2 Analysis of Variations in Ozone & Ozone Precursors

2.6 Day-of-week Differences in Ozone Quenching Near the Ground

2.6.1 Abstract

This chapter presents evidence that day-of-week differences in the destruction (quenching) of ozone by nitric oxide (NO) emissions near ground level may play an important role in determining the ozone WE effect.

Nitrogen oxides (NO_x) are predominantly emitted (90% or more) in the form of nitric oxide (NO). These NO emissions quench ozone (O_3) through a rapid reaction in which NO and O_3 combine to form nitrogen dioxide (NO_2) and oxygen (O_2). Analyses of routine and specialized data indicate that more ozone quenching occurs throughout the day on WD compared to WE. A large part of the ozone WE effect may not be due to complex photochemistry. Instead, it may be due greater NO emissions on WD that quench ozone at the surface and lesser NO emissions on WE that do not quench as much ozone at the surface.

Near ground level, NO is emitted by ubiquitous sources, such as cars, trucks, and off-road engines. In the South Coast Air Basin (SoCAB), ambient levels of NO_x during the daylight hours are about 25% lower on Saturdays and 40% lower on Sundays compared to mid-week levels. Therefore, the amount of ozone quenching at the surface is much less on WE than on WD.

Additional analyses of ozone data from Livermore, CA., oxidant data from ozonesondes during SCOS97, and oxidant (O_3 plus NO_2) from routine monitoring in the SoCAB all indicate substantially greater amounts of surface ozone quenching on WD than on WE.

This issue is important because surface ozone quenching does not represent the ozone-forming system above the surface (100 to 1500 meters aloft), where almost all of the ozone measured at the surface is first formed. Regulations that reduce NO_x emissions may be successful in reducing surface ozone levels by reducing the bulk of ozone formation aloft on all days of the week.

2.6.2 Background

It is well known that nitric oxide (NO) molecules will combine quickly with ozone (O_3) to form nitrogen dioxide (NO_2) and common oxygen (O_2).[1] In the vicinity of freshly emitted NO, this reaction destroys much ozone and is sometimes called "ozone quenching" or "ozone scavenging" or “ozone titration”.

In Chapter 3 of the Staff Report, the seventh hypothesis proposes that surface ozone quenching plays a significant role in causing the ozone WE effect. The hypothesis is concerned with continuous quenching throughout the day, rather than a limited period of quenching in the early morning hours. This possibility is important because the ozone-quenching phenomenon is limited to the air near the surface and does not represent ozone formation and persistence in the air aloft, where most ozone is formed. It is possible, and even likely, that ozone formation aloft is routinely limited by the availability of NO_x (NO_x-limited) though measurements at the surface, where freshly emitted pollutants are always present in relatively large amounts, seem to indicate the system is limited by the availability of VOC (VOC-limited).

2.6.3 Analyses

The four analyses discussed below support the view that ozone quenching depresses surface ozone measurements more on weekdays than it does on weekends.

2.6.3.1 Day-of-week profiles for traffic and NO_x.

Emissions of NO from ubiquitous traffic on roads in urbanized areas are relatively abundant on weekdays compared to weekends, particularly on Sundays.

In Chapter 5.1 and Chapter 5.3, we analyzed patterns in traffic data. In the latter chapter, we also compared these patterns to the corresponding patterns in air quality data. These analyses were limited to the SoCAB, but they yielded significant results that likely represent other urbanized areas.

Motor vehicle activity differs dramatically between weekdays and weekends, especially Sundays. The largest discrepancy between weekdays and weekends is between 6:00 a.m. and 11:00 a.m., with lesser but possibly important differences between 3 p.m. and 7 p.m. **Figure 2.6-1** shows day-of-week composite profiles for hourly volumes of light-duty vehicles at 15 Weigh-in-Motion (WIM) stations in the SoCAB. **Figure 2.6-2** shows these patterns for heavy-duty vehicles for the same stations. These two figures are based on data archived by the California Department of Transportation throughout the year 2000. They are similar to the figures shown in Chapter 5.3, but they represent a full year of more recent data rather than the ozone season of 1997. The most notable feature is the 50-75 percent decrease in traffic on WE mornings compared to the WD commute. During the typical afternoon commute, WE traffic is down 25 percent compared to WD activity. Less noticeable but significant features of traffic are greater midday volumes on WE (especially Saturday) compared to WD and increased activity in the late evening (Friday and Saturday) and early morning (Saturday and Sunday).

Figure 2.6-3 (a copy of Figure 5.3-2) shows composite profiles for day-of-week NO_x measurements at eleven air quality monitors in Los Angeles and Orange Counties, many of them near the WIM stations used to characterize traffic patterns. The profiles for traffic and for NO_x are consistent with emission inventory data for the year 2000 that indicate over 60% of NO_x emissions in the SoCAB are produced by on-road motor vehicles. When all mobile sources are considered, they account for almost 90% of the NO_x emissions in the SoCAB (see Table 5.3-1). Source tests show that anthropogenic NO_x emissions are predominantly in the form of NO, which is converted (oxidized) to NO_2 and other nitrogen-containing species in the atmosphere.[1]

From the air quality and emissions inventory data, it is clear that NO_x emissions are much greater on weekdays than on weekends, especially on Sundays. The opportunity for the NO in NO_x emissions to quench ozone near the surface is, therefore, much greater on weekdays than on weekends.

2.6.3.2 Different weekend effects at two locations in Livermore, CA

The highest ozone concentrations in the San Francisco Bay Area Air Basin are typically measured at Livermore. In 2000, the Livermore monitor was moved about 1.5 km. The move was precipitated by analyses showing that NO emissions from a bus terminal a short distance upwind of the old location were quenching ozone and depressing the measured ozone concentrations. The depressed measurements did not appropriately represent ozone in the general Livermore area.

Like most public transit systems, activity at the Livermore bus terminal was much lower on weekends than on weekdays. Route schedules from the Livermore Amador Valley Transit Authority show greatly reduced service on Saturdays and no service at all on Sundays. At the old monitoring location, daily maximum ozone concentrations on Sundays averaged about 32 percent higher compared to Fridays.

However, for 2000 and 2001, the first two ozone seasons at the new monitoring location, the daily maximum ozone on Sundays averaged only 17 percent higher compared to Fridays. This was not due to a decrease in ozone on Sundays; rather, the emissions from the bus terminal were no longer quenching ozone around the monitor on weekdays. The ozone measurements on Fridays now represent the general Livermore area. As ozone on Fridays increased relative to ozone on Sundays, almost half of the apparent WE effect at Livermore disappeared when the monitoring site was relocated away from the bus terminal.

This analysis shows that a significant portion of the ozone weekend effect can be due to day-of-week differences in ozone quenching at the surface by fresh NO emissions. Emissions from bus activity at the Livermore terminal are a small fraction of the total NO_x emissions in the Livermore area and their effect on general ozone levels would have been minor. However, on-road and off-road motor vehicles are ubiquitous, so "local" NOx sources exist everywhere. It is possible that much of the remaining 17 percent difference between Sundays and Fridays at the new Livermore location is due to ground level suppression of ozone due to quenching by NO emissions from sources that are plentiful on weekdays but relatively scarce on weekends.

2.6.3.3 Vertical profiles for NO_x and ozone

Vertical profiles for NO_x and ozone are not commonly available apart from intensive field studies. Major field studies of ozone in Southern California were conducted in 1987 and 1997. Both studies included some vertical profiles of ozone and/or NO_x measured by some combination of aircraft, ozonesondes (balloons that carry instruments measuring total oxidant, temperature, and relative humidity), or lidar (light detection and ranging) instruments.

The two field studies, however, were not designed with the weekend effect in mind. In fact, the 1987 study sought representative weekday episodes, while the 1997 study sought representative weekend episodes. Also, ambient ozone concentrations and emissions of ozone precursors both declined dramatically in the ten years between these studies. As a result, differences between WD and WE in these studies are not easily generalized to routine conditions.

Nevertheless, an analysis of the ozonesonde data from the 1997 Southern California Ozone Study suggests that afternoon differences between ozone at the surface and ozone at 100 meters aloft are greater on weekdays than on weekends. That is, ozone concentrations at the surface are more depressed (relative to the concentrations at 100 m) on WD than they are on WE.

For each ozonesonde, we estimated the ozone concentration at 100 meters by interpolating between the nearest values below and above 100 meters. The measurements closest to the surface (after equilibration) were used to estimate the surface concentration. The results, shown in **Table 2.6-1**, indicate that ozone on weekdays does not mix down to ground level where surface monitors can measure it. The likely cause is an extra measure of quenching by fresh NO emissions near the surface on weekdays that does not occur on weekends.

2.6.3.4 Comparison of total oxidant on weekdays and weekends

If surface emissions of NO determine a large part of the ozone WE effect by depressing surface ozone concentrations through quenching, the weekend effect for the sum of ozone and NO_2 (total oxidant) should be smaller than the ozone weekend effect. **Table 2.6-2** summarizes the weekend effect for total oxidant in the SoCAB. The total oxidant data represent the maximum hourly values for hours between 10 a.m. and 6 p.m. for the ozone seasons (May through October) from 1998 through 2000. For 22 locations with sufficient data, the largest weekend effect for total oxidant was 9% and the basinwide average was 5%. These are drastically smaller than the values in the SoCAB for the ozone weekend effect at the same 22 locations, for which the largest was 43% and the average was 20%.

The WE effect for total oxidant implies that the ozone WE effect in the SoCAB and elsewhere may be largely due to ozone quenching by NO emissions from sources at ground level that are plentiful on weekdays but scarcer on weekends.

2.6.4 Conclusions

The analyses presented in this chapter strongly support the possibility that a large part of the ozone WE effect is caused by greater quenching of ozone near the surface by NO emissions that are plentiful on WD but relatively scarce on WE.

Ozone concentrations aloft may not follow the WD vs. WE pattern of ozone at ground level, in part because NO emissions are converted to NO_2 within a few tens of meters of the surface. Ozone quenching by NO is, therefore, at a minimum in the air aloft where most ozone is formed.

Although O_3 quenching has always occurred, its impact has become more noticeable (occurs at more sites) as urbanization and traffic have increased.

For this and other reasons, the ozone WE effect is not, as some have suggested, a "real-world" test on the likely impact of NOx emission reductions planned for California in the coming decade(s).

2.6.5 References

1. Harley, R.A. Impact of Improved Emissions Characterization for Nitrogen-Containing Air Pollutants for the South Coast Air Basin, Report to the California Air Resources Board (Contract 93-310), 1996, California Air Resources Board, Research Division, Sacramento, CA.

Table 2.6-1. WD and WE differences between surface ozone and ozone at 100 m above ground level expressed as percent of ozone at 100 m; data from 2 p.m. ozonesondes during the 1997 Southern California Ozone Study.

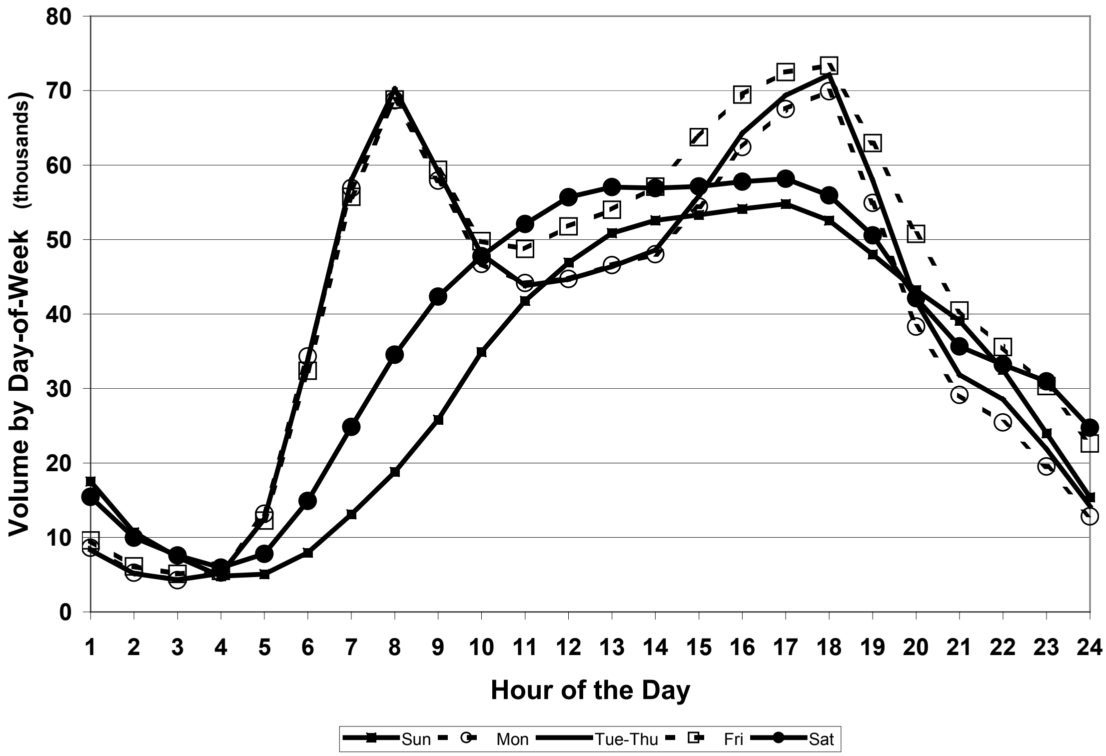
	Weekdays		Weekends	
Location	**Average**	**Maximum**	**Average**	**Maximum**
Anaheim	22% (9)*	78%	13% (4)	17%
Los Angeles	9% (7)	16%	8% (4)	10%
Northridge	17% (8)	34%	13% (4)	20%
Pomona	23% (9)	35%	17% (4)	23%
Riverside	20% (6)	62%	9% (4)	11%

* The number of 2 p.m. ozonesondes available is given in parentheses next to the average.

Table 2.6-2. Comparison of total oxidant (O_3 plus NO_2) at locations in the South Coast Air Basin. Values are means of daily maxima from 10 a.m. to 6 p.m. for May – October from 1998 through 2000.

	Total Oxidant (ppb)		Difference
Location	**WD**	**WE**	**(% of WD)**
Hawthorne	69	71	2.5%
Pasadena	98	103	4.4%
Pico Rivera	97	102	6.1%
San Bernardino	107	116	8.5%
La Habra	85	90	6.9%
Fontana	105	114	8.6%
Reseda	78	79	0.9%
N. Long Beach	76	79	3.6%
Azusa	110	118	7.2%
Upland	109	119	8.7%
Burbank	104	105	0.6%
West L.A	67	69	2.9%
Lynwood	75	78	4.3%
Riverside	94	100	7.2%
Anaheim	78	83	6.7%
Glendora	109	117	7.6%
Santa Clarita	92	94	1.6%
Pomona	106	114	8.1%
Los Angeles - N. Main	91	94	3.0%
Costa Mesa	63	65	3.7%
Lake Elsinore	88	91	3.5%
Banning	95	95	-0.8%
Basin Average			**4.8%**

Figure 2.6-1. Freeway activity of light-duty vehicles – composite of 2000 data from 11 Weigh-in-Motion stations in California's South Coast Air Basin.



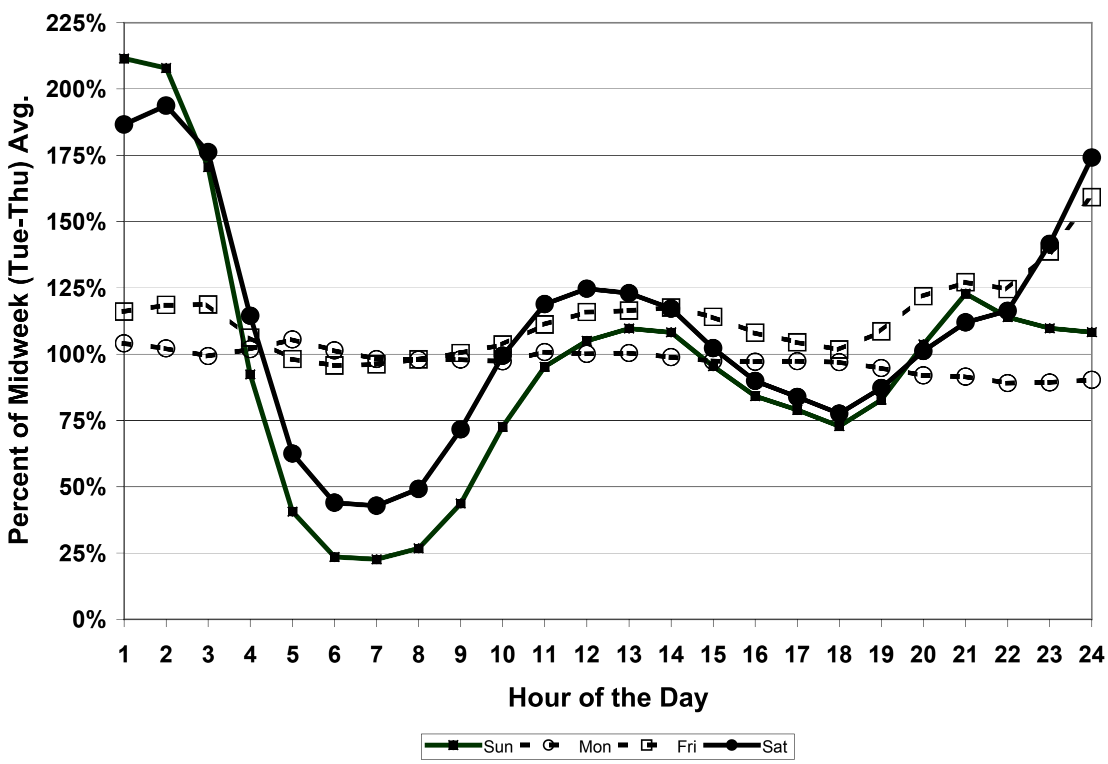
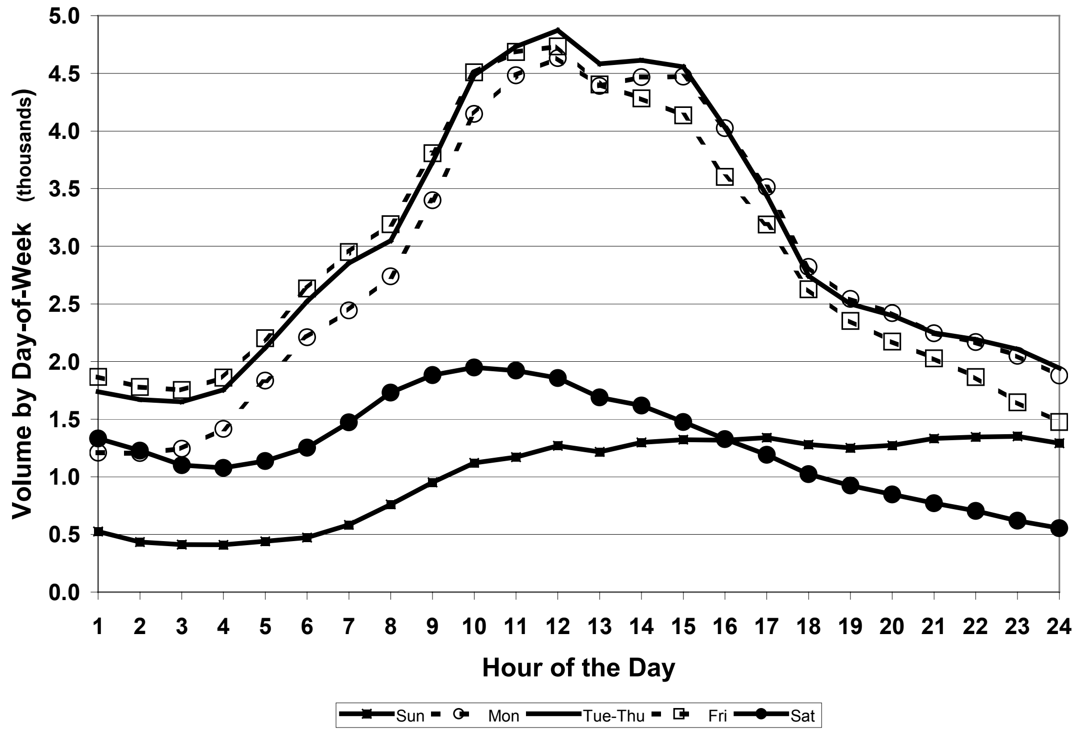


Figure 2.6-2. Freeway activity of heavy-duty vehicles – composite of 2000 data from 11 Weigh-in-Motion stations in California's South Coast Air Basin.



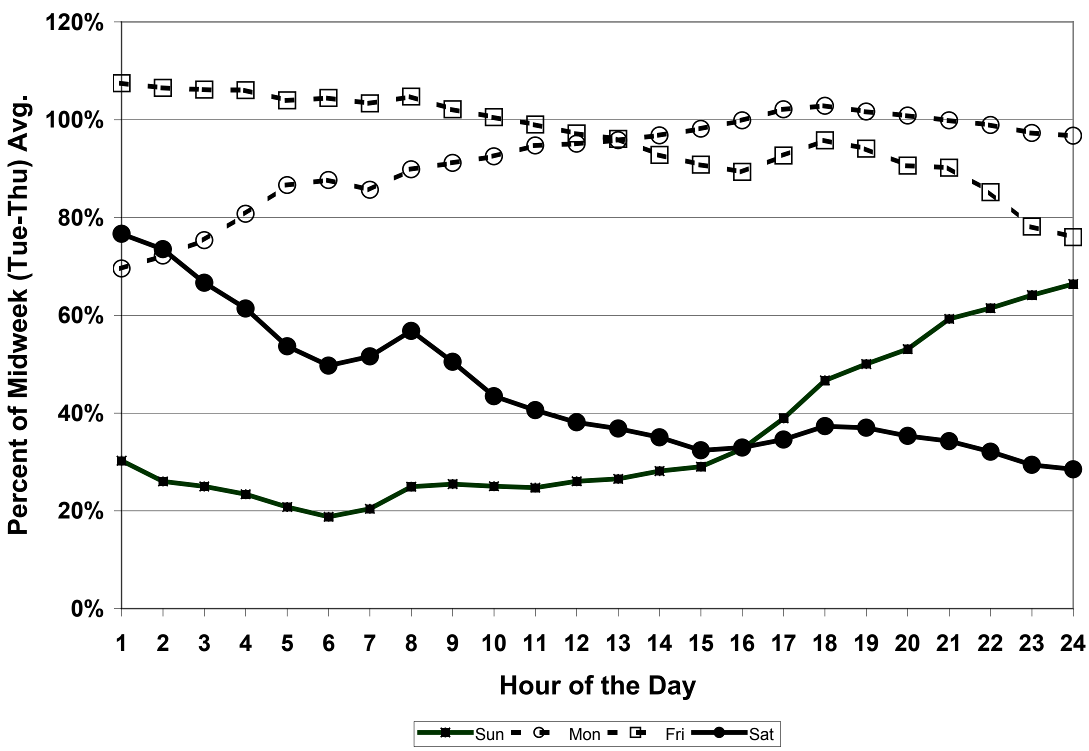
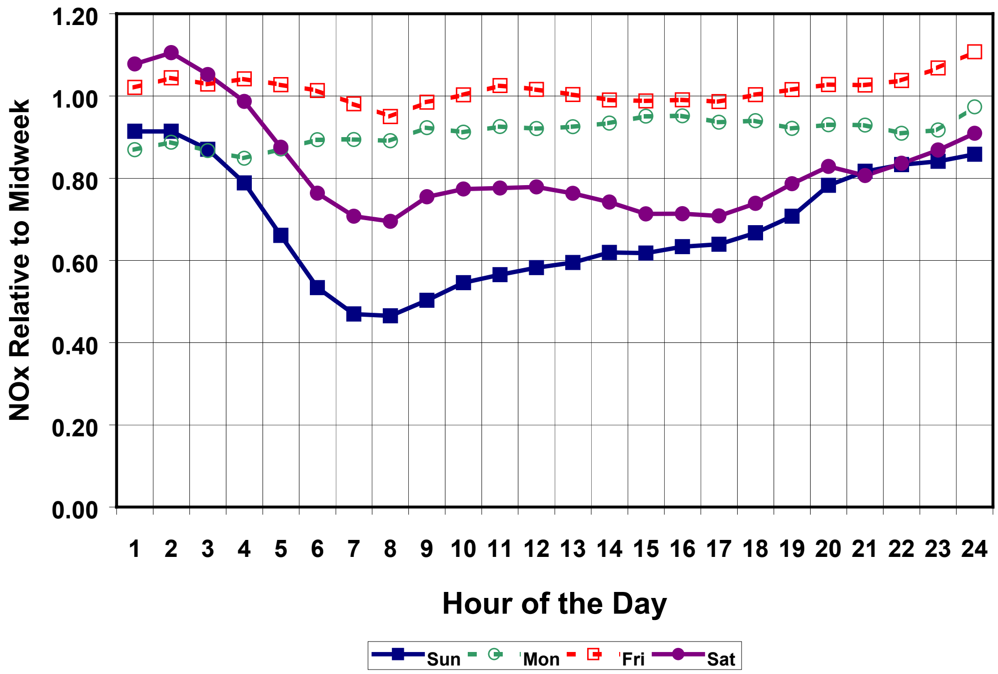


Figure 2.6-3. Hourly values of NO_X by day-of-week expressed as a percent of midweek (Tue-Thu) value; composite of 11 sub-regions of the South Coast. Air Basin



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