the difference
1306300911	24.0	Thursday	19.0	Sunday	5.1	10%
1306700031	21.7	Thursday	17.5	Tuesday	4.2	insignificant
1308900021	24.0	Thursday	17.7	Monday	6.3	5%
1308920011	23.3	Saturday	17.8	Monday	5.5	5%
1312100321	21.9	Saturday	17.4	Monday	4.6	5%
1312100391	25.7	Wednesday	19.9	Sunday	5.7	5%
1312110011	20.4	Friday	17.8	Sunday	2.6	insignificant
1322300031	18.0	Friday	14.4	Monday	3.7	insignificant

Table 4-18. Statistics of mean 24-hour average $PM_{2.5}$ concentrations (μg m^{-3}) by day of the week in Chicago, IL

Site ID	Maximum (μg m^{-3})	Day of maximum	Minimum (μg m^{-3})	Day of minimum	Maximum minus minimum (μg m^{-3})	Statistical significance of the difference
1703100148	25.6	Saturday	11.7	Tuesday	13.8	5%
1703100228	24.0	Wednesday	12.3	Tuesday	11.7	5%
1703100508	24.9	Wednesday	11.4	Tuesday	13.6	5%
1703100528	26.1	Wednesday	15.0	Tuesday	11.1	5%
1703110168	27.0	Saturday	11.9	Tuesday	15.1	5%
1703117018	26.4	Saturday	12.1	Tuesday	14.3	5%
1703120018	24.1	Saturday	12.4	Thursday	11.6	5%
1703133018	25.0	Saturday	11.4	Tuesday	13.6	5%
1703140068	18.7	Friday	11.3	Thursday	7.4	5%
1703142018	21.0	Wednesday	10.4	Tuesday	10.7	5%
1704340028	19.5	Friday	10.5	Tuesday	8.9	5%
1719710028	20.0	Saturday	9.1	Tuesday	10.8	5%
1719710118	17.2	Wednesday	8.9	Tuesday	8.3	5%

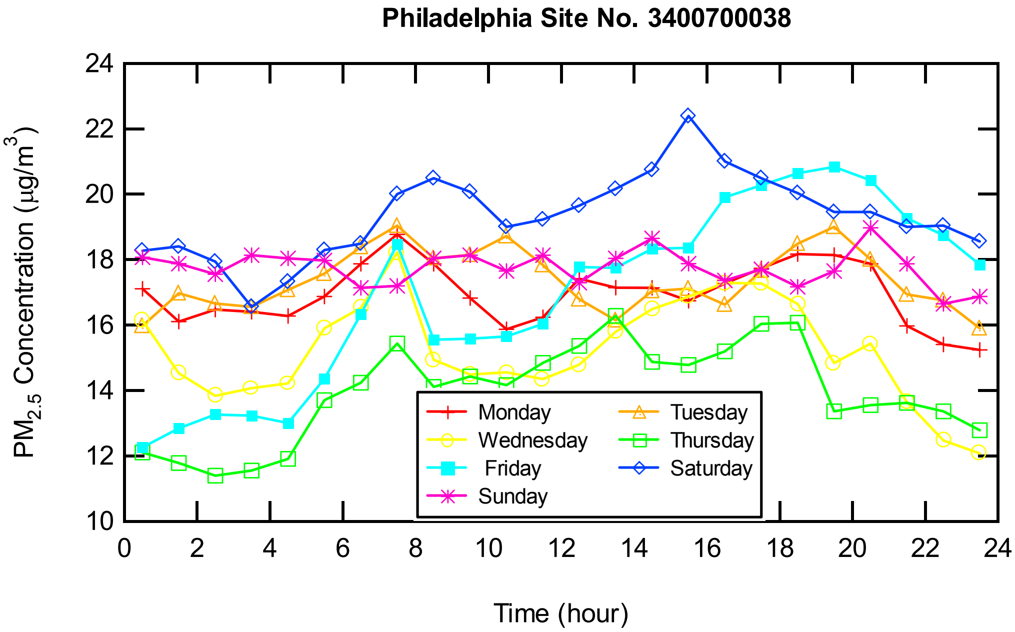


Figure 4-9. Average daily $PM_{2.5}$ profiles at Site 3400700038 in Philadelphia, PA in 1999.

morning on Mondays through Thursdays, but no obvious day-of-the-week behavior was observed.

24-hour average concentrations were calculated for each day of the week. Figure 4-10 displays the mean and standard deviation of the 24-hour average $PM_{2.5}$ concentrations. $PM_{2.5}$ was highest on Saturdays, and second highest on Sundays. Lowest $PM_{2.5}$ concentrations were observed on Thursdays. The difference of about 5 $\mu g\ m^{-3}$ between Thursday and Saturday was significant at the 5% level, as was the difference between Thursdays and Sundays.

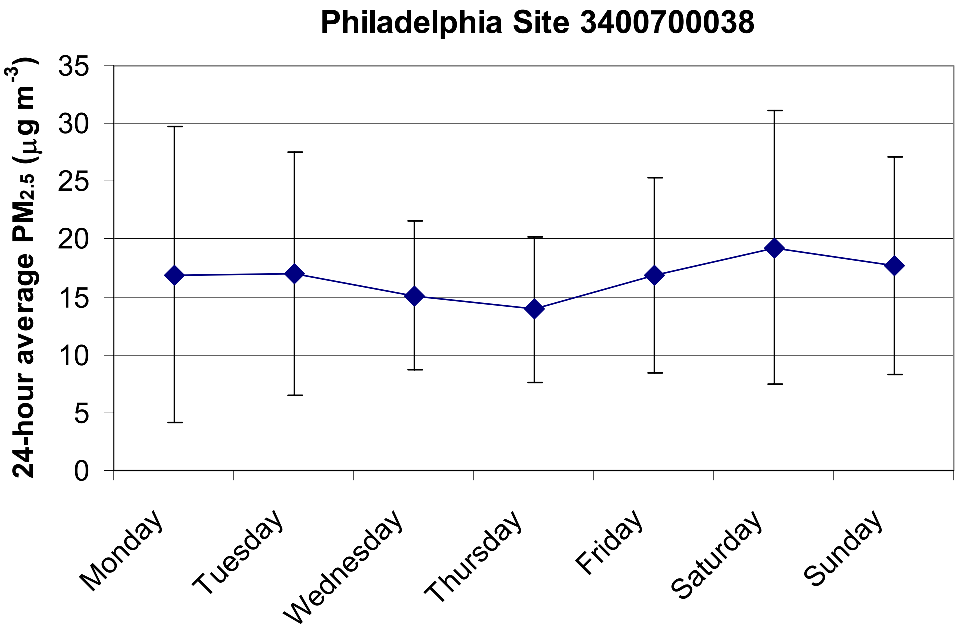


Figure 4-10. Mean 24-hour average $PM_{2.5}$ concentrations by day of the week at Site 3400700038 in Philadelphia, PA. (Error bars represent the standard deviations in the data.)

5. HYPOTHESIS TESTING

The weekly behavior of O_3, a secondary pollutant, is the result of the weekly cycle of anthropogenic emissions. However, the exact causes of the weekly behavior are currently uncertain. The tremendous difference, both in direction and magnitude, of the change from weekdays to weekends, adds to the intrigue of this problem. In this section, we will explore several hypotheses that have been proposed to explain the weekly behavior of O_3. Each subsection contains a description of the hypothesis, the approach taken to test the hypothesis, and results at three locations, Atlanta, Chicago, and Philadelphia. We relied on regression analysis to test the hypothesized relationship between O_3 and other ambient concentrations and other parameters. Details on the regression analysis procedure are provided in Section 3.3.

5.1 Hypothesis 1: Reduction in heavy-duty truck and bus traffic on weekends leads to a greater-than proportionate reduction in NO_x relative to VOC and an increase in the VOC/NO_x ratio. In a VOC-sensitive airshed, the O_3 formation potential will increase with the VOC/NO_x ratio. In a NO_x-sensitive airshed, O_3 formation will decrease with reduced NO_x emissions

Several studies have suggested that the emissions of VOC and NO_x vary significantly from weekdays to weekends (e.g., Levitt and Chock, 1976; Elkus and Wilson, 1977, Hoggan et al., 1989; Altshuler et al., 1995; Dreher and Harley, 1998; Blier and Winer, 1996, 1999). Altshuler et al. (1995) suggested that higher VOC/NO_x ratios observed on weekends compared to weekdays are due to a large decrease in some NO_x emissions (primarily from large diesel-powered trucks and buses, and to a lesser extent from power plants) and a lesser decrease in VOC emissions (some major VOC sources such as biogenic emissions and fuel evaporation remain about constant). If O_3 formation in an area is NO_x sensitive, then the greater VOC/NO_x ratio will lead to lower O_3 formation on weekends than on weekdays. On the other hand, if O_3 formation is sensitive to VOC, then an increase in the VOC/NO_x ratio may lead to an increase in O_3 concentration due to (1) reduced titration of O_3 by NO emissions (that leads to an increase in O_3), and/or (2) an increase in the dynamics of photochemistry because of reduced formation of HNO_3 as a sink for radicals.

We decomposed the hypothesis into two questions: (1) is there a change in the ambient VOC/NO_x ratio from weekdays to weekends? and (2) if there is a change, how does it correlate to O_3 concentrations in the different airsheds? We present the changes in the 24-hour average VOC/NO_x ratio (24-hour average VOC/24-hour average NO_x) and the morning (5 – 8 a.m.) average ratio in Table 5-1 for the three cities of interest. The 24-hour average ratios provided a general indication of the relative availability of the precursors throughout the day, whereas the morning ratios allowed us to focus specifically on traffic related local emissions. Details on the methodology of data processing are provided in Section 3.3. At all three sites, both the 24-hour average and morning average VOC/NO_x ratios increased during weekends from their weekday values. In Atlanta and Chicago, the differences between the weekday and weekend VOC/NO_x ratios were significant at the 5% level; whereas in Philadelphia, the difference was significant at the 10% level.

The increase in VOC/NO_x ratio causes opposite O_3 effects in VOC-sensitive airsheds and in NO_x-sensitive airsheds. From the ratios in the table, it was expected that Chicago may be the most VOC-sensitive location, where NO_x reduction disbenefit may explain the increase in weekend O_3 relative to weekdays. In Philadelphia, high VOC/NO_x ratios would not indicate VOC sensitivity. The observed increases in O_3 during weekends in Philadelphia did not, however, seem to be consistent with NO_x-sensitivity. Atlanta may be NO_x sensitive (modeling studies by Cardelino and Chameides, 1995; Sillman et al., 1997), although the day with the lowest O_3 concentration was Monday rather than Sunday, which had the highest VOC/NO_x ratio.

Another approach to assess the sensitivity of O_3 was to use indicator species (Sillman, 1995, Lu and Chang, 1998). Key indicator species, such as peroxides and nitric acid, were not monitored routinely. In addition, at some sites, available NO_y (total oxidized nitrogen) data were inconsistent with available NO_x data from the same time and location (e.g., NO_y smaller than NO_x data), preventing the calculation of another indicator species $NO_z = NO_y - NO_x$. The indicators NO_y, HCHO/NO_y, and O_3/NO_y (Sillman et al., 1997; Lu and Chang, 1998) were calculated from available (though quite

Table 5-1. VOC/NO_x ratio (ppbC/ppb) on different days of the week in Atlanta, Chicago, and Philadelphia.

	Atlanta, GA	**Chicago, IL**	**Philadelphia, PA**
24-hour average			
Monday	6.2	2.6	10.1
Tuesday	5.9	2.4	9.1
Wednesday	5.6	2.3	9.7
Thursday	6.6	2.3	8.6
Friday	6.2	2.5	10.6
Saturday	7.9	3.1	11.9
Sunday	8.4	3.4	11.5
Morning average (5 – 8 a.m.)			
Monday	5.6	2.4	9.2
Tuesday	4.9	2.1	6.8
Wednesday	5.0	1.9	8.1
Thursday	5.8	1.9	6.6
Friday	4.6	2.3	9.9
Saturday	7.5	2.9	10.3
Sunday	9.5	3.9	11.3

limited) measurements and gave inconsistent results. 24-hour average NO_y concentrations were 27 ppb, 9 ppb, and 59 ppb, respectively in Atlanta, Chicago, and Philadelphia. Since VOC-sensitive locations are expected to have higher NO_y concentrations, these results differ from the conclusions of the VOC/NO_x ratio in terms of the relative level of VOC sensitivity in the three cities. Philadelphia has the highest NO_y concentration and would be classified as VOC sensitive. The transition from NO_x sensitivity to VOC sensitivity occurs at NO_y concentrations of 4-5 ppb; 3-4 ppb; 7-31 ppb; and 10-25 ppb in various studies (Lu and Chang, 1998, and references therein). Using these values, all three locations would be VOC-sensitive or in a transition regime by this indicator. Another indicator is HCHO/NO_y. In a VOC-sensitive airshed, this ratio should be small. The transition values are in the range of 0.5-0.7, 0.6-0.9, and 0.2-0.4 in various studies (Lu and Chang, 1998 and references therein). In Atlanta, the data sets for NO_y and HCHO overlapped only 6 days. The average ratio was 0.9 on those days, which indicated NO_x sensitivity. The mean ratios in Chicago and Philadelphia were 1.3 and 0.2, respectively. According to this ratio, Chicago would be NO_x sensitive, and Philadelphia would be VOC sensitive. The ratio O_3/NO_y was 3.3 in Atlanta, 11.4 in Chicago, and 1.1 in Philadelphia. With a transition value around 6 – 8 (location specific, given in Sillman et al., 1997), Atlanta and Philadelphia would be in a VOC-sensitive regime and Chicago in a NO_x-sensitive regime.

The indicator species approach gave inconsistent results about the VOC or NO_x sensitivity in two out of the three locations. Philadelphia was consistently VOC-sensitive, despite its high VOC/NO_x ratio. The apparent discrepancy may reflect the fact that emission source areas upwind of Philadelphia are VOC-sensitive and that a significant fraction of O_3 observed in Philadelphia is transported from such source areas.

As Sillman et al. (1997) pointed out, the use of indicators has rarely been evaluated at urban locations. Since the application of indicators may be location-dependent, it may not be feasible to compare the characteristics of different locations. In addition, indicator methods are sensitive to uncertainties in the models from which they were developed. On the measurement side, the method is very dependent on the accuracy of NO_y measurements. For example, many of the high O_3/NO_y values in Chicago were direct results of suspiciously low NO_y data. (For example, 24-hour average concentrations less than 0.5 ppb.) Ignoring these data points, the average ratio in Chicago would be 6.4, which would be in a VOC-sensitive regime or a transition regime. Since routine measurements of NO_y and other indicator species are relatively new, and there are renewed controversies about the accuracy of NO_x measurements, it is difficult to assess the uncertainties in the results of the indicators.

We correlated the VOC/NO_x ratio to the maximum one-hour O_3 concentration, grouped by the day of the week. The correlation coefficients (R) and the coefficients of determination (R^2) are presented in Table 5-2, and the regression plots can be found in Appendix D-1. The strongest positive correlation was observed in Chicago between daily maximum one-hour O_3 concentrations and the 24-hour average VOC/NO_x ratios. Similar correlation results were obtained when the morning ratio is substituted for the 24-hour average ratio, with R = 0.93 for the 5-8 a.m. ratio. Therefore, NO_x disbenefit in a VOC-sensitive airshed may explain the positive response in O_3 in Chicago to an increase in the VOC/NO_x ratio on weekends. The correlation was poor in Atlanta, where O_3 built up from Monday to Friday and recovered during the weekend, seemingly out of sync with the weekend increase of the VOC/NO_x ratio. The lack of either a positive or a negative correlation indicates that O_3 production in Atlanta may be driven by factors other than same-day emissions of VOC and NO_x. Such factors may include carry-over and transport. Despite relatively high VOC/NO_x ratios in Philadelphia, the weak but statistically significant (10% level) correlation with the 24-hour ratio in Philadelphia seemed to indicate that (1) the weekend increase in O_3 may be due in part to reduced local O_3 titration by NO or the increased radical concentrations due to reduced formation of HNO_3 and (2) the formation of O_3 may occur in part in upwind locations that are VOC-sensitive, whereas locally, there may be abundant VOC emissions. (Note that the VOC concentrations used in the correlation analyses were not spatial averages, since measurements were only available from one site.) An insignificant correlation of the morning VOC/NO_x ratio with the daily one-hour O_3 maximum provides additional circumstantial evidence that Philadelphia is affected by upwind transport, and same-day local emissions play a smaller role in O_3 production. This conclusion also seemed consistent with the analysis of indicators discussed above.

Table 5-2. Correlation between maximum one-hour average O_3 concentrations and VOC/NO_x ratios in three cities.

	Atlanta, GA	**Chicago, IL**	**Philadelphia, PA**
24-hour average VOC/NO_x ratio			
correlation coefficient (R)	0.04[(1)]	0.95[(2)]	0.72[(3)]
coefficient of determination (R^2)	0.00	0.90	0.52
Morning (5 - 8 a.m.) average VOC/NO_x ratio			
correlation coefficient (R)	-0.20[(1)]	0.93[(2)]	0.58[(1)]
coefficient of determination (R^2)	0.04	0.86	0.34

(1) Statistically insignificant at the 10% level.

(2) Statistically significant at the 5% level.

(3) Statistically significant at the 10% level.

5.2 Hypothesis 2: Increased traffic on Friday and Saturday evenings leads to increased precursor concentrations that carry over to the next day, thereby increasing the O_3 forming potential, and vice versa.

Social activities on Friday and Saturday evenings may result in increased Friday and Saturday night traffic. Therefore, late night vehicular emissions may be carried over to Saturday and Sunday. If an airshed is sensitive to pollutant carry-over, an increase/decrease in O_3 may be a direct result of increased/decreased concentrations of precursors in the boundary layer when photochemistry is initiated at sunrise the next morning.

Mobile sources emit both VOC and NO_x precursors to O_3. We first analyzed the day-of-the-the-week profiles of CO and NO_x to identify any change in the nighttime traffic. CO was used as a surrogate for automobile VOC emissions (Fujita et al., 2000), for which fewer measurements were available. Further discussion of temporal profiles will be provided in Section 5.3. Next, we quantified the changes in late night CO and NO_x emissions on Fridays and Saturdays by analyzing the predawn concentrations of precursors on Saturday and Sunday. To test the hypothesis that the weekly behavior of O_3 may be related to late night emissions or predawn concentrations of CO and NO_x, we correlated the maximum one-hour O_3 concentrations with the predawn CO and NO_x concentrations by the day of the week.

Averaged diurnal profiles of CO and NO_x are provided in Appendix D.3. We focused only on the late night concentrations on Fridays and Saturdays and the predawn concentrations on Saturdays and Sundays to test the current hypothesis. In Atlanta, both CO monitoring sites showed highest CO concentrations on Saturday evenings and early Sunday mornings. At one site, high CO concentrations were also observed on Friday nights/Saturday mornings. Predawn concentrations of NO_x tended to be lower on late Saturday and Sunday nights than on week nights at all 6 sites in Atlanta. Corresponding low NO_x was also observed on early Sunday and Monday mornings.

Except at a rural site near Chicago, predawn CO concentrations were highest on Saturdays or Sundays. Corresponding high late night CO concentrations were also observed on Fridays or Saturdays in Chicago. Sunday nights/Monday mornings and

Saturday nights/Sunday mornings consistently showed low NO_x concentrations at 12 out of 14 sites in Chicago. High predawn NO_x concentrations were observed on Wednesdays, Thursdays, or Fridays at about half the sites and on Saturday mornings at about 1/3 of the sites.

All 6 CO monitors in Philadelphia showed higher predawn concentrations on Saturdays and Sundays than on weekdays. Corresponding high concentrations were observed on Friday nights and Saturday nights at some sites. NO_x concentrations were highest overnight on Thursday nights/Friday mornings and lowest on Saturday nights/Sunday mornings and Sunday nights/Monday mornings at a single monitoring site that reported NO_x in the Philadelphia area.

Table 5-3 lists the predawn (midnight to 4 a.m.) concentrations of NO_x and CO in Atlanta, Chicago, and Philadelphia. In Atlanta, Chicago, and Philadelphia, NO_x before dawn on weekdays (Tuesdays through Fridays) was higher by 8 to 12 ppb on average than on Sundays, while Monday concentrations were only 2-3 ppb higher than those on Sundays. CO was higher on weekends than on weekdays by 160 ppb, 70 ppb, and 160 ppb in Atlanta, Chicago, and Philadelphia, respectively. The differences in the precursor concentrations in the predawn hours were statistically significant at the 5% level.

Predawn CO was higher on weekends than on weekdays. Predawn NO_x was lower on Sundays and Mondays than on other weekdays. This result was somewhat unexpected, because one would expect predawn concentrations of CO and NO_x to show the same trend on weekends vs. weekdays, assuming they are both indicators of traffic emissions. The use of summer data precludes wintertime domestic fireplace usage (when people stay up on Friday and Saturday nights) as a significant CO source. It is well known that heavy duty vehicles (e.g., trucks) are a major source of NO_x; however, they are only a minor source of CO emissions (Sawyer et al., 2000). Therefore, CO may be viewed as a surrogate for VOC emissions from light duty vehicles (e.g., passenger cars). One possible explanation for the increased predawn CO concentrations and decreased NO_x concentrations on weekends is that passenger car traffic increases on Friday and Saturday nights, resulting in higher CO concentrations at predawn hours on the weekends, while heavy duty traffic decreases on weekends (CARB, 2000) and weekend mornings, resulting in lower NO_x concentrations at the same hours. The predawn

Table 5-3. Average predawn (midnight to 4 a.m.) concentrations of CO (ppm) and NO_x (ppb) on different days of the week in Atlanta, Chicago, and Philadelphia.

	Atlanta, GA		Chicago, IL		Philadelphia, PA	
	CO	**NO_x**	**CO**	**NO_x**	**CO**	**NO_x**
Monday	0.78	28	0.73	38	0.66	27
Tuesday	0.76	34	0.72	44	0.66	29
Wednesday	0.80	36	0.76	51	0.62	28
Thursday	0.76	36	0.74	47	0.63	32
Friday	0.83	38	0.76	48	0.68	35
Saturday	0.90	33	0.82	46	0.81	30
Sunday	0.99	26	0.80	36	0.82	24

concentrations of VOC could ideally be used to corroborate the observations in the CO weekly trend. However, due to more limited data, statistically significant differences between weekday and weekend predawn VOC concentrations were not observed in the Chicago and Philadelphia data. Atlanta did show a statistically significant (5%) difference between high weekend predawn VOC (especially on Saturdays) and low weekday VOC (especially on Mondays).

Due to a difference in atmospheric lifetimes of CO and NO_x, chemical reactions may also contribute to the lack of correlation between these two pollutants in the predawn hours compared to time periods that are dominated by fresh emissions, such as the morning commute or a 24-hour average.

Correlation statistics between daily maximum one-hour average O_3 and predawn CO and VOC concentrations are shown in Table 5-4. Note that since VOC data were more limited, the uncertainties in the spatially-aggregated VOC data for each day of the week were higher. As a result, correlation coefficients in Chicago and Philadelphia, where insignificant weekday-weekend differences in VOC were found, should be interpreted with caution. Regression plots can be found in Appendix D2. No O_3-CO or O_3-VOC correlation was observed in Atlanta. In Chicago and Philadelphia, positive O_3-VOC correlations were observed despite limited VOC data. In Chicago, a statistically significant positive correlation between O_3 and CO was consistent with the observations from the O_3-VOC/NO_x correlation in a VOC sensitive airshed. The equally strong positive correlation between O_3 and predawn concentrations of CO in Philadelphia as in Chicago provided some evidence that the availability of VOC precursors and VOC carry-over could be important to the formation of O_3 there.

The negative correlations (Table 5-4) between predawn NO_x concentrations and O_3 in Chicago and Philadelphia were consistent with the O_3 vs. VOC/NO_x ratio correlations. However, these correlations were weak and statistically insignificant. In Atlanta, there was some positive correlation between O_3 and the NO_x concentration before the morning rush hour, despite the lack of correlation with the VOC/NO_x ratio. Production of O_3 in Atlanta may be sensitive to NO_x carry-over, as discussed next.

Table 5-4. Correlation between maximum one-hour average O_3 concentrations and average predawn concentrations of CO and NO_x in three cities.

	Atlanta, GA	**Chicago, IL**	**Philadelphia, PA**
CO			
correlation coefficient (R)	0.11[(2)]	0.85[(3)]	0.85[(3)]
coefficient of determination (R^2)	0.01	0.72	0.72
VOC[(1)]			
correlation coefficient (R)	0.44[(2)]	0.45[(2)]	0.78[(3)]
coefficient of determination (R^2)	0.19	0.19	0.61
NO_x			
correlation coefficient (R)	0.70[(4)]	- 0.52[(2)]	- 0.52[(2)]
coefficient of determination (R^2)	0.50	0.27	0.27

(1) Day-of-week difference in predawn VOC in Chicago and Philadelphia insignificant due to limited data.
(2) Statistically insignificant at the 10% significance level.
(3) Statistically significant at the 5% significance level.
(4) Statistically significant at the 10% significance level.

5.2.1 Hypothesis 2a: Carry-over of precursors and/or O_3 from one day to the next drives the weekly cycle of O_3.

At sites that seemed to be sensitive to the predawn concentrations of precursors, there is a distinct possibility that it is not only the nighttime emissions, but also the carry-over of precursors that drive the weekly behavior of O_3 concentrations. We investigated the correlations of O_3 vs. previous day's O_3, NO_x, NO_y, CO, and VOC, focusing on NO_x and NO_y for Atlanta and VOC and CO for Chicago and Philadelphia, based on the predawn concentration correlations. The results are reported in Table 5-5, and regression plots are provided in Appendix D2.2.

Daily maximum concentrations of O_3 did not correlate well with the concentration of O_3 from the previous day. The daily maximum O_3 in Atlanta correlated well with previous day's 24-hour average NO_x, NO_y and CO concentrations. In fact, the R^2 values were much higher than the corresponding relationship with the NO_x, NO_y and CO concentrations from the same day. For example, the correlation between the maximum one-hour average concentration of O_3 and 24-hour average concentration of NO_x from the same day resulted in a correlation coefficient of +0.25, but that with previous day's 24-hour average NO_x was +0.75, statistically significant at the 5% level. The positive correlation coefficients indicated that NO_x and NO_y from the previous day fueled O_3 production, rather than scavenged O_3. The VOC correlation was much weaker (for both same day and with a 1-day lag). Therefore, the weekly O_3 behavior in Atlanta, including minimum O_3 concentrations on Mondays, may be driven in part by the amount of NO_x and NO_y carried over from previous day (or days). On the other hand, it is not sensitive to VOC carry-over, as expected from the VOC/NO_x ratio. In Chicago and Philadelphia, carry-over of nitrogen precursors seemed to play a small role; weak or negligible correlations were observed with O_3 concentrations. (For example, in Chicago, the correlation coefficient between O_3 and the same day's 24-hour average NO_x was -0.97, vs. a mere -0.22 with NO_x concentration of the previous day.) The weekly O_3 behavior in Philadelphia also seemed independent of the carry-over of VOC and CO from the previous day at the same location, whereas O_3 in Chicago was weakly correlated to the carry-over of VOC from the previous day.

Table 5-5. Correlation between maximum one-hour average O_3 concentrations and concentrations of O_3, CO, VOC, NO_x and NO_y from the previous day in three cities.

	Atlanta, GA		**Chicago, IL**		**Philadelphia, PA**	
	R	**R^2**	**R**	**R^2**	**R**	**R^2**
O_3	0.02(1)	0.00	0.30(1)	0.09	0.15(1)	0.02
NO_x	0.75(2)	0.56	- 0.12(1)	0.01	- 0.18(1)	0.03
NO_y	0.87(2)	0.76	0.12(1)	0.01	0.59(1)	0.35
CO	0.81(2)	0.65	0.16(1)	0.03	0.25(1)	0.06
VOC	0.28(1)	0.08	0.76(2)	0.58	0.17(1)	0.03

(1) Statistically insignificant at the 10% significance level.

(2) Statistically significant at the 5% significance level.

5.3 Hypothesis 3: Different driving activity during weekends (vs. weekdays) results in different temporal emission patterns, and hence in variations in O_3 concentrations.

Weekday traffic is strongly affected by work-related commutes. During the work week, emissions from mobile sources peak in the morning and early evening. These peaks are less pronounced on weekends and, in some areas, may well be non-existent. The change in the timing in precursor injection may affect the photochemistry of O_3 formation.

In Section 5.2, we concluded that significant differences exist between the predawn concentrations of NO_x and CO on weekdays and those on weekends. This change may be attributed to increased passenger car traffic on Friday and Saturday nights and reduced truck traffic on weekends. We have shown that carry-over may affect O_3 production. The reduction in predawn NO_x on Sundays and Mondays in Atlanta and the accumulation of CO in Chicago and Philadelphia before the start of photochemistry with sunrise were correlated to the peak one-hour average O_3 concentrations in the afternoon. In this section, we turn to the diurnal profiles of CO and NO_x to identify changes in the traffic patterns from weekdays to weekends, focusing on daytime concentrations.

Example diurnal profiles of CO and NO_x, grouped by the day of the week, are shown in Figure 5-1 for Chicago, IL. Appendices D3.1 to D3.3 contain additional CO and NO_x diurnal profiles from Atlanta, GA, Chicago, IL, and Philadelphia, PA. VOC diurnal profiles were much more variable, and were not analyzed. In general, day-of-the-week specific diurnal profiles of NO_x and CO show many similar characteristics. It is, therefore, not surprising that the 24-hour average concentrations of these two pollutants correlate quite well. In particular, the morning traffic peaks were very pronounced on weekdays in both CO and NO_x diurnal concentration profiles. A few sites also showed an afternoon peak that corresponded to the afternoon commute peak, but generally the afternoon commute peak was not observed, probably due to increased mixing layer height relative to the morning commute peak. As the nocturnal boundary layer decreases in height, concentrations of the primary pollutants CO and NO_x increased, reaching peak concentrations late at night. On the weekends, the morning commute signal was weaker

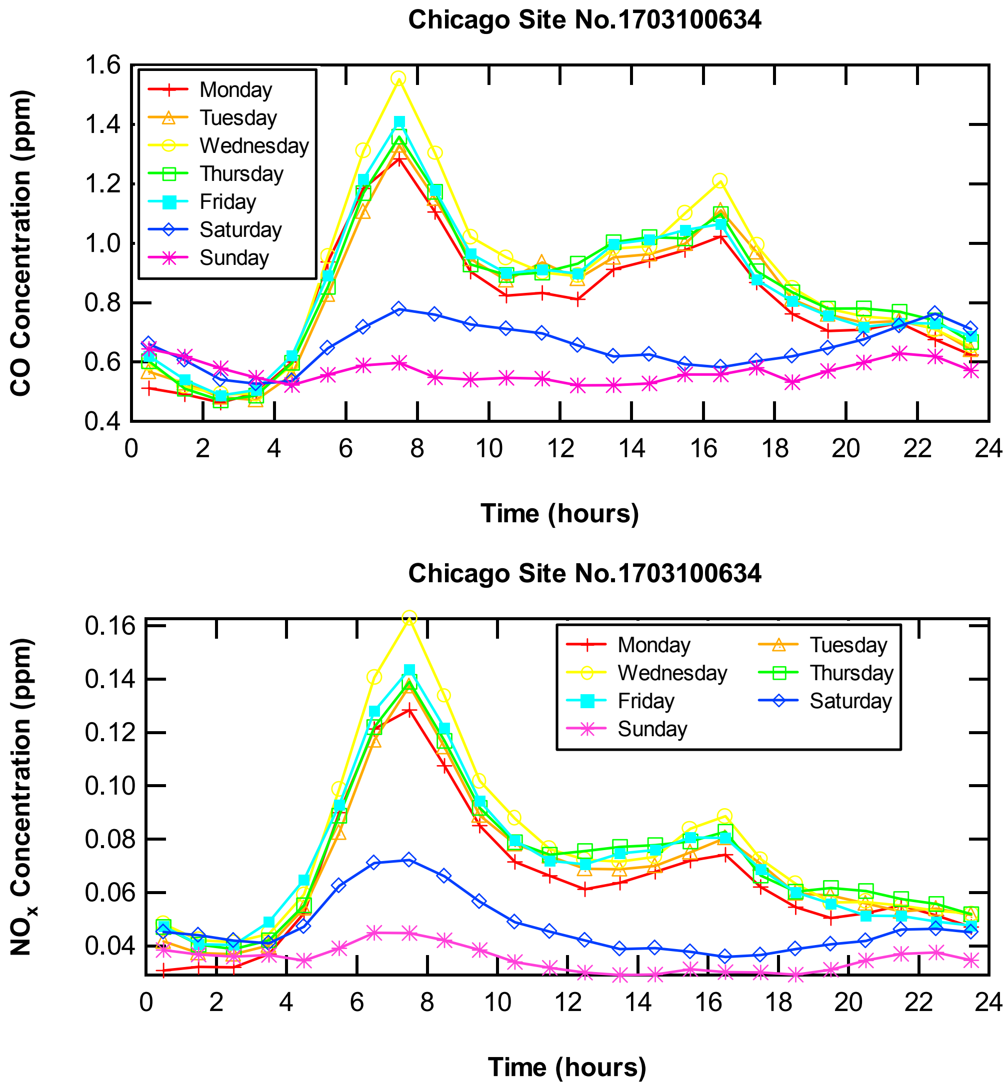


Figure 5-1. Sample diurnal profiles of CO and NO_x from Chicago, IL Site 1703100634.

or non-existent (especially on Sundays). Except for the predawn hours, ambient CO concentrations on weekends were lower than or comparable to concentrations on weekdays. (The only exceptions were two sites in Chicago where CO concentrations between 10 a.m. and 1 p.m. were higher on Saturdays and/or Sundays than on weekdays.) The same is also true for NO_x concentrations.

The largest day-time difference between weekday and weekend CO and NO_x profiles occurred during the morning rush hour, from 5 a.m. to 8 a.m. The average morning concentrations are listed in Table 5-6 by the day of the week. Note that since both CO and NO_x seemed to be driven by traffic emissions, there were very tight correlations between the two in all three cities. The correlation coefficients were 0.94, 0.99, and 0.98 in Atlanta, Chicago, and Philadelphia, respectively.

The correlation results between daily maximum one-hour average O_3 concentrations and morning average concentrations of CO and NO_x are summarized in Table 5-7. Correlation plots are found in Appendix D3.4. The maximum one-hour average O_3 concentrations in Atlanta did not correlate well with morning average CO or NO_x concentrations, a behavior consistent with a strong dependence on carried over precursors to drive photochemical production of O_3. Both Chicago and Philadelphia showed negative correlations between O_3 and morning NO_x, indicating the role of titration of O_3 by NO emissions in the morning, which served to delay O_3 accumulation. The titration effect was further supported by the morning O_3-morning NO_x correlations, which were even tighter than those listed in Table 5-7. At sites where titration of O_3 occurred in the morning, the time when the NO concentration equaled O_3 concentration in the morning, the so-called "O_3-NO cross-over time," was accelerated by two hours on average on Sundays relative to weekdays in Chicago. Reduced NO_x emissions on weekends also lead to reduced formation of HNO_3; thereby increasing the availability of OH for O_3-producing photochemical reactions. The negative correlation between morning CO concentration and maximum O_3 was probably not a direct cause-effect relationship, but rather a consequence of the high correlation between CO and NO_x in the morning.

Table 5-6. Average morning (5 a.m. to 8 a.m.) concentrations of CO (ppm) and NO_x (ppb) on different days of the week in Atlanta, Chicago, and Philadelphia.

Morning Concentrations	Atlanta, GA		Chicago, IL		Philadelphia, PA	
	CO	NO_x	CO	NO_x	CO	NO_x
Monday	1.25	40	1.04	62	1.05	47
Tuesday	1.26	47	1.01	61	1.05	49
Wednesday	1.27	50	1.12	75	1.01	44
Thursday	1.26	45	1.04	66	1.03	49
Friday	1.29	51	1.04	68	1.04	53
Saturday	0.90	34	0.85	45	0.82	32
Sunday	0.81	25	0.71	31	0.69	25

Table 5-7. Correlation between maximum one-hour average O_3 concentrations and average morning concentrations of CO and NO_x in three cities.

CO	**Atlanta, GA**	**Chicago, IL**	**Philadelphia, PA**
correlation coefficient (R)	0.01[1]	- 0.94[2]	- 0.75[2]
coefficient of determination (R^2)	0.00	0.88	0.56
NO_x			
correlation coefficient (R)	0.29[1]	- 0.91[2]	- 0.81[2]
coefficient of determination (R^2)	0.08	0.83	0.66

(1) Statistically insignificant at the 10% significance level.

(2) Statistically significant at the 5% significance level.

5.4 Hypothesis 4: Different driving activity during weekends (vs. weekdays) results in different spatial emission patterns, and hence in variations in O_3 concentrations.

In the previous section, we have shown that significant changes occurred in the temporal distribution of traffic emissions from weekdays to weekends, resulting in changes in the diurnal distribution of primary pollutants such as CO and NO_x. In addition to temporal changes, traffic patterns are also expected to change spatially from weekdays to weekends. For example, commute trips to and from work, which dominate the weekday traffic pattern, will be replaced by errands and trips to recreational destinations. Therefore, the locations at which mobile source emissions are released into the atmosphere may differ from weekdays to weekends, and this change can result in changes in O_3 chemistry.

The analysis of the spatial distribution of pollutants is limited by the available monitors. In areas with only a few CO or NO_x monitors, the changes in spatial distribution are difficult to assess. Due to the spatial variability of primary pollutants, the area of representativeness of each monitor may also be different. Therefore, the analysis presented here will illustrate if any spatial difference can be detected in the weekday vs. weekend emissions, and may not necessarily reflect how the spatial emissions pattern change within an urban area.

Due to the subtle difference between the weekday vs. weekend diurnal profiles at different sites (see Appendix D3), we used a 24-hour average concentration as the metric to compare concentrations at different sites. Our approach is to rank the concentrations at different monitors on different days of the week. If there is a consistent change in ranking, the monitor may represent a location that is frequented on weekdays or on weekends.

In Atlanta, there were only two CO monitors. On every day of the week, the 24-hour concentration at Site 1312100994 (commercial area in Atlanta) was greater than that at Site 1308910024 (residential area in Clarkston). Five NO_x monitors in the Atlanta area were located in urban, suburban, and rural settings. Their daily average NO_x concentrations and ranks are listed in Table 5-8. The farthest sites from Atlanta, Sites

Table 5-8. 24-hour average concentrations of NO_x and ranks at Atlanta area sites.

Site ID	Weekday[1] (ppb)	Weekday rank	Saturday (ppb)	Saturday rank	Sunday (ppb)	Sunday rank
1308900024	57	1	44	2	36	2
1308930014	26	3	20	3	16	3
1312100484	53	2	46	1	37	1
1322300034	7.2	5	6.4	5	5.3	5
1324700014	11	4	8.2	4	6.6	4

(1) Average Monday through Friday 24-hour average concentrations

1322300034 and 1324700014, recorded the lowest NO_x. These sites are located in rural/ agricultural areas due west and east of Atlanta, respectively. The classification of Site 1308930014 is rural and residential, and is closer to Atlanta than the sites measuring lower concentrations. There seemed to be a shift in traffic from the suburban site in Decatur (east of Atlanta) (Site 1308900024) to the urban site in Atlanta (Site 1312100484) on weekends.

Table 5-9 presents the 24-hour average CO concentrations at various Chicago monitoring sites. The lowest (suspiciously low) CO concentrations in the Chicago area were found at Site 1719710114, a background site. The highest concentrations were recorded in Maywood, a suburb to the east of Chicago along Route 290. The high concentrations may well be a direct result of the site's proximity to Route 290. The site that showed the most significant relative decrease from weekdays to weekends was Site 1703100634. This site is located downtown at the Chicago Transit Authority Building. With a "mobile" designation, this site is highly affected by weekday commutes. The site that showed the most significant increase in relative concentrations of CO is Site 1703180034, located along Highway 94 in Calumet City south of Michigan. It is possible that the increase in CO reflects areas along the south shore of Lake Michigan as weekend destinations.

Table 5-10 shows the same analysis for NO_x monitoring sites in the Chicago Area. The highest NO_x concentrations were also recorded at the Maywood site. Significant shifts in traffic occurred at Sites 1703100374, 1703100754, and 1808910164, the first two showed an increase in relative NO_x concentrations on the weekends and the latter showed a decrease. Sites 1703100374 and 1703100754 were both located near the lakeshore north of Chicago. Site 1703100754 was also within 1 km of Wrigley Field. Therefore, it is possible that these two sites represented popular weekend destinations. Site 1808910164 was located in Gary, Indiana, an industrial city in transition after the collapse of the steel industry.

Of the six CO monitoring sites in Philadelphia, the highest concentrations were measured at Site 4210100274. Located within 15 feet of a 6-lane traffic route, local emissions probably dominated the measurements at this site. Lowest concentrations were recorded at Site 3400700034, located in Camden, NJ, across the river. No change in the

Table 5-9. 24-hour average concentrations of CO and ranks at Chicago area sites.

Site ID	Weekday[1] (ppm)	Weekday rank	Saturday (ppm)	Saturday rank	Sunday (ppm)	Sunday rank
1703100374	0.94	2	0.92	2	0.89	2
1703100634	0.87	4	0.65	8	0.55	9
1703131014	0.79	8	0.68	7	0.58	7
1703131034	0.79	7	0.72	6	0.66	6
1703140024	0.87	3	0.84	3	0.80	3
1703140044	0.67	9	0.63	9	0.57	8
1703141014	0.60	10	0.56	10	0.54	10
1703160044	1.61	1	1.64	1	1.47	1
1703180034	0.83	6	0.80	4	0.78	4
1719710114	0.29	11	0.30	11	0.29	11
1808900214	0.84	5	0.79	5	0.70	5

(1) Average Monday through Friday 24-hour average concentrations

Table 5-10. 24-hour average concentrations of NO_x and ranks at Chicago area sites.

Site ID	Weekday[(1)] (ppb)	Weekday rank	Saturday (ppb)	Saturday rank	Sunday (ppb)	Sunday rank
1703100374	65	4	57	3	48	2
1703100634	77	3	51	4	38	4
1703100644	40	9	33	9	27	9
1703100724	25	12	26	12	21	12
1703100754	38	10	37	7	28	7
1703131014	89	2	62	2	48	3
1703131034	95	1	72	1	54	1
1703140024	49	6	43	6	35	6
1703142014	32	11	28	11	22	11
1703180034	57	5	45	5	36	5
1709710074	10	14	10	14	7.4	14
1709710114	11	13	10	13	8.6	13
1808900224	43	8	36	8	28	8
1808910164	46	7	32	10	24	10

ranking of the concentrations was observed at any site between weekdays and weekends. Since NO_x data were downloaded only at one site in the Philadelphia area, the spatial distribution of NO_x was not investigated.

We were able to identify some changes in the distribution patterns of CO and NO_x in Atlanta and Chicago during the weekends that may have resulted from a shift in the traffic pattern. However, we could not correlate these patterns to the weekly patterns of O_3 concentrations. When O_3 correlated strongly with the spatially averaged concentrations of CO and NO_x, the change in total emissions from weekdays to weekends had such a strong effect that any effect of the changes in the spatial distribution of emissions on O_3 would be masked. When O_3 did not correlate strongly with the spatially averaged concentrations, it also did not correlate to any significant extent with concentrations at individual sites.

5.5 Hypothesis 5: Emissions from sources other than on-road mobile sources vary from weekday to weekend.

Sources other than mobile emissions may also exhibit differences between weekday and weekend emissions. Our approach to identify such sources involves the analysis the composition of particles for changes in the (relative) concentration of key tracer species. Theoretically, the composition of organic gases may also be used in identifying changes in VOC sources. Unfortunately, VOC species routinely measured in the PAMS network, such as simple alkanes, alkenes, aromatics, and small aldehydes, are quite ubiquitous and typically dominated by mobile emissions. Measurements of fingerprint species that may be tracers for specific sources, such as levoglucosan for wood burning or fatty acids for meat cooking (Schauer and Cass, 2000), are not routinely available.

Routine monitoring of PM composition is not conducted in the ambient monitoring stations in the NAMS, SLAMS, and PAMS networks. The new PM supersites program may eventually provide useful long-term and short-term data in several key metropolitan areas. At this time, IMPROVE is the only routine monitoring network to provide PM composition data. The goal of IMPROVE is to monitor visibility by monitoring fine particle concentrations and compositions. The majority of IMPROVE sites are established in pristine areas and do not provide relevant information for the study of weekday/weekend differences in metropolitan areas. However, one urban site that follows the IMPROVE protocol is operational in Washington D.C. For illustrative purposes, we analyze the composition of PM to test if weekday/weekend differences in emission sources can be identified in an urban area.

The protocol for IMPROVE monitoring sites was to measure 24-hour average PM concentrations and compositions on Wednesdays and Saturdays. Therefore, the data obtained for 1988 to 1997 were separated into two groups, and the concentration of each component is normalized by the $PM_{2.5}$ mass measured on the same day. Key species that showed a statistically significant (at the 10% significance level) weekday-weekend difference in composition are listed in Table 5-11.

Silicon (Si) and calcium (Ca) are indicators of crustal minerals, which in a city are likely to reflect road dust resuspended by traffic. Therefore, a decrease in the contribution of these species is consistent with reduced traffic on weekends. Of particular interest is the decrease in EC. We also tested the ratio of OC to EC from this data set. The average Wednesday ratio was 1.73 and the Saturday ratio was 1.93. The difference is significant at the 1% level. This observation is consistent with a decrease in the relative importance of diesel-fueled vehicles (refer to Hypotheses 1 and 2) and an increase in the relative importance of other PM sources that have higher OC/EC ratios. In addition to gasoline vehicles, this latter category includes woodsmoke and meat cooking. A detailed investigation of source activities, which is beyond the scope of the current project, will reveal changes of the relative contributions of various organic aerosol sources.

5.6 Hypothesis 6: A decrease in PM concentrations reduces light extinction of the atmosphere, and accelerates the photochemistry for O_3 production, and vice versa.

This hypothesis treats the possible relationship between PM and O_3 through the light extinction properties of PM. Fine particles contain primary and secondary

Table 5-11. PM species with significantly different compositions between weekdays and weekends at the IMPROVE monitoring station in Washington D.C.

Species of increased contribution [(1)]	**Species of decreased contribution**
Sulfur (S)	Silicon (Si)
Potassium (K)	Calcium (Ca)
Rubidium (Rb)	Titanium (Ti)
Strontium (Sr)	Manganese (Mn)
Molybdenum (Mo)	Iron (Fe)
Nitrite ion (NO_2^-)	Copper (Cu)
	Zinc (Zn)
	Elemental Carbon (EC) [(2)]

(1) Species with only a few valid measurements are excluded (e.g., P)
(2) EC is the sum of 3 components that are oxidized at different temperatures.

components. A key primary component is elemental carbon, which has strong light absorption properties. Secondary components, such as sulfate, nitrate, and ammonium, may scatter rather than absorb light. On weekends, one expects that the decreased traffic, especially heavy duty vehicle traffic, will lead to reduced emissions of fine particles. If primary components dominate fine particles, a decrease in primary emissions will reduce the light extinction by fine particles on weekends. In Section 4, we investigated the weekly behavior in $PM_{2.5}$. $PM_{2.5}$ was lowest on Sundays and Mondays in Atlanta, Tuesdays and Thursdays in Chicago, and Thursdays in Philadelphia. Therefore, an overall decrease in $PM_{2.5}$ was not observed with the expected decrease in primary emissions by heavy duty vehicle traffic.

Even though we could not identify specific changes in $PM_{2.5}$ over the weekend, it is still our goal to test any correlations in the day-of-the-week behavior in PM, radiation, and O_3. To that end, we analyzed the day-of-the-week behavior of radiation (see Table 5-12). We tested the weekday-weekend differences in both solar and UV radiation. Solar and UV measurements were downloaded from four sites in Atlanta. The data record for solar radiation (4-5 years) was longer than the UV records (2-3 years). The 24-hour average solar radiation was higher on weekends in Atlanta by about 10 W m^{-2}, a 3% increase. The Wednesday-Sunday difference was significant when tested by bootstrap sampling at the 10% level. UV radiation was also higher on weekends than on weekdays in Atlanta, by about 0.0005 Langley min^{-1} (0.5 mCal cm^{-2} min^{-1}). This difference was not statistically significant at the 10% level, but the Sunday-Wednesday difference was. We have also tested the morning averaged solar and UV radiation values. The weekday-weekend difference in morning averaged values were not significant at the 10% level (except the morning UV difference between Sundays and Thursdays). In Chicago, the averaged weekend solar radiation was also higher than weekday values. The difference of 0.012 Langley min^{-1} was not statistically significant at the 10% level. UV radiation was also not statistically different between weekends and weekdays. In Philadelphia, higher solar radiation was observed on weekends. The difference of 0.024 Langley min^{-1} was statistically significant at the 10% level, despite a single site and a relatively short data record (3 years). No UV data were downloaded for Philadelphia.

Table 5-12. 24-hour average solar and UV radiation on different days of the week in Atlanta, Chicago, and Philadelphia (solar radiation only).

Radiation (Langley min^{-1})	**Atlanta, GA**		**Chicago, IL**		**Philadelphia, PA**	
	Solar	**UV**	**Solar**	**UV**	**Solar**	**UV**
Monday	0.464	0.0145	0.508	0.0204	0.506	--
Tuesday	0.477	0.0144	0.504	0.0201	0.514	--
Wednesday	0.481	0.0141	0.511	0.0203	0.508	--
Thursday	0.472	0.0142	0.492	0.0197	0.491	--
Friday	0.490	0.0145	0.512	0.0204	0.542	--
Saturday	0.489	0.0146	0.510	0.0205	0.543	--
Sunday	0.494	0.0152	0.524	0.0209	0.530	--

Next we investigated any correlations between $PM_{2.5}$ and radiation. The results are listed in Table 5-13 (see also Appendix D4.1). In Philadelphia, solar radiation was positively related to $PM_{2.5}$. Instead of $PM_{2.5}$ causing light extinction, increased solar and UV radiation may enhance the production of secondary components of $PM_{2.5}$. No significant correlation was found in Atlanta and Chicago.

A second component of this hypothesis is that an increase in ground level solar/UV radiation accelerates O_3 production. Correlation results between radiation and O_3 are shown in Table 5-14 and Appendix D4.2. There was a weak but significant correlation between O_3 and UV in Chicago. No other significant correlations were found between maximum one-hour concentrations of O_3 and UV or solar radiation.

In Chicago, both O_3 and $PM_{2.5}$ increased during weekends (although there was no significant correlation between O_3 and $PM_{2.5}$). The positive PM-radiation correlation results did not support the hypothesis that the observed increase in weekend solar radiation was caused by reductions in $PM_{2.5}$ emissions. No statistically significant correlations were found between $PM_{2.5}$, solar or UV radiation, and O_3 in Atlanta and Philadelphia. However, daily maximum one-hour average O_3 concentrations and 24-hour average $PM_{2.5}$ concentrations correlate positively at both sites. (The correlation coefficients of 0.8 and 0.79 were statistically significant between O_3 and $PM_{2.5}$.) In Chicago, though insignificant, the correlation between O_3 and $PM_{2.5}$ was also positive. It seems unlikely at this time that $PM_{2.5}$ significantly reduces solar radiation and production of O_3. However, there may be a relationship between primary EC (e.g., from mobile sources) and O_3, at locations where EC is an important component of PM. EC absorbs light and a decrease in EC on weekends should lead to an increase in radiation. It has also been suggested that nitrogen species may be removed on the surface of carbonaceous PM. The possible relationship between fine PM and O_3 should be revisited when better $PM_{2.5}$ and possibly component data (e.g., EC measurements or coefficient of haze, which correlates to EC measurements (S. Altshuler, Pacific Gas and Electric Co., private communication, 2000)) are available.

Table 5-13. Correlation between 24-hour average $PM_{2.5}$ concentrations and 24-hour average solar and UV radiation in three cities.

	Atlanta, GA	**Chicago, IL**	**Philadelphia, PA**
Solar Radiation			
correlation coefficient (R)	0.59[(1)]	0.61[(1)]	0.81[(2)]
coefficient of determination (R^2)	0.35	0.37	0.66
UV Radiation			
correlation coefficient (R)	- 0.37[(1)]	0.60[(1)]	--
coefficient of determination (R^2)	0.14	0.36	--

(1) Statistically insignificant at the 10% significance level.

(2) Statistically significant at the 5% significance level.

Table 5-14. Correlation between maximum one-hour average O_3 concentrations and 24-hour average solar and UV radiation in three cities.

	Atlanta, GA	**Chicago, IL**	**Philadelphia, PA**
Solar Radiation			
correlation coefficient (R)	0.42[(1)]	0.63[(1)]	0.41[(1)]
coefficient of determination (R^2)	0.18	0.39	0.17
UV Radiation			
correlation coefficient (R)	- 0.09[(1)]	0.69[(2)]	--
coefficient of determination (R^2)	0.01	0.47	--

(1) Statistically insignificant at the 10% significance level.

(2) Statistically significant at the 10% significance level.

6. WEEKLY BEHAVIOR OF OZONE: 1986 - 90 VS. 1995 - 99

6.1 Atlanta

24-hour profiles of each day of the week. The averaged diurnal profiles at 4 sites are shown in Appendix E1. In general, there were only small day-of the week differences in the diurnal profiles from this earlier period. O_3 concentrations in mid morning (8 to 10 a.m.) were typically higher on weekends than on weekdays. Peak O_3 occurred at roughly the same time. At three out of four sites, the profiles of O_3 from different days of the week looked very similar (with small differences in the morning O_3, which was consistently higher on weekends). At site 1312100534, noticeable differences in the morning O_3 concentrations between weekdays and Saturdays and Sundays were presumably related to reduced NO titration of O_3 on weekends. This difference translated into higher afternoon O_3 concentrations on Saturdays and Sundays at this particular site. When compared to the averaged profiles from the same sites in Appendix A1, some differences are observed. The day-of-the-week differences seemed to be magnified in the later data set. The lowest concentration profiles observed on Mondays in the 1990's were not at all obvious in the earlier data set, possibly due to similar profiles on all weekdays.

Maximum one-hour average concentration. The daily one-hour maximum concentrations, averaged for each day of the week, are presented in Table 6-1. As expected from the similarity in the diurnal profiles, differences between the maximum daily one-hour average O_3 were rather small. The mean and standard deviation of the maximum one-hour average concentrations are listed in Appendix E2 by the day of the week. When the differences were tested using bootstrap sampling, only one site showed a statistically significant difference. The site was Site 1312100534, a site in the city of Atlanta classified as urban/center city. Highest concentrations were observed on Sundays and lowest concentrations were observed on Tuesdays. The differences between Sunday and Monday concentrations were also significant. Note that all sites showed high concentrations on Fridays and low concentrations on Mondays in the later time period (Table 4-1). The day-of-the-week differences were statistically insignificant at the other three sites. These three sites were located in the suburban and rural areas of Decatur,

Table 6-1. Statistics of mean daily maximum one-hour average ozone concentrations (ppm) by day of the week in Atlanta, GA, 1986 – 1990.

Site ID	Maximum (ppm)	Day of maximum	Minimum (ppm)	Day of minimum	Maximum minus minimum (ppm)	Statistical significance of the difference
1308900024	0.0623	Sunday	0.0597	Thursday	0.0026	insignificant
1309700024	0.0614	Tuesday	0.0591	Wednesday	0.0022	insignificant
1312100534	0.0589	Sunday	0.0548	Tuesday	0.0041	10%
1324700014	0.0647	Friday	0.0621	Thursday	0.0026	insignificant

Tucker, and Conyers. Note that the larger differences in the 1995-1999 time period at these sites (Table 4-1) seemed to be driven by higher maximum concentrations.

The lack of a (statistically significant) weekly cycle in O_3 concentrations was unexpected, due to the working hypothesis that the weekly cycle in anthropogenic emissions interacts with transport and chemistry to produce a weekly cycle in O_3. We put forth the following conjecture. If the difference in the weekly cycle at suburban and rural sites between the 1980s and the 1990s was due to the growth of the Atlanta metropolitan area, it is possible that O_3 was regionally distributed back in the 1980's in the southeastern United States, and the formation of O_3 on the regional scale may have been less sensitive to anthropogenic emissions. Further investigation will be needed to elucidate the relationships between the emission patterns and the behavior of O_3.

6.2 Chicago

24-hour profiles of each day of the week. The average diurnal profiles from Chicago area sites from 1986 to 1990 are shown in Appendix F1. The increase in day-time O_3 on Saturdays and Sundays compared to weekdays was observed from this earlier data set. At a majority of sites, O_3 concentrations on Sunday mornings (e.g., 7 or 8 a.m.) were higher than on any other day of the week, indicating reduced titration by NO on Sunday mornings. With a higher starting concentration, O_3 built up faster on Sunday mornings. Saturdays also showed higher O_3 in the mornings compared to weekdays. Sunday afternoon O_3 typically peaked earlier than that on Saturday. At about 12 sites, O_3 accumulated at a faster rate on Saturday mornings and eventually caught up with or exceeded the Sunday O_3 concentrations. Weekday diurnal profiles looked rather similar to one another at many sites, with peak O_3 at 3 or 4 p.m.

Maximum one-hour average concentration. The maximum one-hour average concentrations were calculated for each day, and the mean value and standard deviation for each day of the week are presented in Appendix F2. The maximum, minimum and difference at each site are presented in Table 6-2. The difference between the maximum and minimum one-hour average O_3 concentrations ranged from 4 ppb to 10 ppb.

Like in the late 1990s, the highest one-hour concentrations were recorded on weekends. However, Saturdays recorded higher mean maximum one-hour concentrations than Sundays at 9 sites. Two sites in Indiana recorded high Thursday concentrations. The weekly trend was somewhat less consistent among different sites than it was in the late 1990 period, when all sites in the metropolitan area recorded highest daily one-hour maximum concentrations on Sundays. Also, unlike the late 1990s, the day on which the lowest one-hour maximum concentrations were most frequently recorded was Friday rather than mid week, although Tuesdays recorded the next highest number of low concentrations.

The standard deviations associated with the maximum one-hour concentrations were high (Appendix F2). We applied bootstrap sampling to test the statistical significance of the difference in the mean values from different days of the week. The smallest difference between maximum and minimum concentrations that was statistically significant at the 5% level was about 5 ppb, given the long data records. Note that the Friday-Sunday difference was statistically significant at 12 sites at the 5% significance level and at 14 sites at the 10% level.

6.3 Philadelphia

24-hour profiles of each day of the week. Six sites recorded O_3 diurnal concentrations in Philadelphia, PA during the 1986 – 1990 period. Like Chicago, the diurnal profiles, shown in Appendix G1, displayed a cyclical behavior with higher concentrations on Saturdays and Sundays. Relatively low concentrations were observed on Thursdays at most sites, and Wednesdays and Fridays at some hours. The weekly diurnal profiles showed a decrease in O_3 during the morning rush hour (6 to 8 a.m.) that was not prominent on Saturdays and Sundays. Therefore, in the mornings, O_3 was consistently higher on Sundays. Weekday morning concentrations were quite similar and lower than the weekend concentrations. The differences in the morning concentrations translated into the afternoon peaks on Sundays at most sites, since the rates of O_3 accumulation were similar on weekends and weekdays. The time of peak O_3 was most frequently at 3 or 4 p.m., although at several sites, Sunday's peak concentration

Table 6-2. Statistics of mean daily maximum one-hour average ozone concentrations (ppm) by day of the week in Chicago, IL, 1986 – 1990.

Site ID	Maximum (ppm)	Day of maximum	Minimum (ppm)	Day of minimum	Maximum minus minimum (ppm)	Statistical significance of the difference
1703100014	0.0606	Sunday	0.0508	Friday	0.0097	5%
1703100324	0.0564	Sunday	0.0499	Friday	0.0065	5%
1703100374	0.0507	Saturday	0.0444	Tuesday	0.0063	5%
1703100504	0.0487	Sunday	0.0408	Tuesday	0.0079	5%
1703100644	0.0591	Sunday	0.0491	Tuesday	0.0099	10%
1703110024	0.0514	Sunday	0.0458	Thursday	0.0056	insignificant
1703110034	0.0548	Saturday	0.0464	Friday	0.0084	5%
1703116014	0.0557	Saturday	0.0484	Friday	0.0074	5%
1703140024	0.0529	Sunday	0.0457	Tuesday	0.0072	5%
1703140034	0.0547	Saturday	0.0471	Friday	0.0076	5%
1703170024	0.0592	Saturday	0.0545	Tuesday	0.0047	10%
1704360014	0.0520	Saturday	0.0443	Friday	0.0077	5%
1709700014	0.0544	Saturday	0.0478	Friday	0.0066	5%
1709710024	0.0567	Saturday	0.0504	Friday	0.0063	5%
1709730014	0.0540	Saturday	0.0480	Friday	0.0060	5%
1808910164	0.0485	Sunday	0.0434	Wednesday	0.0050	5%
1808920084	0.0585	Thursday	0.0550	Tuesday	0.0035	insignificant
1812700244	0.0638	Thursday	0.0595	Friday	0.0043	insignificant

occurred earlier and/or Saturday's peak concentration occurred at a later time so that the peak concentration on Saturdays caught up with that on Sundays. Site 4210100234, which showed the most significant difference between weekday and weekend diurnal profiles, was an urban and center city site located near a power plant and 8-lane approach to a PA-NJ bridge. Therefore, this site is probably affected by local titration of O_3 by NO emissions throughout the day. Higher variability at a site close to a NO_x source would also result in somewhat more jagged profiles, despite the long data record length of five years used in determining the average profile. The significant difference in diurnal profiles, while probably not representative of urban-scale O_3 distribution, provided some indication on the extent of reduction of NO pollution throughout the day on weekends.

Maximum one-hour average concentration. A mean value was calculated for the maximum one-hour concentrations on each day of the week. The maximum differences in this quantity are presented in Table 6-3. The mean value and standard deviation are shown in Appendix F.2. Highest maximum one-hour concentrations occurred on Sundays at three out of 6 sites and Saturdays at the other three sites. Lowest concentrations occurred on Thursdays or Wednesdays (1 site). All differences were significant at the 5% or 10% level. In the later time period, minimum concentrations were also observed on Fridays, and the weekend-weekday difference was slightly smaller, with lower average concentrations.

Table 6-3. Statistics of mean daily maximum one-hour average ozone concentrations (ppm) by day of the week in Philadelphia, PA, 1986 – 1990.

Site ID	Maximum (ppm)	Day of maximum	Minimum (ppm)	Day of minimum	Maximum minus minimum (ppm)	Statistical significance of the difference
3400530014	0.0629	Saturday	0.0559	Thursday	0.0069	5%
3400700034	0.0638	Saturday	0.0580	Thursday	0.0058	10%
4204500024	0.0663	Sunday	0.0583	Thursday	0.0080	10%
4210100144	0.0634	Sunday	0.0594	Thursday	0.0040	10%
4210100234	0.0644	Sunday	0.0574	Wednesday	0.0070	5%
4210100244	0.0535	Saturday	0.0417	Thursday	0.0118	5%

7. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

In the period 1995 to 1999, Atlanta showed a weekly cycle where O_3 concentrations were highest on Fridays and lowest on Mondays. Chicago and Philadelphia, on the other hand showed weekend increases in O_3. All three areas shared common features in O_3 diurnal profiles, notably higher morning O_3 on Sundays, followed by Saturdays, relative to weekdays. The higher morning concentrations were a result of reduced titration by NO emitted by traffic. However, the dynamics of O_3 production differed and led to differences in the peak O_3 behavior by day of the week.

PM_{10} at all three sites showed lower concentrations on weekends relative to weekdays. Diurnal PM_{10} profiles were particularly informative in Philadelphia, where they showed a behavior characteristic of primary emissions. $PM_{2.5}$ monitoring started in 1999. In Atlanta, high $PM_{2.5}$ concentrations were typically observed late in the work week, and low $PM_{2.5}$ concentrations were observed on Mondays and Sundays. In Chicago and Philadelphia, $PM_{2.5}$ concentrations were high on some weekend days and some weekdays. The short $PM_{2.5}$ record period prevents us from drawing any meaningful conclusions from the $PM_{2.5}$ data.

We examined several hypotheses for the weekly behavior of O_3 in Atlanta, Chicago, and Philadelphia. The ones most likely to explain the weekend increase in O_3 in Chicago and Philadelphia were (1) the increased VOC/NO_x ratio during weekends, (2) the reduced O_3 titration by NO emissions during morning commute on weekends, and (3) the carry-over of VOC (CO as surrogate) in the predawn hours. The weekly cycle of O_3 in Atlanta seemed to be driven by the carry-over of NO_x or NO_y. VOC/NO_x ratio and NO titration in the morning had little effect on O_3. We identified some changes in the spatial distribution of NO and CO emissions during the weekends, but could not correlate them to the weekly behavior of O_3. Changes in PM composition in a metropolitan area seemed to be driven by reduced traffic and possibly a higher dominance of gasoline vehicles (compared to diesel vehicles) in the urban weekend traffic fleet. The possible relationship between PM, solar/UV radiation, and O_3 was not supported by ambient measurements available for this study.

The weekly behavior of O_3 has changed from the late 1980's to the late 1990's. In Atlanta, the difference in O_3 between different days of the week has increased. In Chicago and Philadelphia, weekend increases in O_3 were observed in both periods, but the day with the lowest O_3 seemed to be different in the two time periods.

Our recommendations for future work are as follows:

1. Investigate the reasons for long-term changes in weekly behavior.

Long-term changes in the weekly behavior from the late 1980s to the late 1990s could have important implications for future trends. The small differences in weekday vs. weekend O_3 in the Atlanta metropolitan area data set of 1986 to 1990 is particularly interesting. We hypothesized that the impact of anthropogenic pollution on O_3 may have been smaller in the earlier time period. An analysis of the concentration of O_3 precursors, such as NO_x and VOC (CO as a surrogate) may reveal the reasons for the long-term changes in the weekly behavior. For Chicago and Philadelphia, it would be interesting to test if the same hypotheses (VOC/NO_x ratio, morning NO emissions, and carry-over of CO or VOC) can explain the weekly behavior of O_3.

2. Reanalyze $PM_{2.5}$ day-of-the-week behavior when more data are available

The $PM_{2.5}$ data records analyzed in this work were only one year in length, since $PM_{2.5}$ monitoring started in 1999. More consistent day-of-the-week trends will likely be obtained if $PM_{2.5}$ can be reanalyzed in a few years' time.

3. Analyze VOC/PM composition data when better data are available.

Routine VOC monitoring does not seem to generate the detailed measurements required for the analysis of different sources or source contributions between weekday and weekends. Routine PM composition monitoring is conducted in very few metropolitan areas. As mentioned in Section 5, some PM supersites may provide useful data for analysis of PM sources in the not-so-distant future. One possibility is to analyze data from special field programs. However, such programs provide episodic information that may lack in statistical power when used to analyze weekend-weekday differences.

Under CRC and NREL sponsorship, a field program has been conducted to specifically investigate weekday/weekend changes in emissions activities. A similar program may be used to generate the speciated VOC (including fingerprint species) and PM composition information that could be used to identify different VOC/PM source emissions.

4. Reanalyze NO_y when more and better data available.

NO_y has been shown to correlate with O_3 in Atlanta. In addition, it is an important indicator species. More reliable indicator results can be obtained when more NO_y data are available with corresponding VOC (e.g., formaldehyde) data. However, current NO_y data may be unreliable and suffer from artifacts. The calculation of NO_z, another indicator species, relies on accurate NO_x and NO_y measurements. In some cases, it is difficult to interpret the results without knowing what NO_y comprises exactly. Therefore, some of the hypotheses may be worth revisiting once more and better NO_y data are available.

5. Incorporate meteorological considerations.

The direction and magnitude of the weekend-weekday difference maybe a function of location (e.g., CARB, 2000). However, a spatial analysis of the weekly behavior would only be meaningful if a location can be defined meteorologically as upwind or downwind. In the metropolitan areas studied in this work, a well-defined wind direction was not identified using monthly wind rose data. It may be necessary to analyze hourly/daily meteorology to determine if a site is upwind or downwind at a given time. Then, meaningful results regarding the geographic variability of the weekly behavior within a metropolitan area can be displayed using clock plots and maps.

6. Airshed modeling

The causes of the weekly behavior of O_3 identified in this data analysis study should be verified by airshed modeling. Of particular interest is the weekly behavior of O_3 in Atlanta. Atlanta's weekly cycle of concentrations is very different from those observed in Chicago and Philadelphia in this study. The latter two areas show similar O_3 increases in the weekend as the Los Angeles basin. The measurement campaign and modeling studies currently being conducted to understand the weekend O_3 increase in Los Angeles will likely provide a good understanding of the weekend O_3 increases in those two areas as well. Atlanta's weekly cycle may be driven by different factors, e.g. NO_x or NO_y carry-over. Regional modeling could be used to elucidate the governing processes of this weekly behavior, and to investigate the relationships between O_3 and the concentrations of NO_x, NO_y, and CO for different time periods.

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