4. STATISTICAL COMPARISONS OF WEEKDAY AND WEEKEND MEASUREMENTS

The objective of this section is to characterize weekday and weekend variations of ambient concentrations of PM, particulate nitrate, and nitric acid (HNO_3) as completely as possible. Previous work has shown that concentrations of PM_{10} mass in the SoCAB are lower on weekends than on weekdays, whereas PM nitrate concentrations do not show consistent weekday/weekend changes (Austin et al., 2001). This section first examines gas-phase measurements from several special studies, then compares weekend and weekday values of particulate species using special-study data, and finally provides comparisons using routine monitoring data. It will be shown that both routine and special-study data exhibit lower weekend than weekday concentrations of key primary species, including NO_x, CO, VOCs, PM_{10}, and TSP. In contrast, HNO_3 and particulate nitrate show no statistically significant differences between weekdays and weekends, and thus appear nonresponsive to significant variations in ambient concentrations of NO_x.

Special Studies: Ozone, PAN, and HNO_3

The CSMCS-1986, SCAQS-1987, CADMP-1993, and SCOS-1997 special studies provide useful information for evaluating the weekend effect. Data from the CSMCS indicate elevated ozone and PAN concentrations on weekends, as well as hourly variations in HNO_3 concentrations at Glendora (see Figure 6). However, over a 24-hour period, the weekend and weekday levels of HNO_3 were not very different. Similarly, there was little 24-hour change in HNO_3 concentrations, but some hourly differences at Claremont during the SCAQS study (see Figure 7). The CADMP evaluation in 1993 measured elevated ozone and luminol-measured PAN on weekends compared to weekdays at Azusa; again, there was little variation in the 24-hour average HNO_3 (see Figure 8). The SCOS reveals evidence for weekday/weekend differences in NO_y (NO_x + other oxidized nitrogen species), PAN, and HNO_3 measurements during the summer of 1997: Figure 9 shows weekday NO_y levels were higher than weekend NO_y at several sites (the NO_y was predominantly NO_x). Data from the northern end of the SoCAB (Calabasas and Cajon Pass), as shown in Figure 10, also showed higher NO_y concentrations and lower PAN values on weekdays than weekends. Azusa and Simi Valley had higher weekend than weekday PAN concentrations during this same period (see Figure 11). Finally, HNO_3 showed little if any 24-hour concentration difference between weekend and weekday measurements at Azusa, Simi Valley, Banning and UC Riverside (see Figure 12).

The CSMCS-1986, SCAQS-1987, CADMP-1993, and SCOS-1997 special studies together suggest that weekend levels of HNO_3 typically were not significantly different from weekday concentrations, when averaged over 24-hour periods. This result is important in several ways. First, it is a different response than was shown by PAN or ozone, both of which had higher weekend than weekday concentrations. Second, it indicates a general lack of responsiveness of HNO_3 to changes in NO_x levels. Finally, because HNO_3 is the immediate precursor of particulate nitrate, the results imply that there may exist a similar lack of responsiveness of particulate nitrate to changes in NO_x levels.

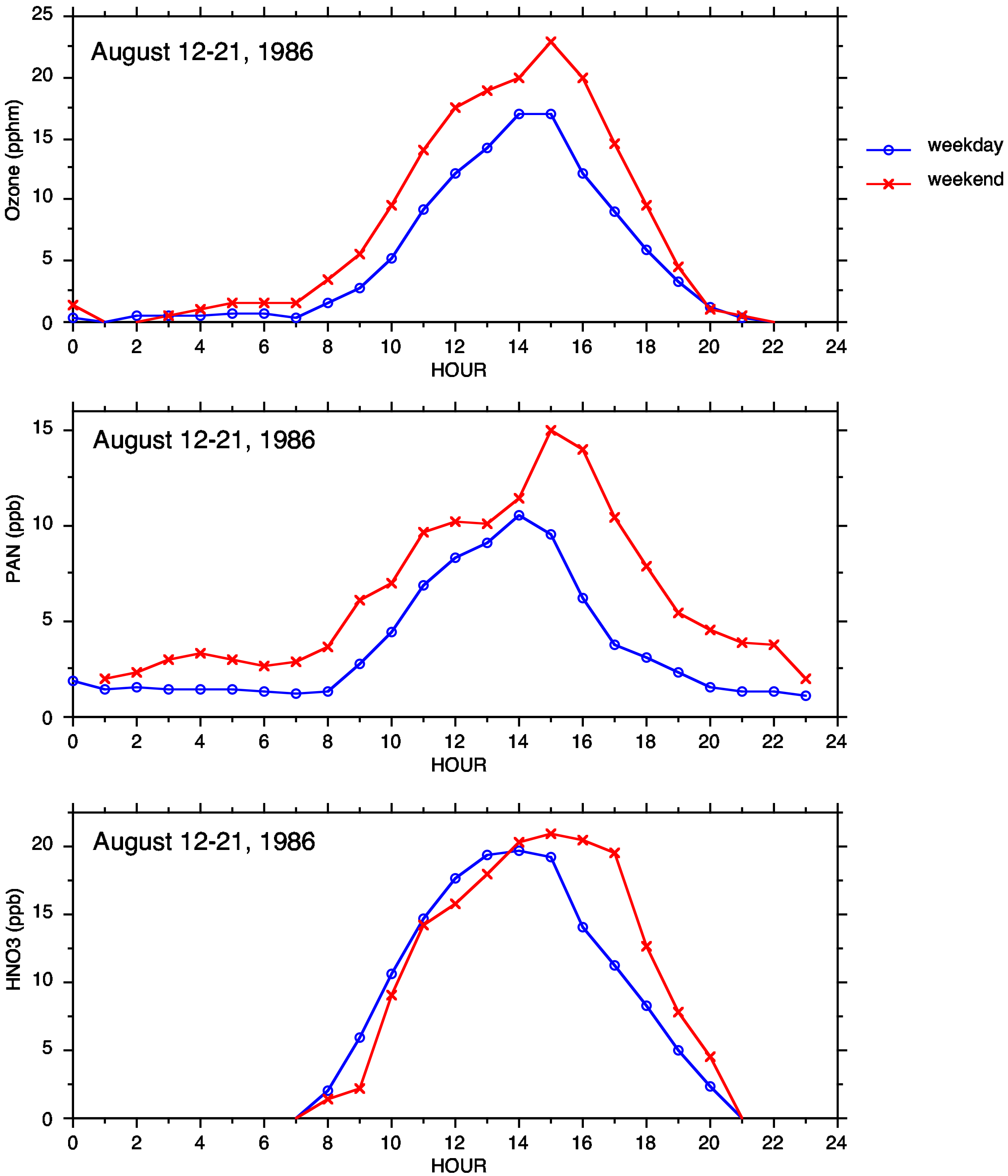

Figure 6. Hourly differences between weekday and weekend measurements of ozone, PAN, and HNO_3 at Citrus College (~2 mi east of Azusa) on Aug. 12-21, 1986 (Tuazon et al., 1995; data from CSMCS).

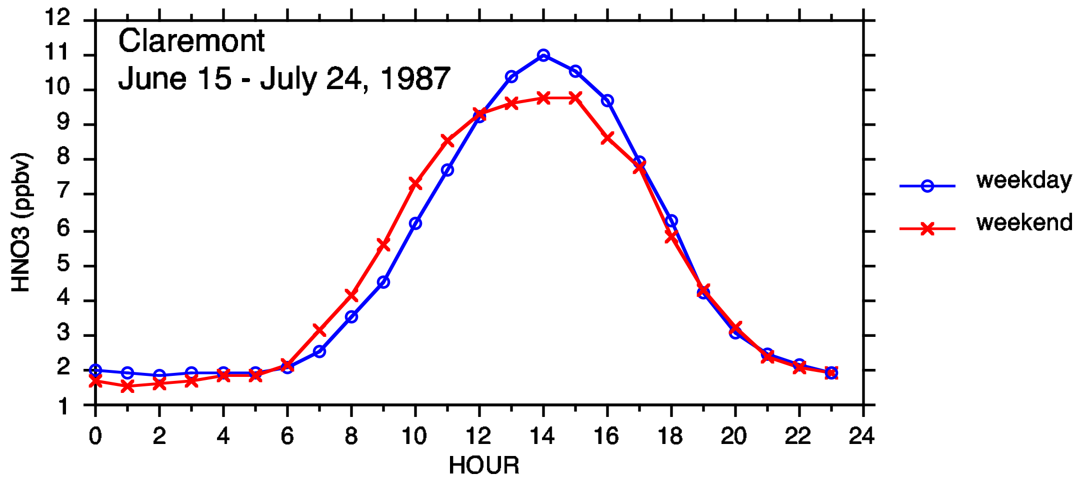

Figure 7. Hourly differences between weekday and weekend measurements of HNO_3 at Claremont on June 15-July 24, 1987 (Tuazon et al., 1995; data from SCAQS).

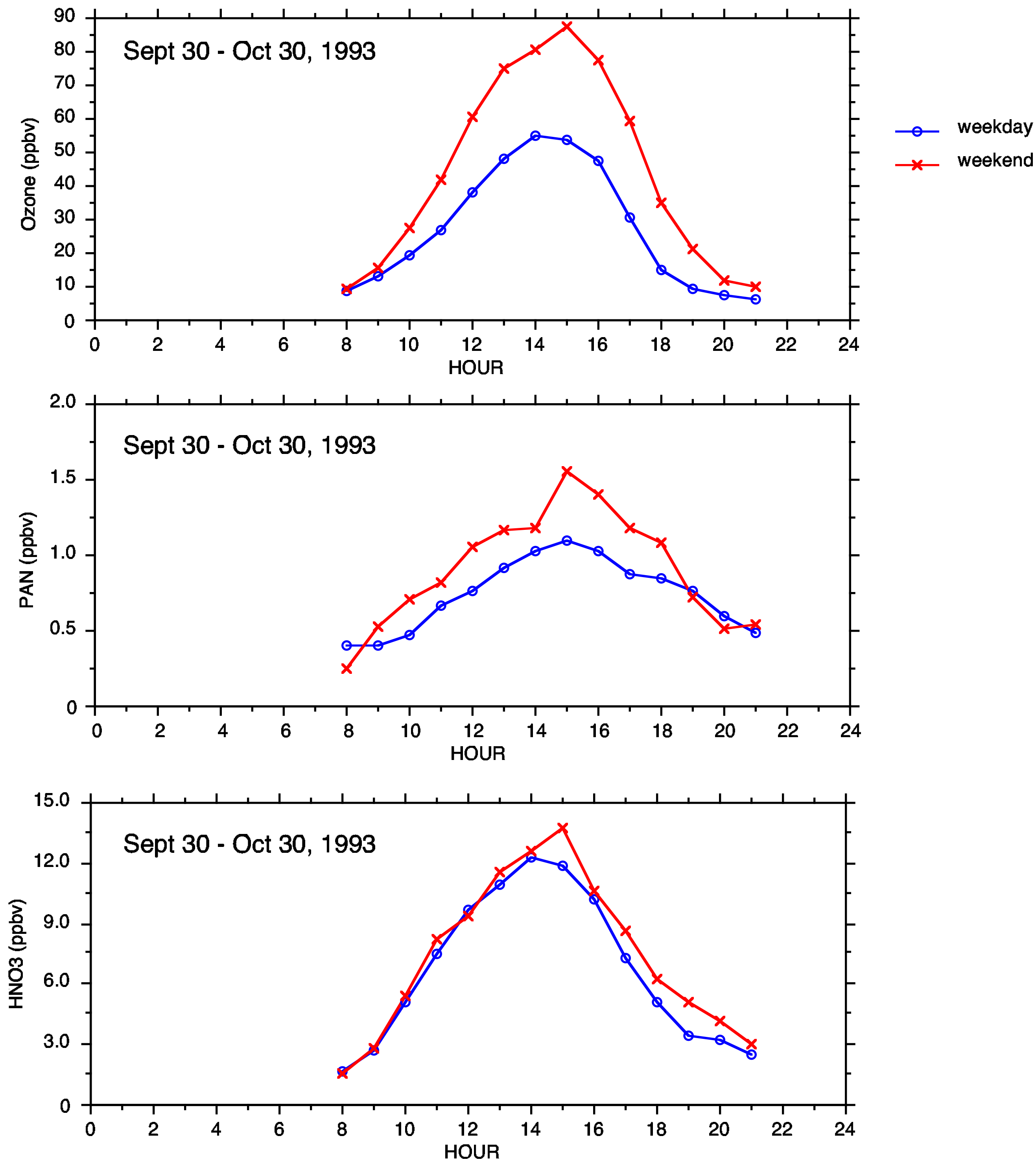

Figure 8. Hourly differences between weekday and weekend measurements of ozone, PAN, and HNO_3 at Azusa on Sept. 30-Oct. 30, 1993 (Tuazon et al., 1995). PAN was measured using the luminol method. HNO_3 was measured by tunable diode laser absorption spectroscopy (TDLAS).

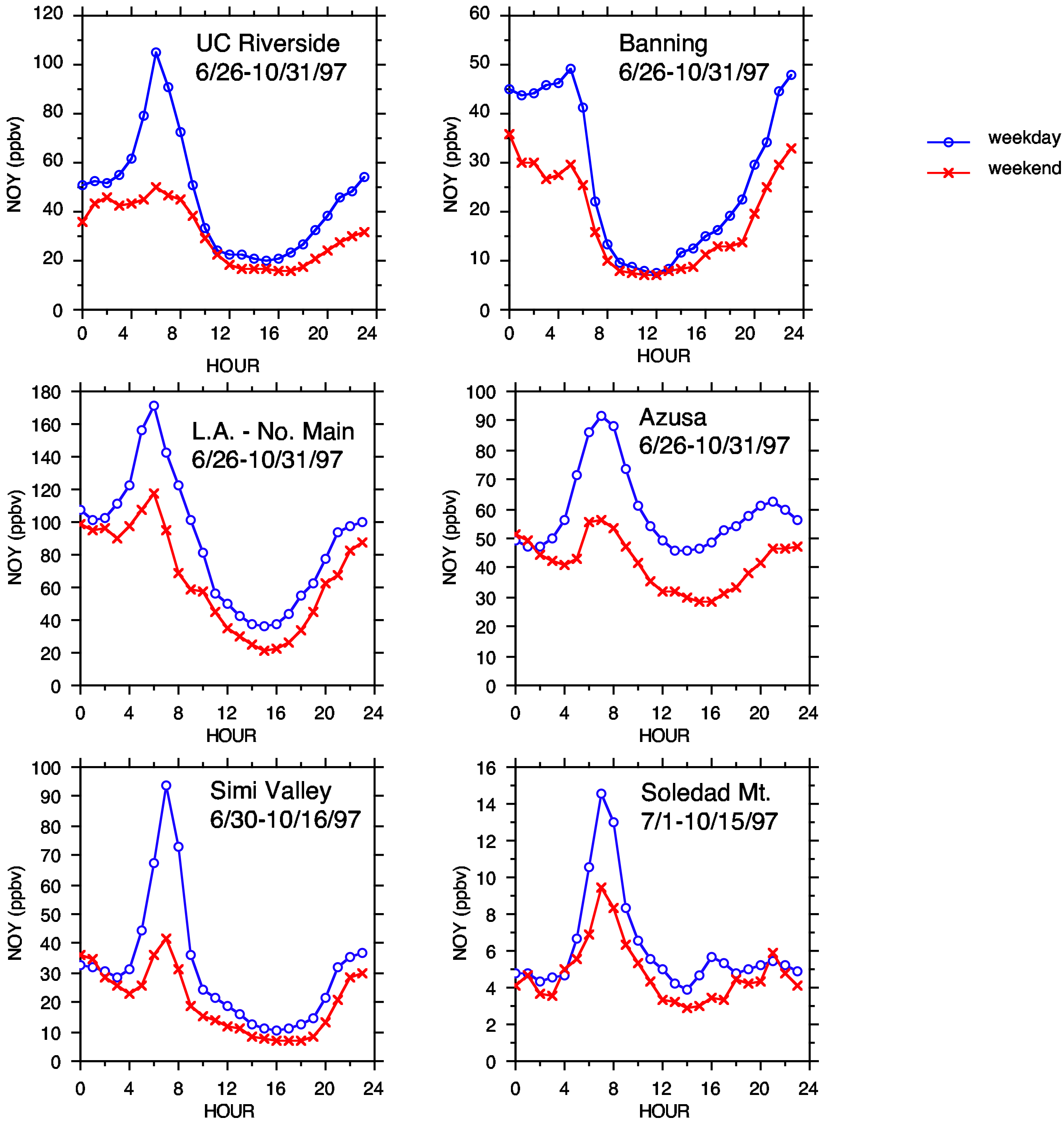

Figure 9. Hourly differences between weekday and weekend measurements of NOy at selected southern California sites on June-Oct. 1997 (Fujita et al., 1999; CE-CERT data).

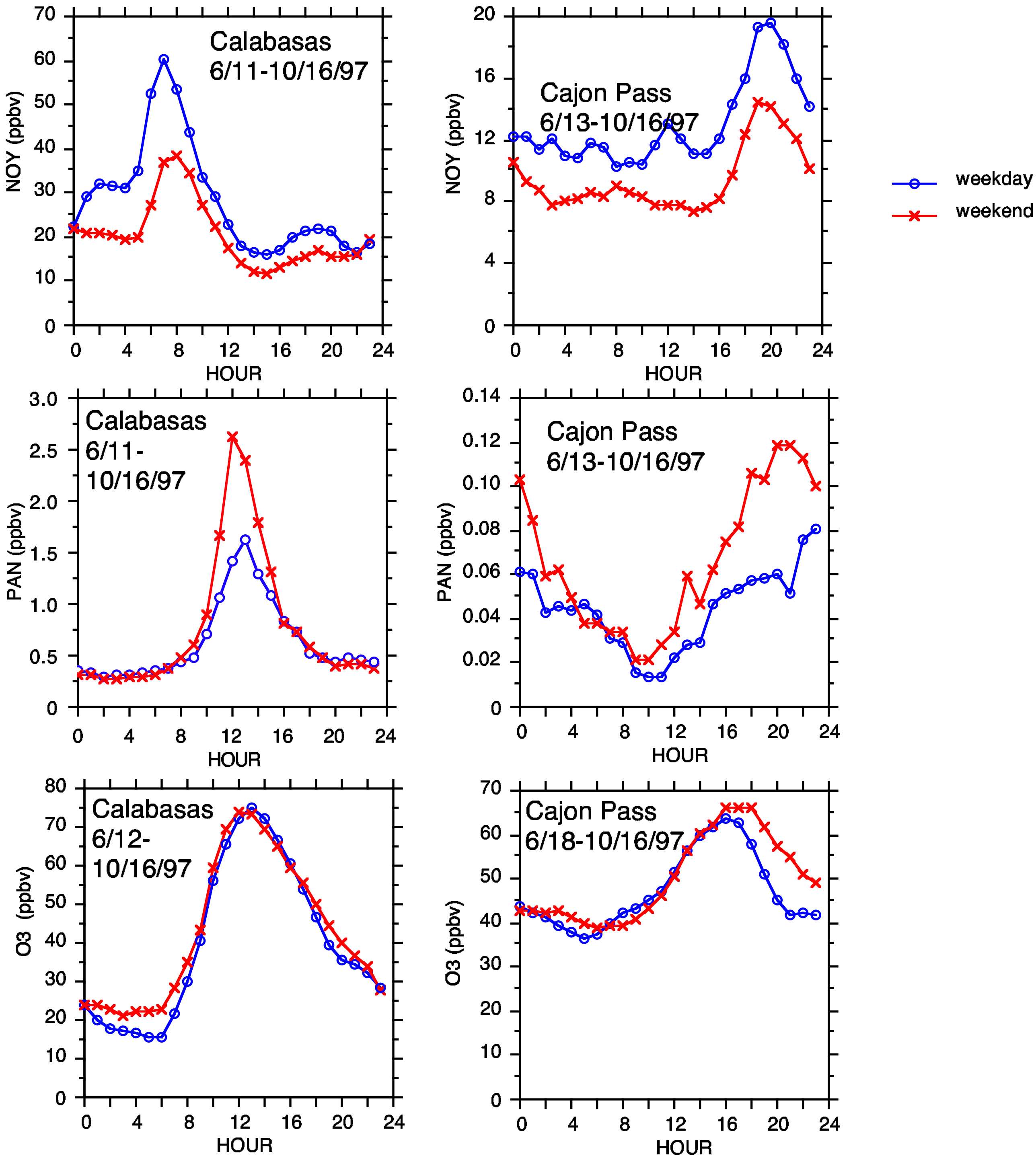

Figure 10. Hourly differences between weekday and weekend measurements of NOy, PAN and ozone at Calabasas and Cajon Pass on June - Oct. 1997 (Fujita et al., 1999; AVES data).

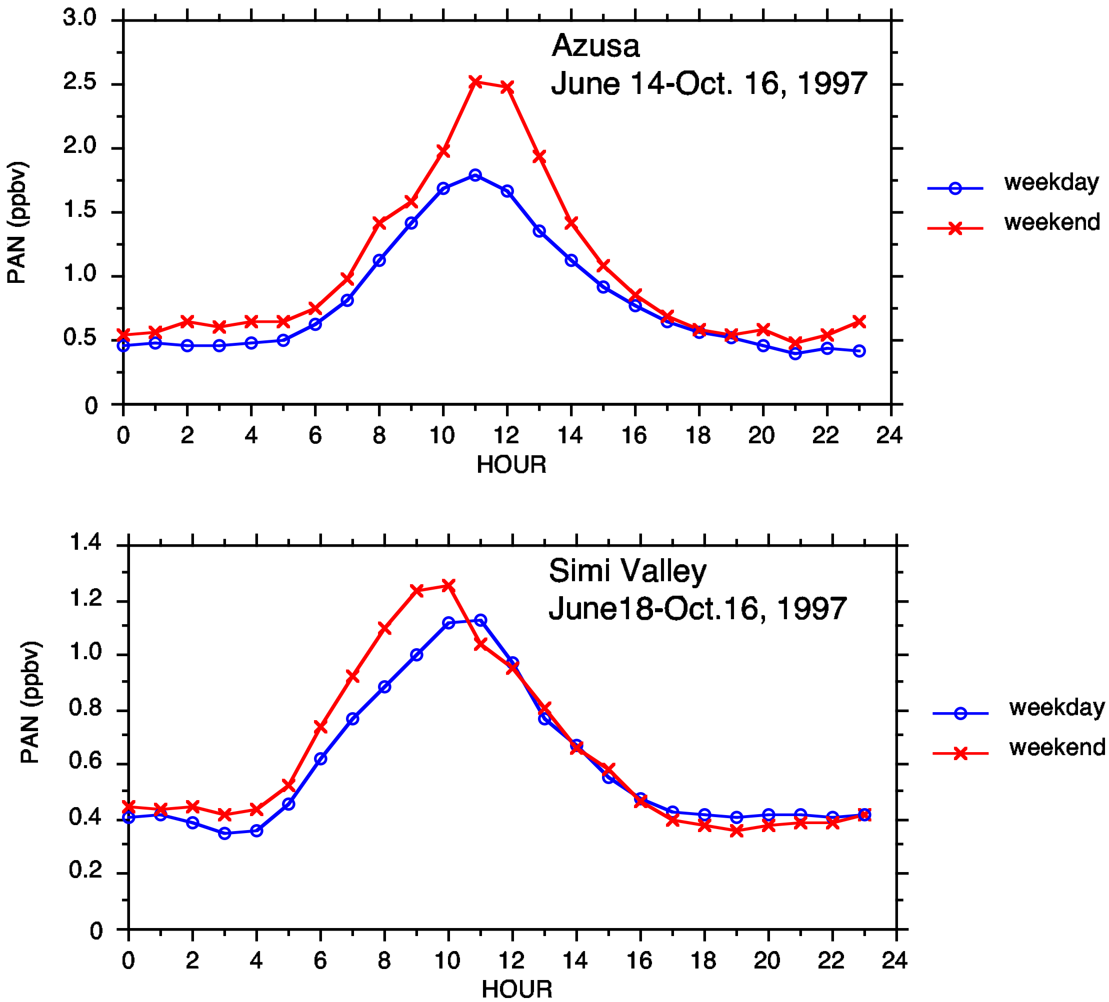

Figure 11. Hourly differences between weekday and weekend measurements of PAN at Azusa and Simi Valley on June - Oct. 1997 (Fujita et al., 1999; DGA data).

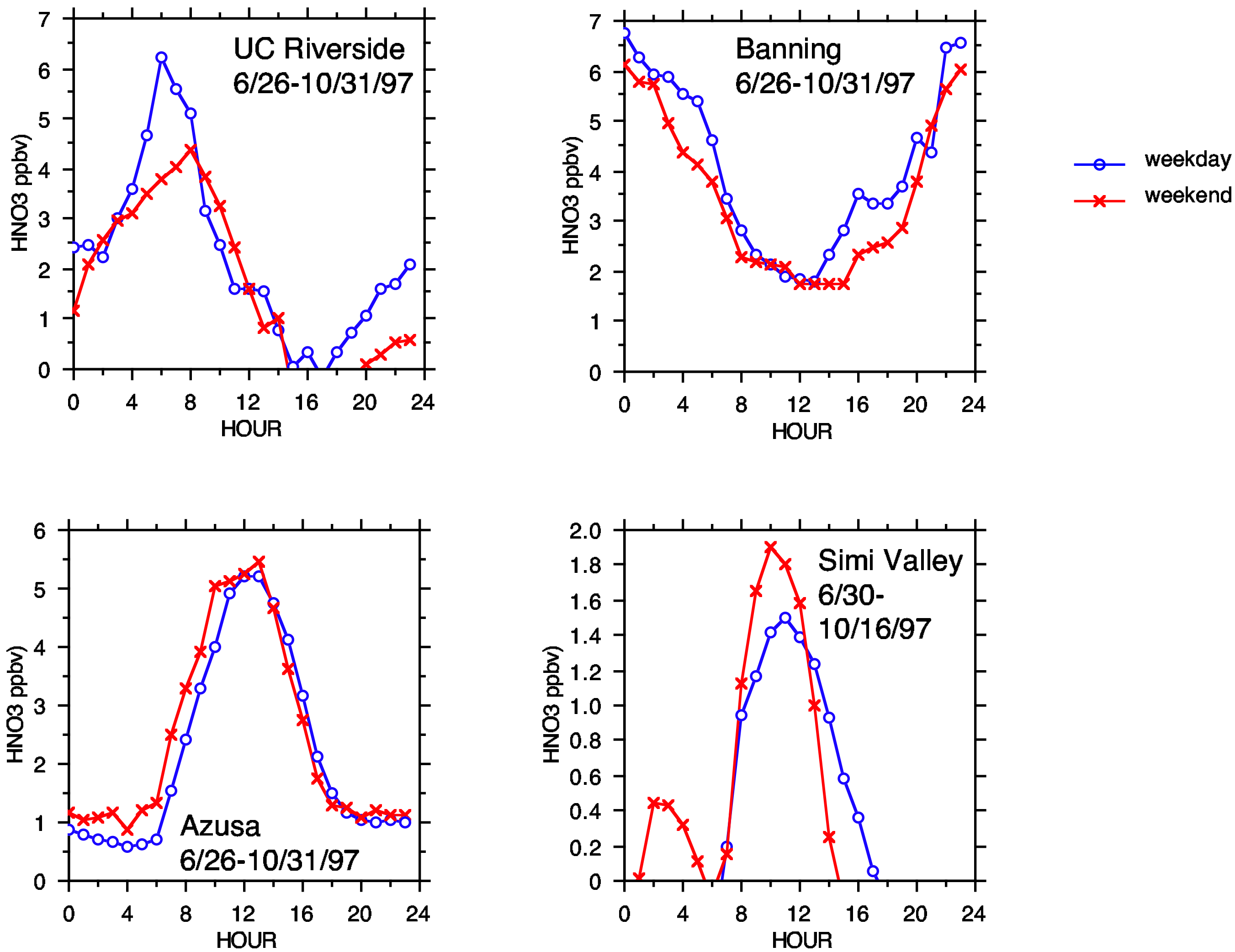

Figure 12. Hourly differences between weekday and weekend measurements of HNO_3 at Azusa, Simi Valley, Banning and UC Riverside on June - Oct. 1997 (Fujita et al., 1999; CE-CERT data).

CADMP Particulate and Gas-Phase Measurements

The CADMP operated three sites in southern California (Long Beach, downtown Los Angeles, and Azusa) from 1988 through 1994 on a once-per-six days, twice-a-day (6 am to 6 pm and 6 pm to 6 am) schedule. Because both daytime and nighttime samples were collected for several species (PM_{10}, $PM_{2.5}$, SO_2, NO_2, NH_3, HNO_3), weekday/weekend differences may be investigated separately by day or night as well as for cool/wet (Oct-March) and warm/dry seasons (April-Sept.). The CADMP sampler employed redundant measurements (both $PM_{2.5}$ and PM_{10} mass and speciation; two separate measures of particulate nitrate and of HNO_3). All three sites show statistically significant ($p<0.01$) daytime decreases of NO_2 from weekdays to weekends, but no significant changes in HNO_3 (either by denuder difference, DD HNO_3, or as HNO_3 without employing a denuder) or particulate nitrate (Figures 13 through 18). At Azusa, statistically significant decreases in PM_{10} and $PM_{2.5}$ mass also occurred. The sites showed few significant differences at night. (Statistical significance was evaluated using a t-test of differences in means. This test was deemed adequate because data were collected once every six days over a period that was short enough that temporal trends were not expected to bias the results).

CADMP samples include redundant measurements of HNO_3 and nitrate, collected on filter packs both with and without denuders. The measurements were compared to identify possible biases. Published studies have documented substantial nitrate losses from conventional filter-pack systems due to the volatilization of particulate ammonium nitrate (Hering and Cass, 1999). Figure 19 shows that the CADMP filter-pack HNO_3 (no denuder) concentrations were higher than the denuded HNO_3, whereas the $PM_{2.5}$ nitrate levels were lower than the denuded nitrate concentrations. Since the sampler was designed with a Teflon filter (for particulate nitrate) placed in front of a nylon filter (for HNO_3) in the channel lacking a denuder, the comparisons indicate that the filter-pack HNO_3 (nylon filter, not denuded) was biased high by NH_4NO_3 volatilization from the Teflon filter. Correspondingly, the Teflon-filter $PM_{2.5}$ nitrate measurements were biased low by loss. Volatilization was greatest during daytime in the warm/dry season. These comparisons indicate that routine PM nitrate measurements (which are made in a manner similar to the nondenuded CADMP Teflon filter) may be 20 to 70 percent too low. Such losses introduce additional uncertainties into the comparison of weekend and weekday particulate nitrate levels.

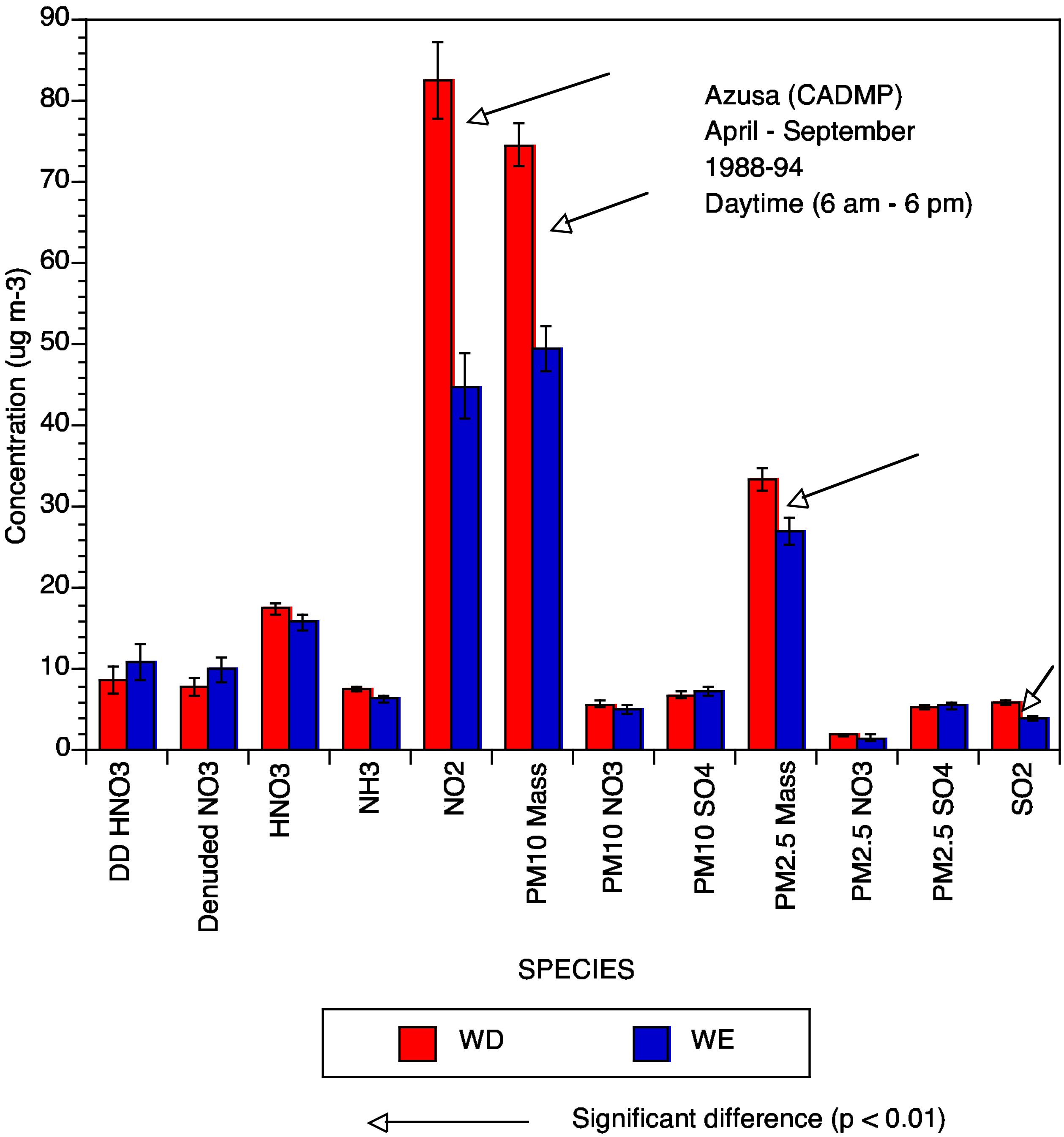

Figure 13. Average daytime, warm/dry season differences between weekday and weekend for Azusa, 1988-94 (CADMP data). Error bars are one standard error.

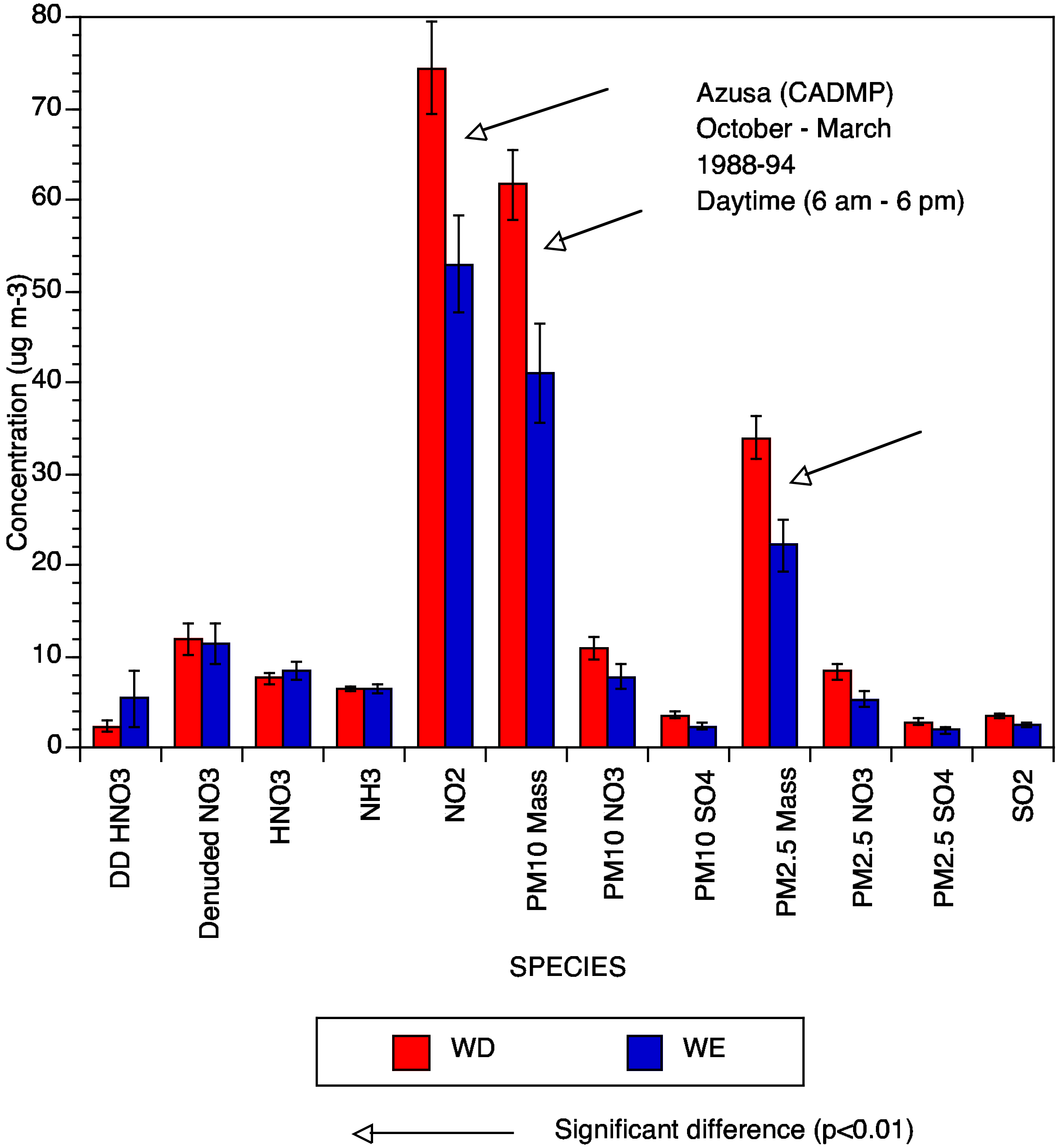

Figure 14. Average daytime, cool/wet season differences between weekday and weekend for Azusa, 1988-94 (CADMP data). Error bars are one standard error.

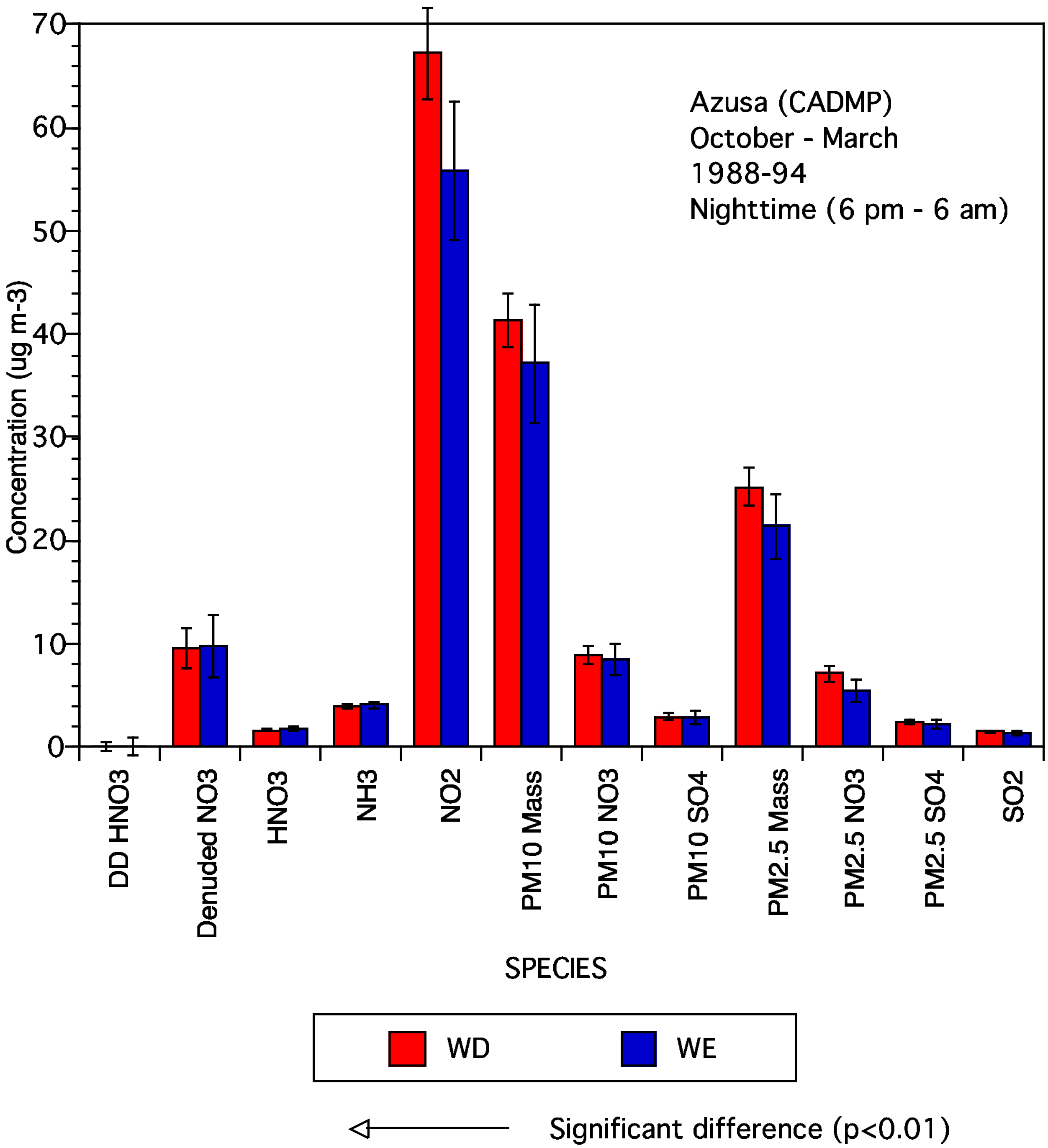

Figure 15. Average nighttime, cool/wet season differences between weekday and weekend for Azusa, 1988-94 (CADMP data). Error bars are one standard error.

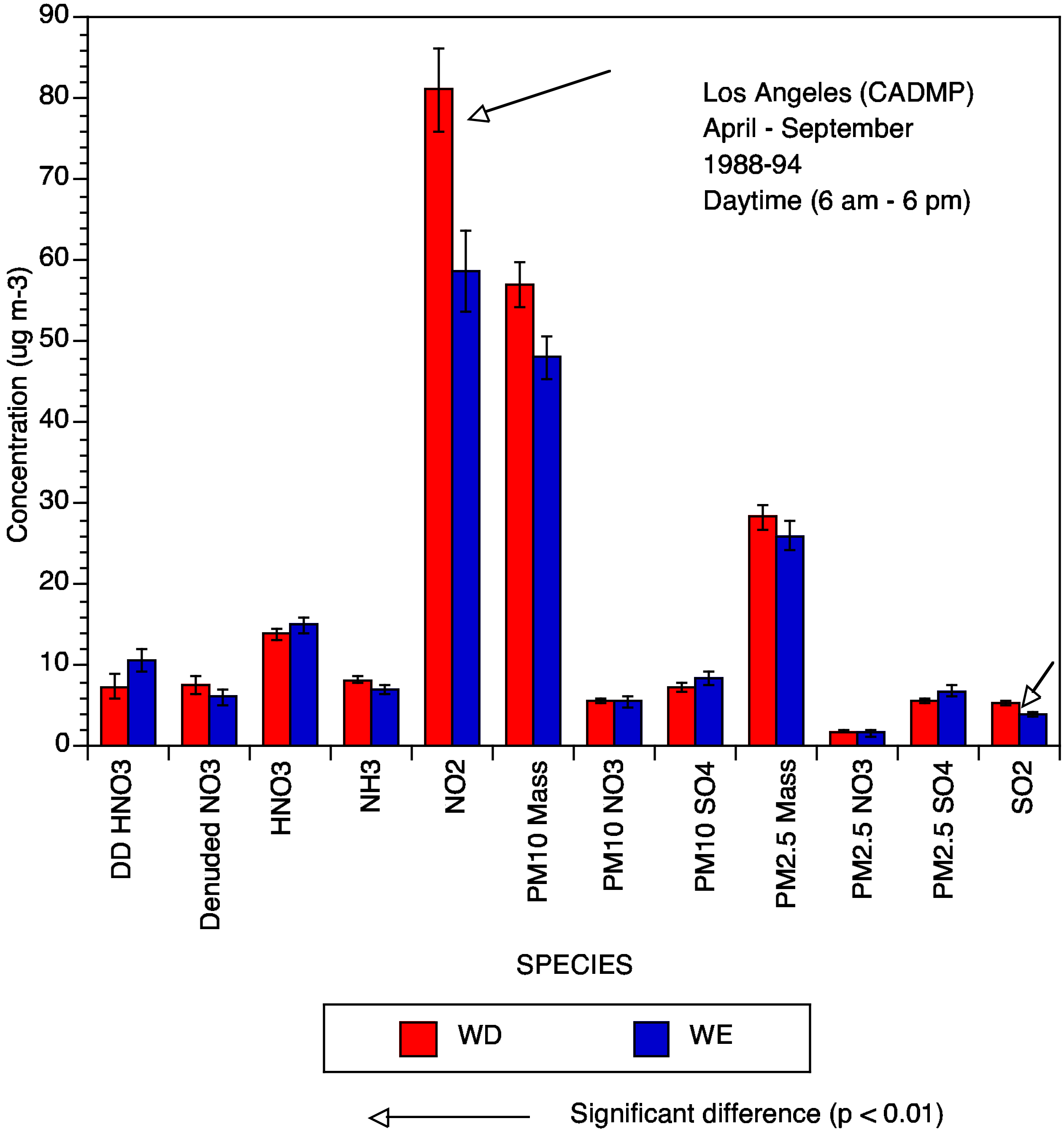

Figure 16. Average daytime, warm/dry season differences between weekday and weekend for downtown Los Angeles, 1988-94 (CADMP data). Error bars are one standard error.

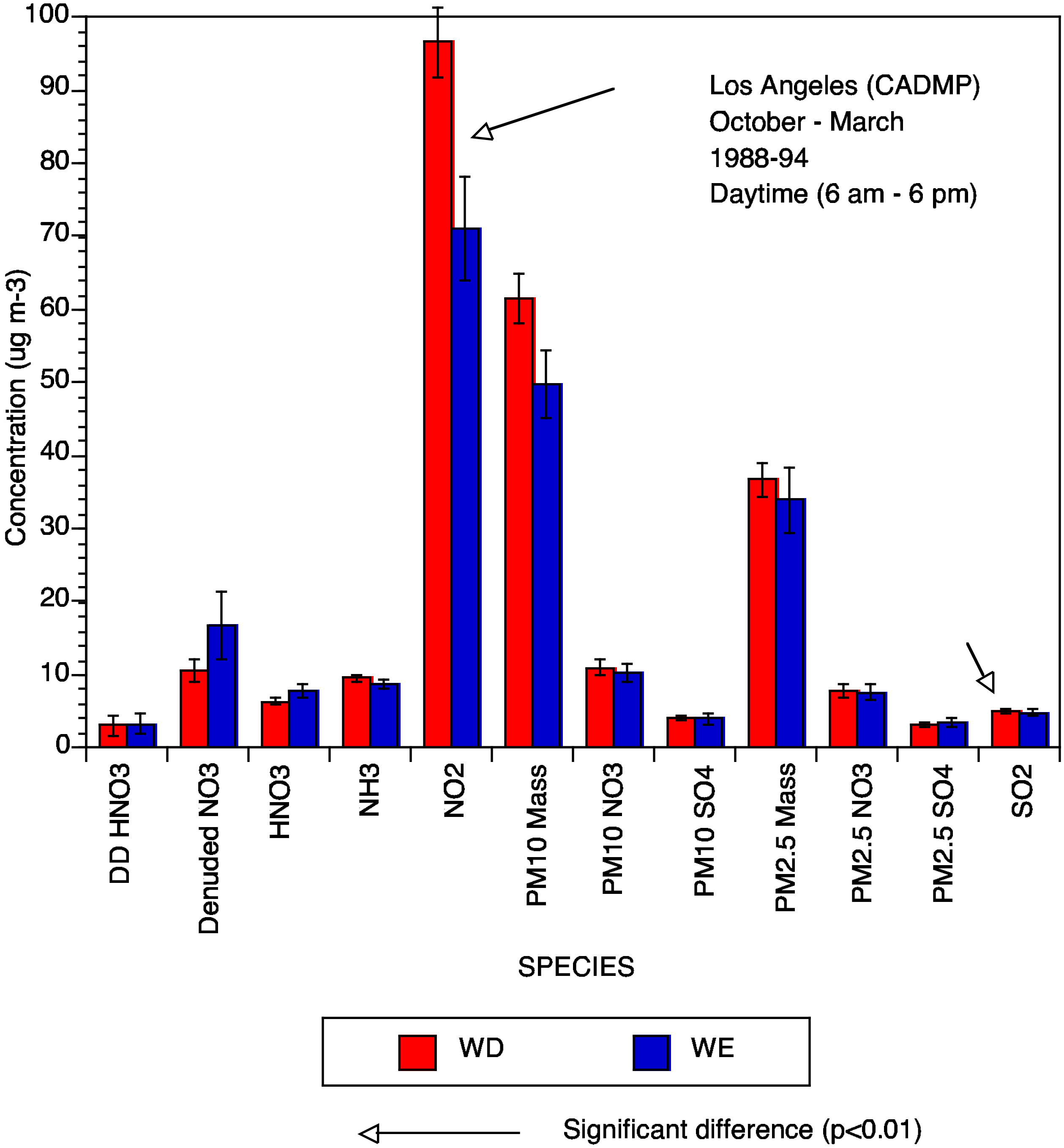

Figure 17. Average daytime, cool/wet season differences between weekday and weekend for downtown Los Angeles, 1988-94 (CADMP data). Error bars are one standard error.

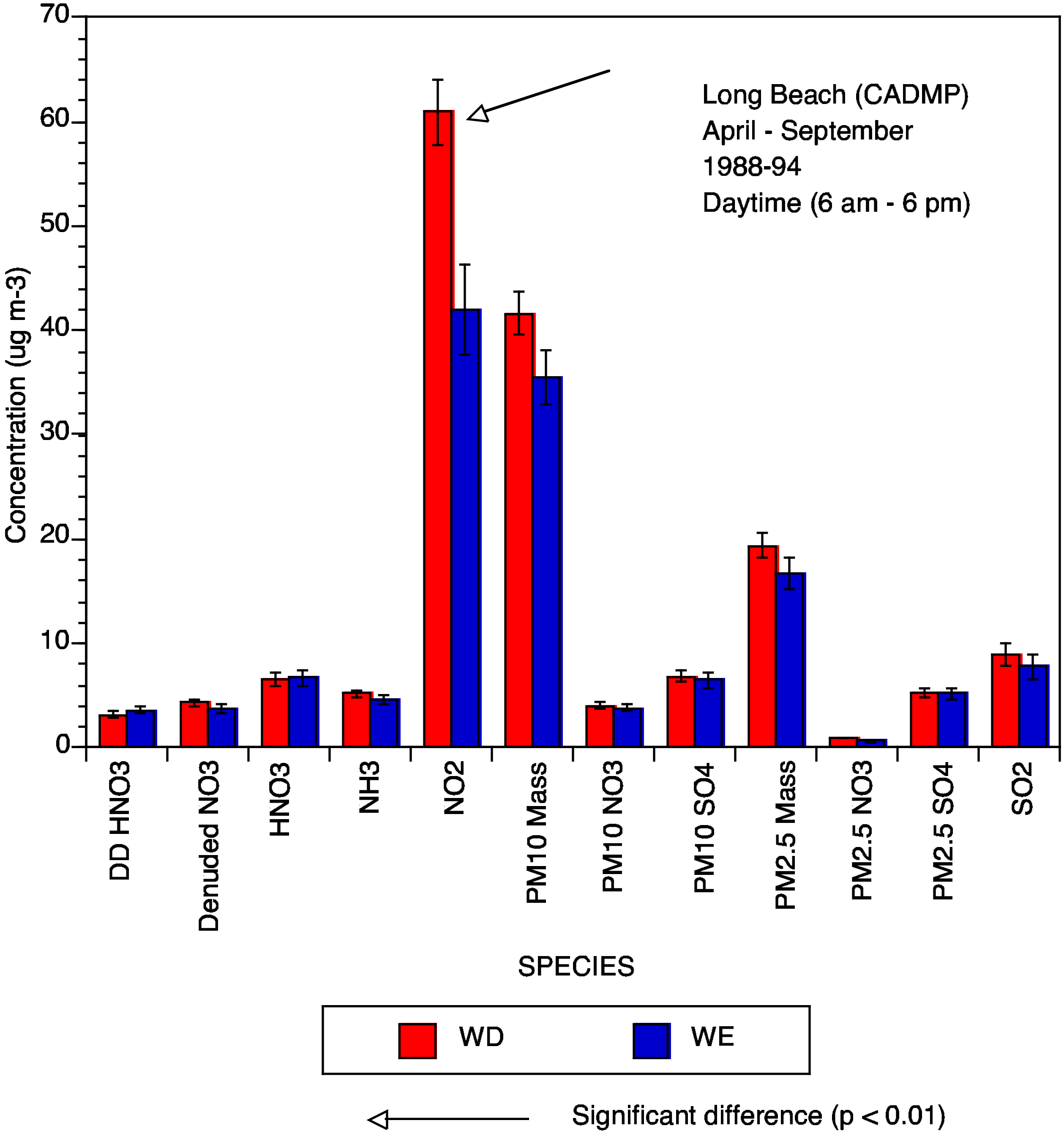

Figure 18. Average daytime, warm/dry season differences between weekday and weekend for Long Beach, 1988-94 (CADMP data). Error bars are one standard error.

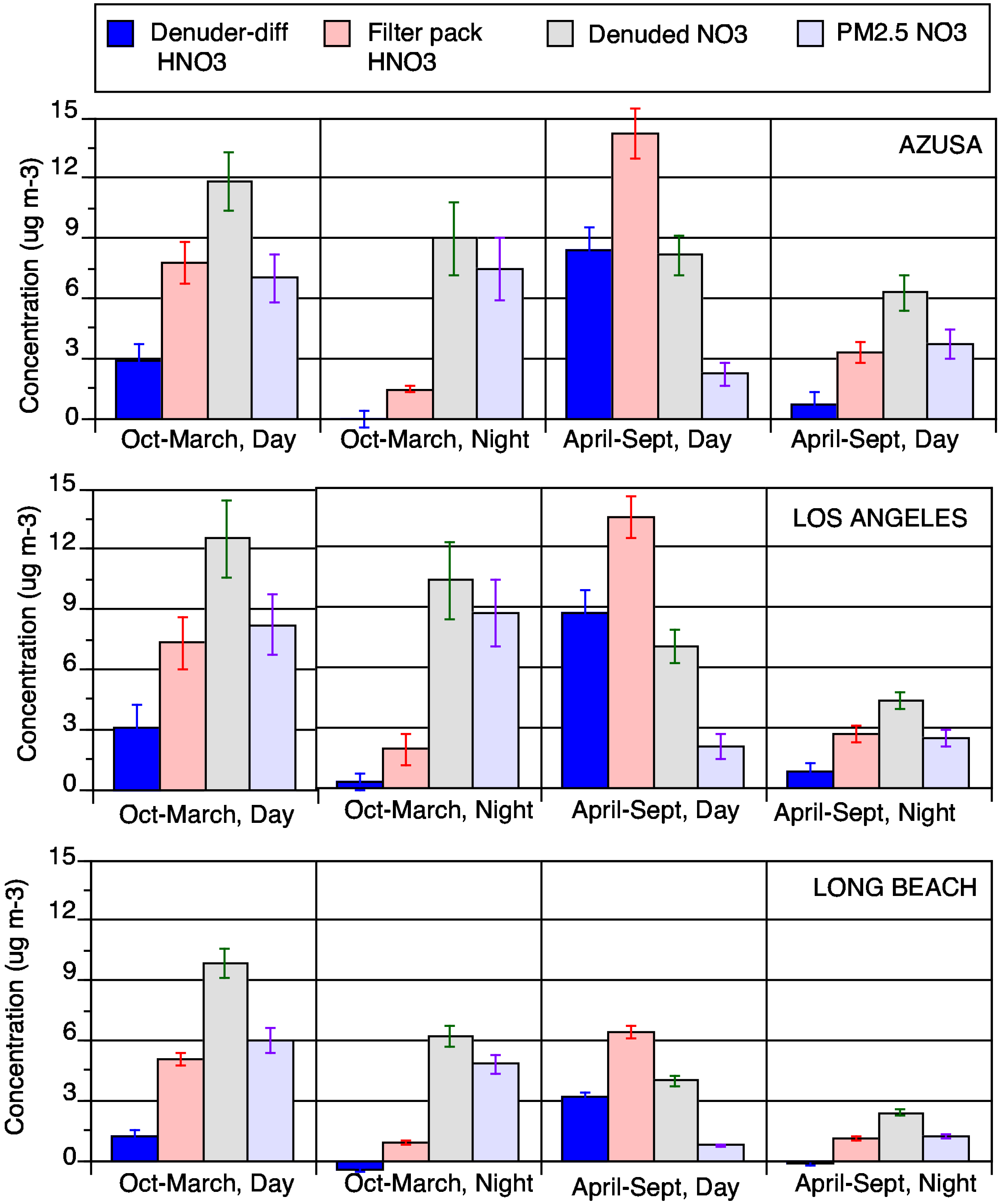

Figure 19. Comparison of denuder-difference HNO_3 with filter pack HNO_3 and comparison of denuded NO_3 with Teflon-filter $PM_{2.5}$ nitrate at Azusa, Los Angeles, and Long Beach, for cool/wet and warm/dry seasons and day and night (CADMP data).

PTEP and SCOS Particulate Measurements

The PM measurements made during the 1995-96 PTEP Study show no statistically significant differences in nitrate concentrations at any of the five monitoring sites for either the $PM_{2.5}$ or PM_{10} size fractions (Figures 20 and 21). The PTEP study also measured concentrations of nitric acid and ammonia, as well as other particulate species such as sulfate. The full PTEP database was used to model the relation of particulate nitrate to HNO_3, ammonia, and sulfate (see Section 6).

The 1997 SCOS included four intensive-sampling periods during which measurements were collected on both a weekday and a weekend day: August 22-23, September 4-6, September 28-29, and October 3-4. These data were examined by pairing each Friday or Monday with the adjacent Saturday or Sunday. Because the number of sample points was so limited, we simply compared the weekday and weekend values without testing for statistical significance. However, statistical tests were carried out for longer-term routine monitoring data (described in the next section of this chapter).

At seven of the eight SCOS weekday/weekend pairs, morning NMOC concentrations decreased from weekday to weekend (Figure 22). NMOC/NO_x ratios increased on all four weekday/weekend pairs at Azusa, North Main Street, and Anaheim, and on two of three pairs at Burbank (Figure 23). Thus, these data indicate that lower NMOC concentrations occurred on weekends, but differential decreases of VOC and NO_x emissions resulted in higher NMOC/NO_x ratios on weekends.

Morning concentrations of NO_x, NO_y, NMOC, and CO were consistently lower on weekend days at both Azusa and Los Angeles-North Main (Figures 24 and 25). In contrast, afternoon concentrations of ozone were consistently higher on weekends. The afternoon concentrations of HNO_3 were sometimes higher and sometimes lower on weekends (Figures 24 and 25). Morning concentrations of both ozone and HNO_3 tended to be higher on weekend days.

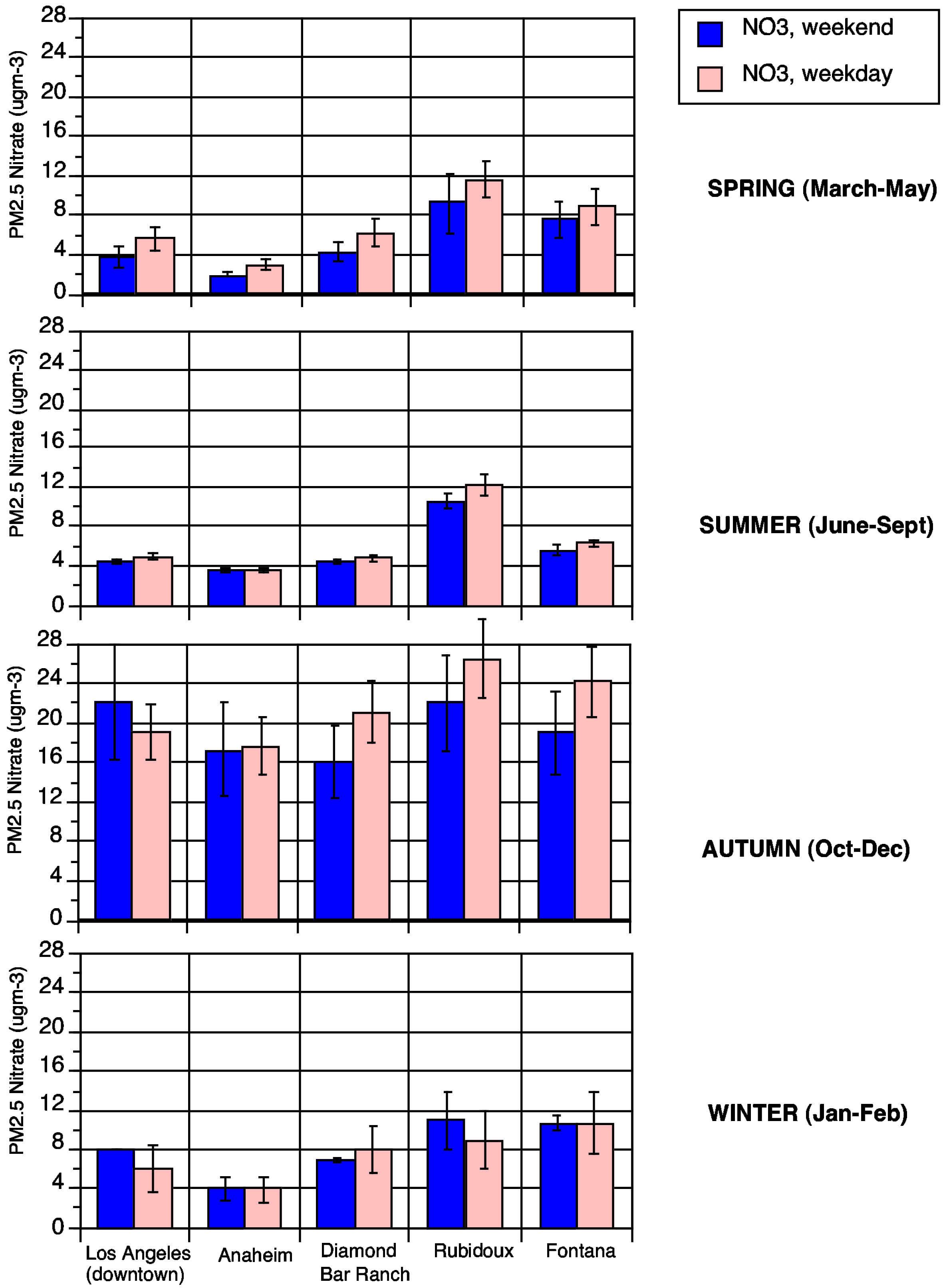

Figure 20. Mean weekday and weekend $PM_{2.5}$ nitrate concentrations at five locations during the 1995-96 PTEP study. Error bars are one standard error.

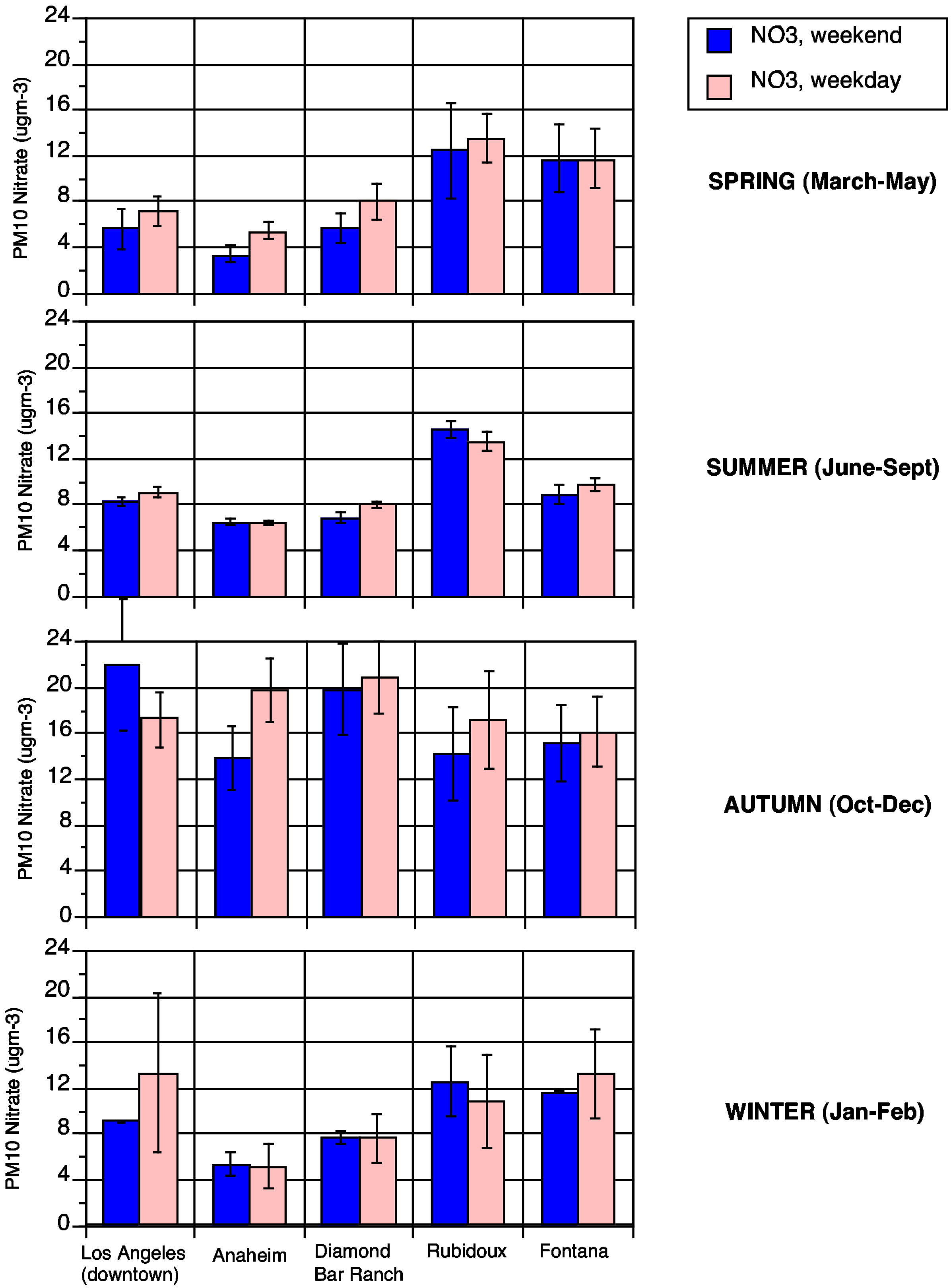

Figure 21. Mean weekday and weekend PM_{10} nitrate concentrations at five locations during the 1995-96 PTEP study. Error bars are one standard error.

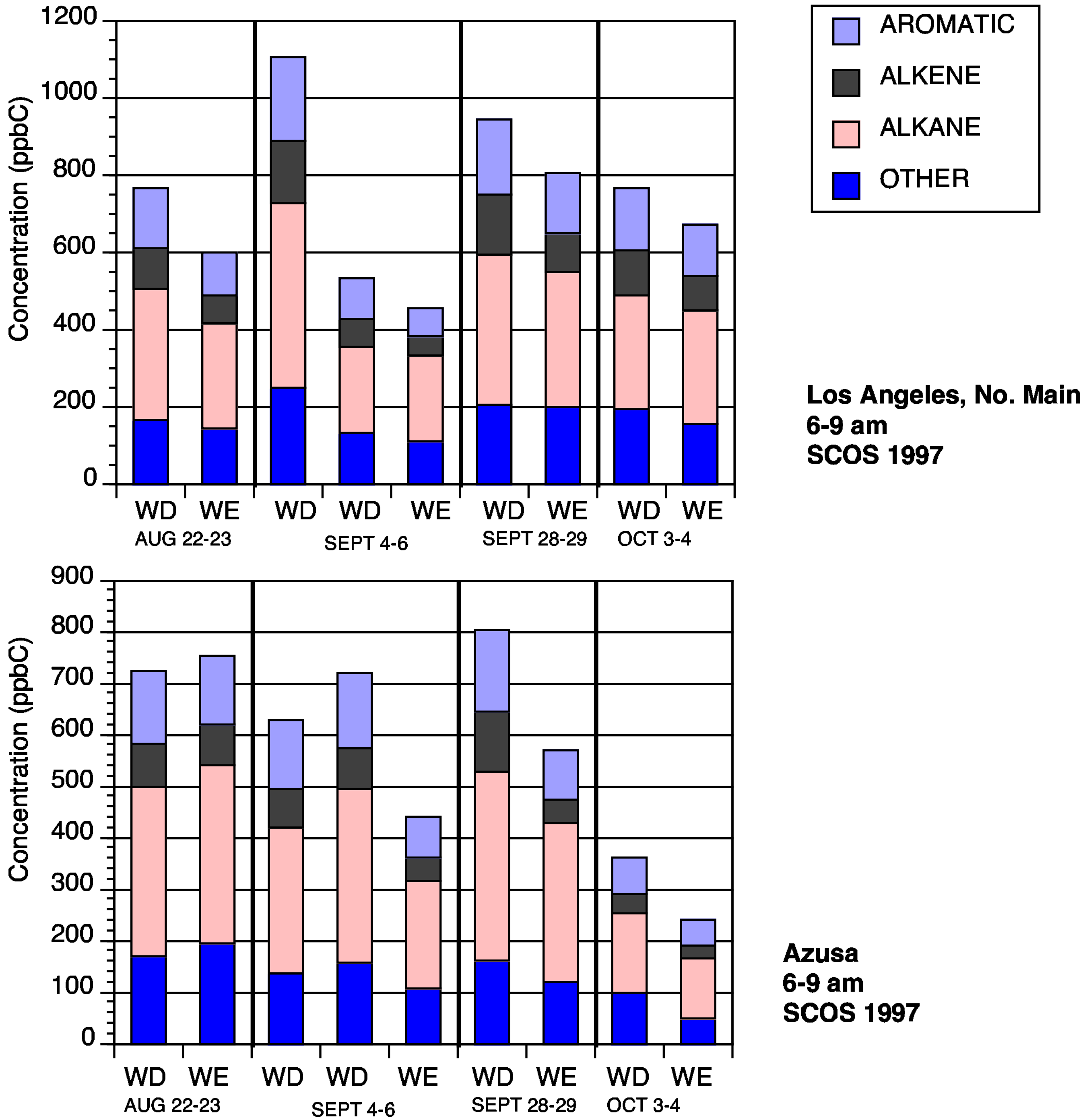

Figure 22. Comparisons of morning NMOC concentrations on sequential weekdays and weekend days at North Main Street and Azusa during the 1997 SCOS.

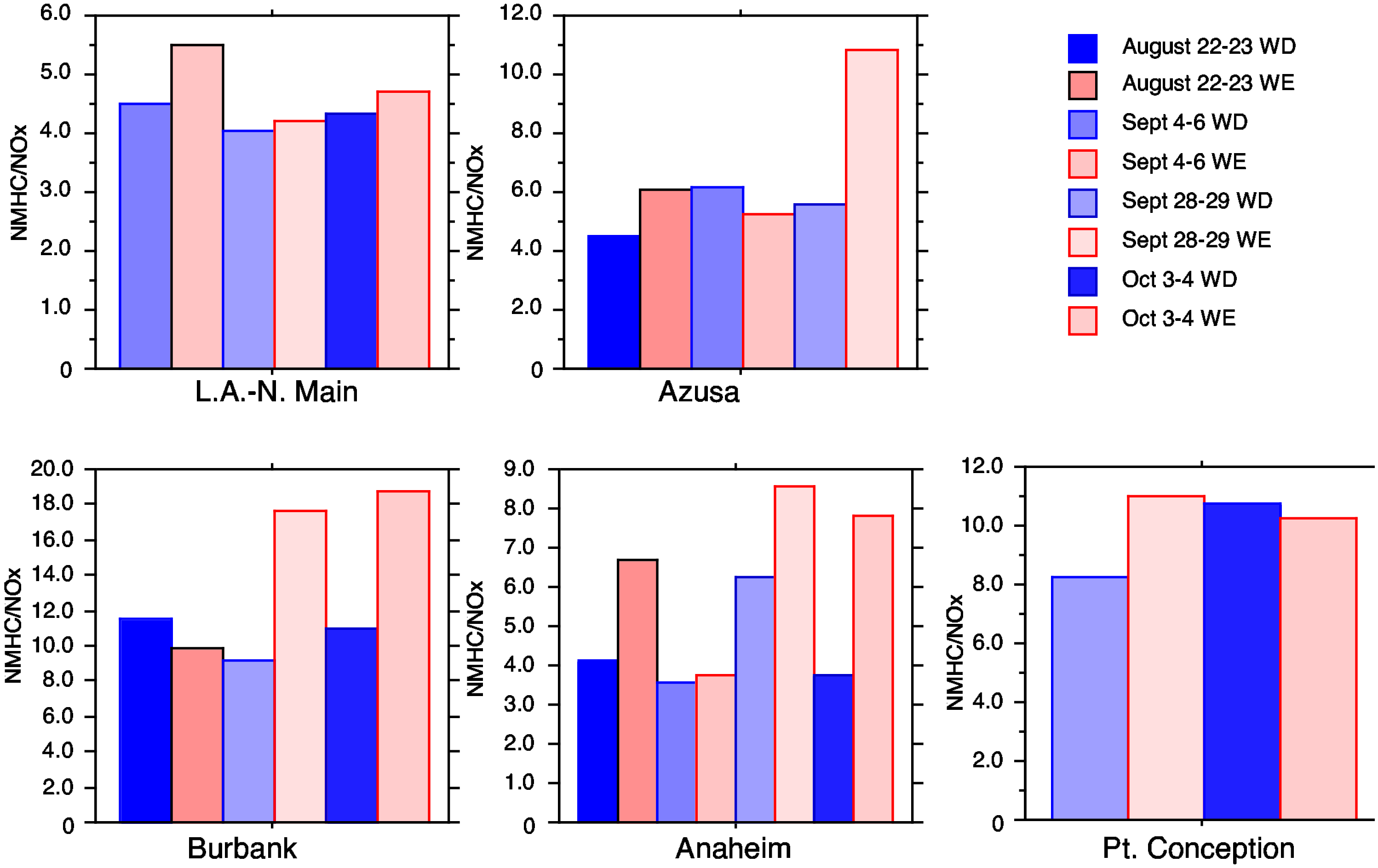

Figure 23. Ratios of hydrocarbons to NO_x on sequential weekdays and weekend days at five sites during the 1997 SCOS. The hydrocarbon canister samples were collected from 6 am through 9 am and were paired with NO_x measurements averaged over the same times. For Los Angeles and Azusa, the NMHC values are the total of identified plus unidentified hydrocarbon compounds. The total identified oxygenate concentrations were also available in the data from Anaheim, Burbank, and Point Conception and were added to the total of identified plus unidentified hydrocarbon concentrations.

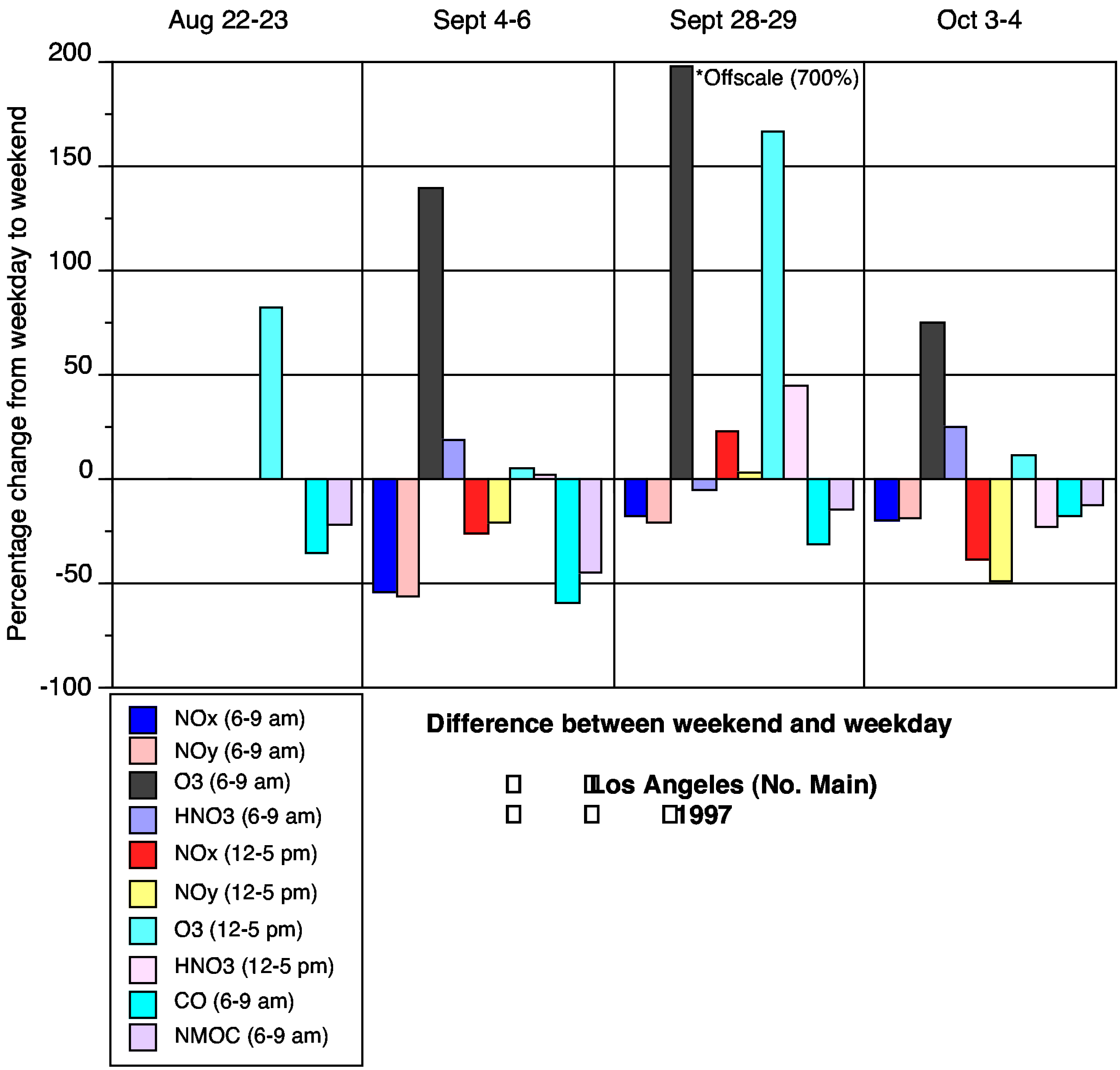

Figure 24. Percent differences between weekend and weekday concentrations of NO_x, NO_y, ozone, HNO_3, CO and NMOC at Los Angeles-North Main Street on four sets of dates (Aug 22-23, Sept 4-6, Sept 28-29 and Oct 3-4, 1997).

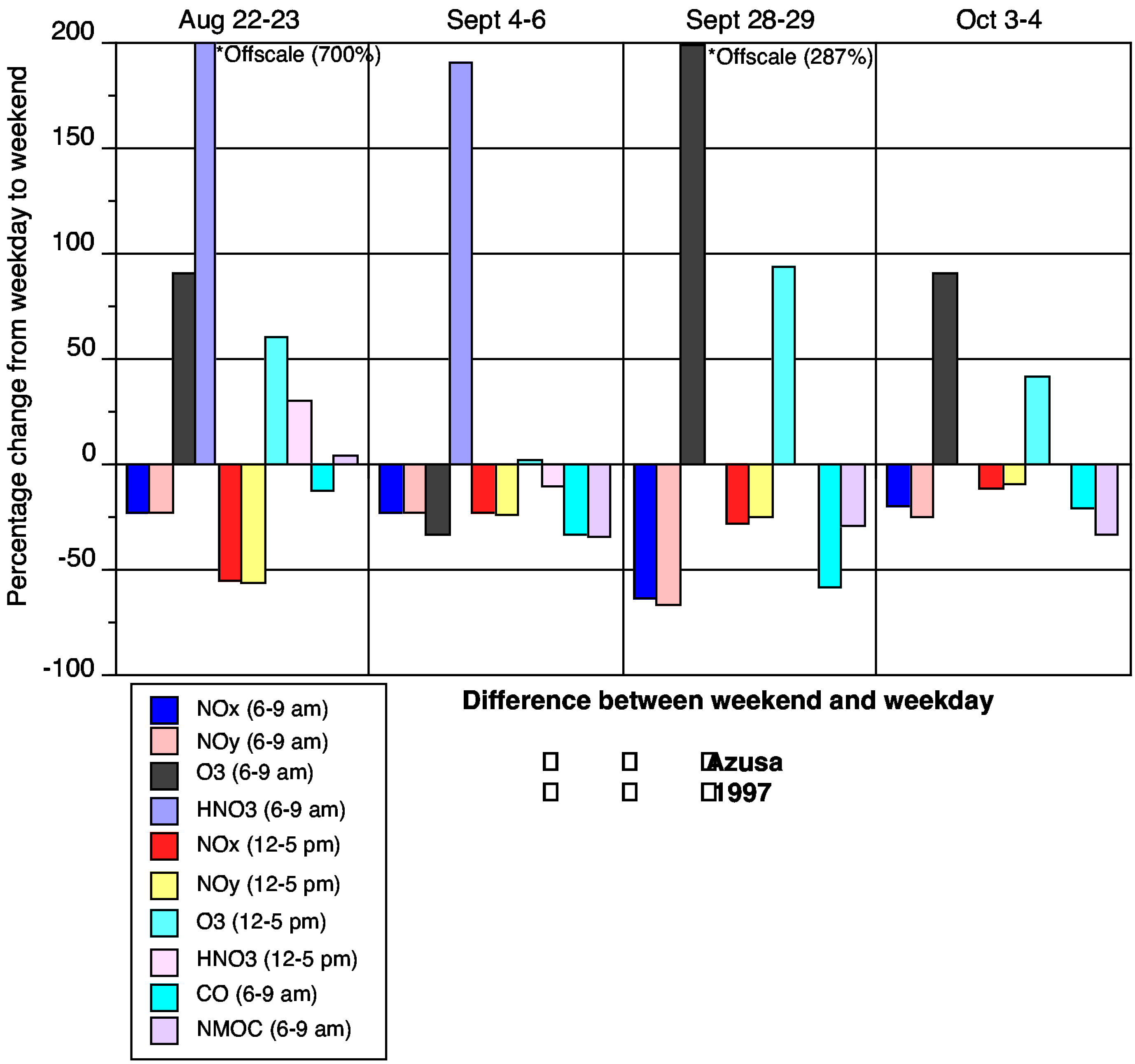

Figure 25. Percent difference between weekend and weekday concentrations of NO_x, NO_y, ozone, HNO_3, CO and NMOC at Azusa on four sets of dates (Aug 22-23, Sept 4-6, Sept 28-29 and Oct 3-4, 1997).

Routine Monitoring Data

Day-of-week variations of PM_{10} mass, PM_{10} nitrate and PM_{10} sulfate concentrations are noticeable in CARB routine data, as shown for Azusa and Riverside-Rubidoux over the time period 1985 through 1999 (see Figures 26 and 27). Differences are evident between cool/wet (October – March) and warm/dry (April – September) seasons, with cool/wet values consistently lower than warm/dry values. Also, PM_{10} mass shows lower weekend values, whereas PM_{10} nitrate and PM_{10} sulfate show little evidence for either lower or higher weekend values. Over the entire time period, PM_{10} mass shows decreasing values at both Azusa and Riverside. A much slighter declining trend is evident for PM_{10} sulfate at both sites. Warm/dry season PM_{10} nitrate measurements exhibit decreasing values at Riverside and Azusa over the 15-year period, whereas little or no decrease in cool/wet season PM_{10} nitrate is evident at those sites. (Note that although the samples were PM_{10} size fraction, on some or many samples, nitrate could have been present primarily as fine particles.)

A comparison of 24-hour mean weekday and weekend concentrations shows that the differences are statistically significant for some species during the cool/wet season (see Figure 28). Specifically, weekend concentrations were lower than weekday concentrations at statistically significant levels at 6 out of 8 sites for PM_{10}, 12 out of 15 sites for CO, 15 out of 16 sites for NO_x, and 14 out of 23 sites for TSP. Weekend concentrations were higher than weekday concentrations at statistically significant levels for 14 out of 23 sites for ozone and 17 out of 27 sites for the ratio of CO to NO_x. There was no significant change in nitrate--some sites showed a decrease and some sites showed an increase between weekends and weekdays. The ratio of nitrate to both NO_x and PM_{10} mass was higher on weekends, although most differences were not statistically significant. Comparisons for the warm/dry season yielded nearly identical numbers and proportions of significant differences as for the cool/dry season (Figure 29).

Statistical tests were also carried out to compare weekend/weekday differences between VOC concentrations and VOC/NO_x ratios. VOC samples are routinely collected once every six days, during 3-hour intervals during the day; data are available for summer months (June-September) only. Our analysis was further restricted to sites with more than one year of data and at least seventy percent of collection days (see Table 3). One site (El Rio) showed increasing VOC levels from weekday to weekend and four sites (Los Angeles, Pico Rivera, Burbank and Azusa) showed lower weekend VOC concentrations. VOC-to-NO_x ratios increased from weekday to weekend at two sites (Azusa and Los Angeles), and decreased at one site (Pico Rivera). However, none of the differences were statistically significant.

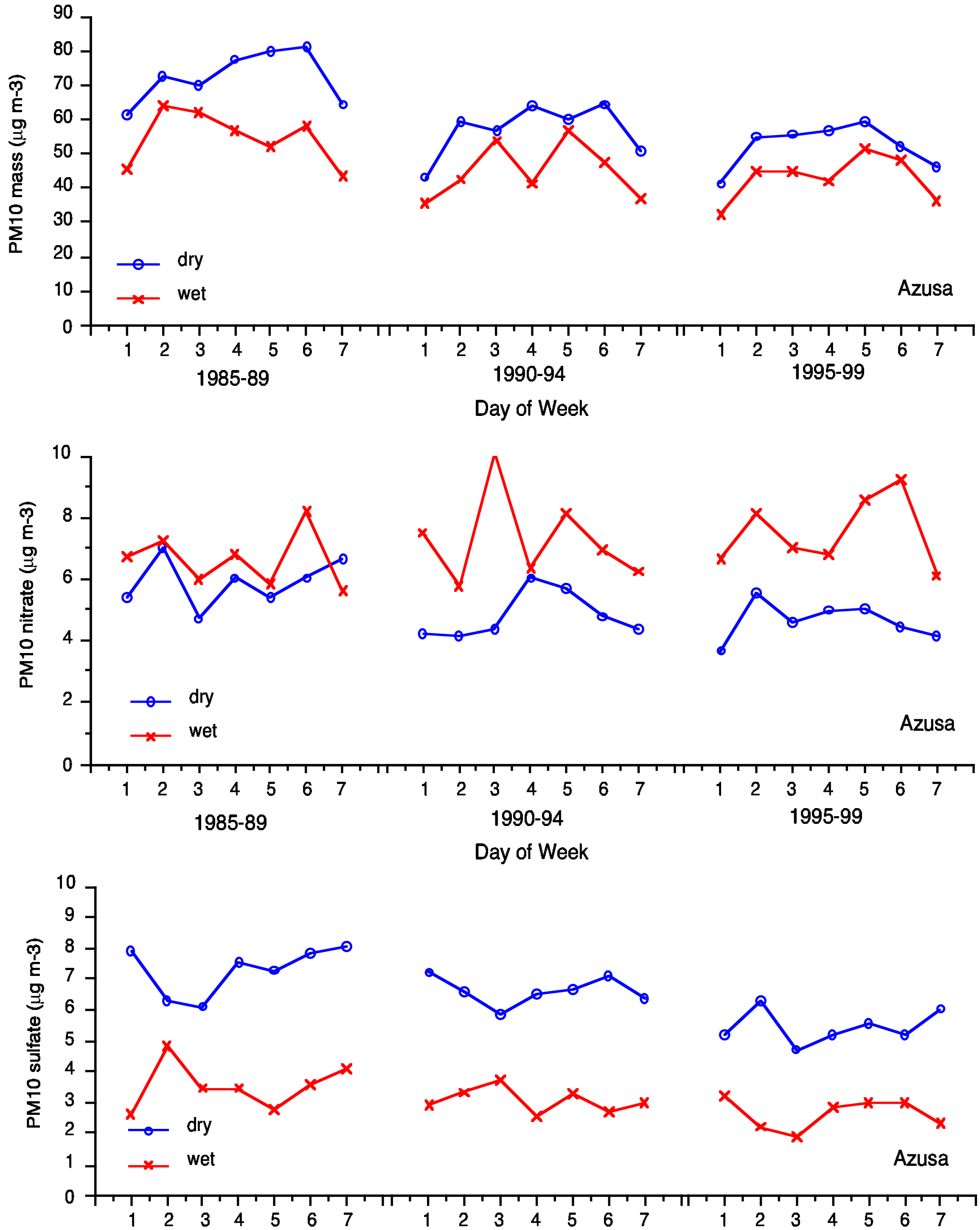

Figure 26. Day of week variations of PM_{10} mass, PM_{10} nitrate concentration, and PM_{10} sulfate by season (cool/wet is Oct-March and warm/dry is April-Sept) at Azusa. The samples were collected once every six days from 1985 through 1999. Each point is the average of 60 to 66 samples.

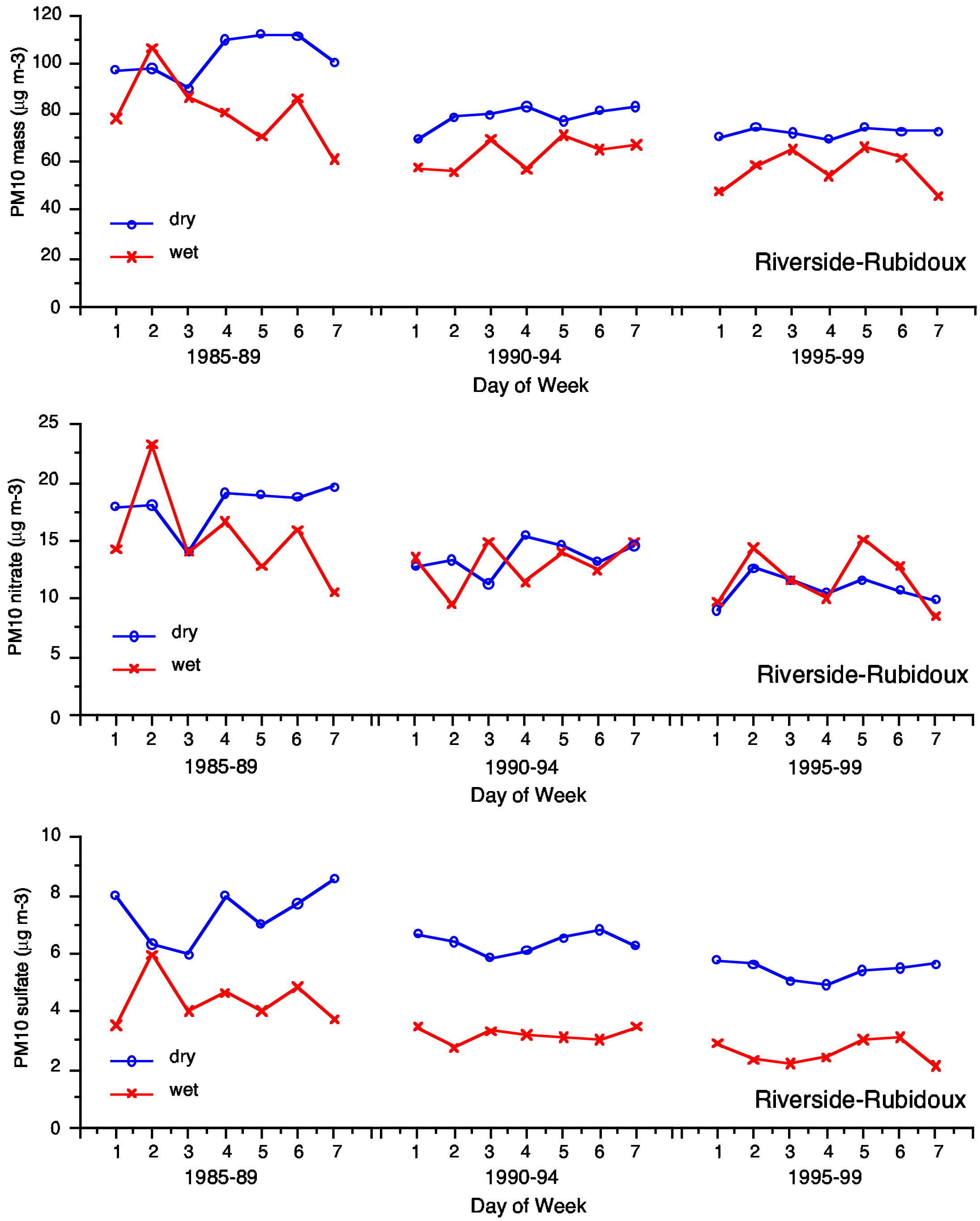

Figure 27. Day of week variations of PM_{10} mass, PM_{10} nitrate concentration, and PM_{10} sulfate by season (cool/wet is Oct-March and warm/dry is April-Sept) at Riverside. The samples were collected once every six days from 1985 through 1999. Each point is the average of 60 to 66 samples.

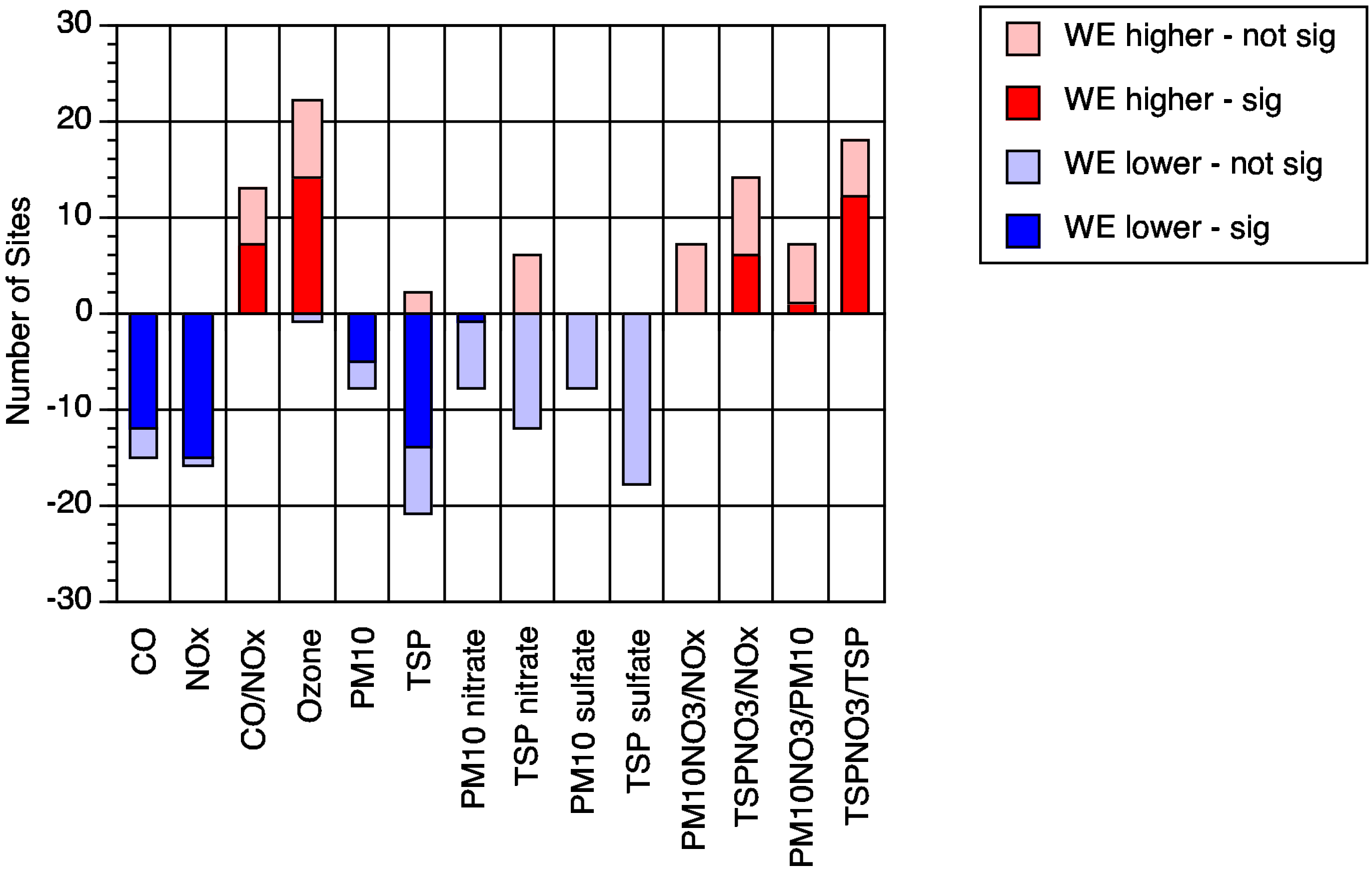

Figure 28. Number of sites showing statistical significance ($p<0.01$) of differences in 24-hour mean weekday and weekend concentrations for the cool/wet season (Oct-March), 1985-1999. A t-test was applied to the means of the weekday and weekend concentrations for each year. The yearly tests were summed and approximated as a normal statistic.

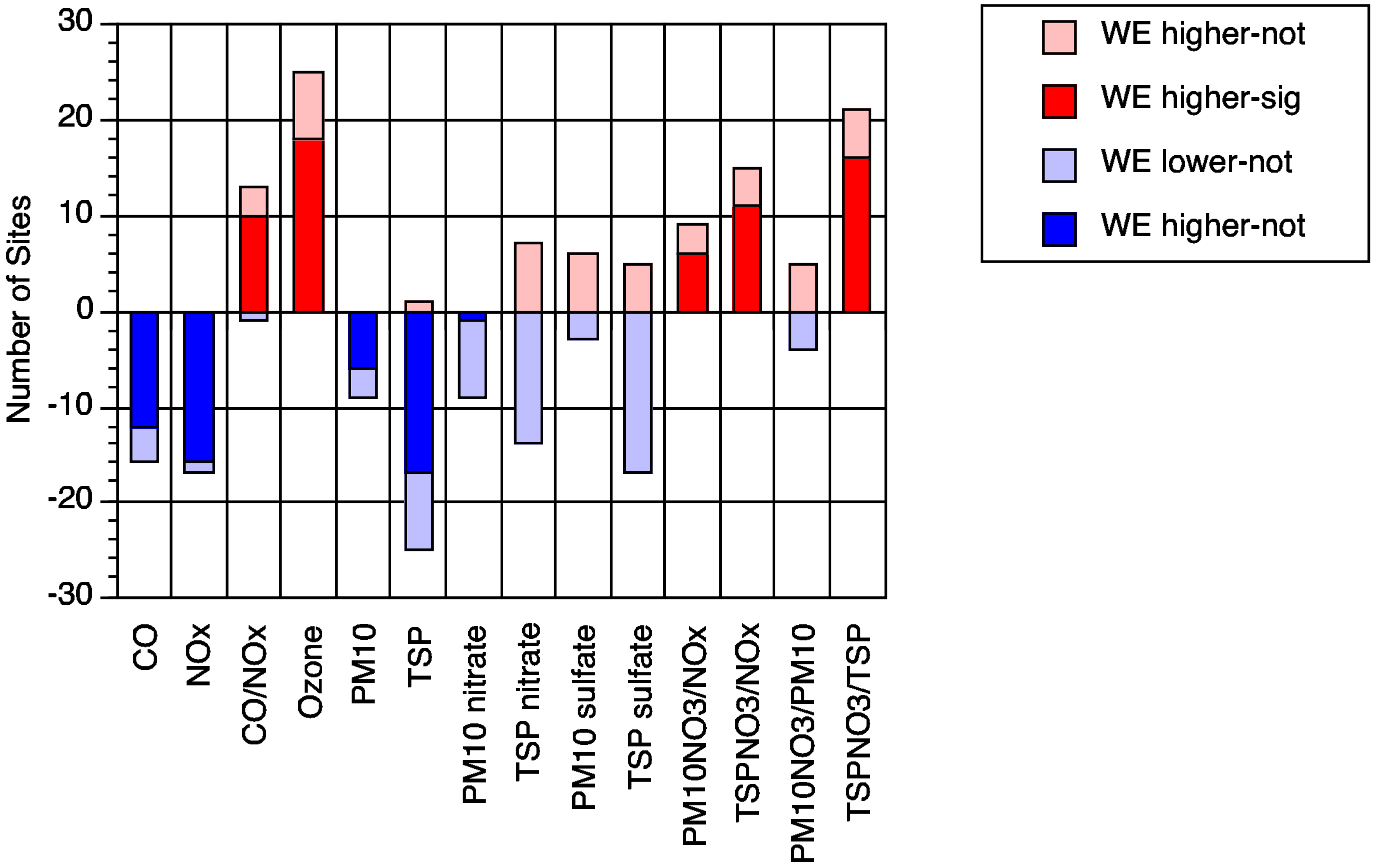

Figure 29. Number of sites showing statistical significance ($p<0.01$) of differences in 24-hour mean weekday and weekend concentrations for the warm/dry season (April-Sept), 1985-1999. A t-test was applied to the means of the weekday and weekend concentrations for each year. The yearly tests were summed and approximated as a normal statistic.

Table 3. VOC and VOC/NO_x weekday/weekend differences at selected sites, showing statistical significance, number of samples per day, and number of years of available data.

Measurement	Site	Weekday /Weekend Difference*	Significance Probability < .01	# Samples per Day	Years
VOC's	Los Angeles	-	no	2	94-99
	Azusa	-	no	7	98-99
	Burbank	-	no	8	98-99
	Pico Rivera	-	no	8	98-99
	El Rio	+	no	2	95-99
VOC/NO_x	Los Angeles	+	no	2	94-99
	Azusa	+	no	7	98-99
	Pico Rivera	-	no	8	98-99

* Negative denotes lower weekend values.

The routine data over the full twenty year period (1980-1999) were used to calculate the mean percentage change from weekdays to weekends, averaged over all sites in the South Coast, South Central Coast, and Mojave Desert air basins (Figure 30). The mean percentage change for PM_{10} nitrate was about half of the decrease in NO_x; however, the standard errors of the weekday-to-weekend decreases in mean PM_{10} nitrate concentrations were nearly as large as the decreases themselves. Thus, no weekday-weekend nitrate differences were statistically significant (and the averages could be much different depending on which days are sampled). There was no weekend decrease in TSP nitrate. The ratios of both PM_{10} and TSP nitrate to NO_x increased at most sites, although not all such increases were statistically significant.

Spatial patterns over time (1980-1999) were examined to evaluate whether some sites are responding differently than others. Figures 31-43 display maps showing geographic patterns of cool/wet season (Oct-March) differences in the 24-hour mean concentrations of the following species: CO, NO_x, CO/NO_x, ozone, PM_{10} mass, TSP mass, PM_{10} sulfate and nitrate, TSP sulfate and nitrate, PM_{10} nitrate/NO_x, TSP nitrate/NO_x, PM_{10} nitrate/PM_{10} mass, TSP nitrate/TSP mass. (These figures depict the same statistical tests that are summarized in a different way in Figure 28: a t-test was applied to the means of the weekday and weekend concentrations for each year and the yearly tests were summed and approximated as a normal statistic.) Few, if any, pronounced spatial gradients are evident. For example, CO, NO_x, PM_{10} mass, and TSP mass concentrations are lower on weekends than on weekdays at all sites, and these differences are statistically significant at most or nearly all monitors. Conversely, CO/NO_x ratios and ozone concentrations are higher on weekends at most sites.

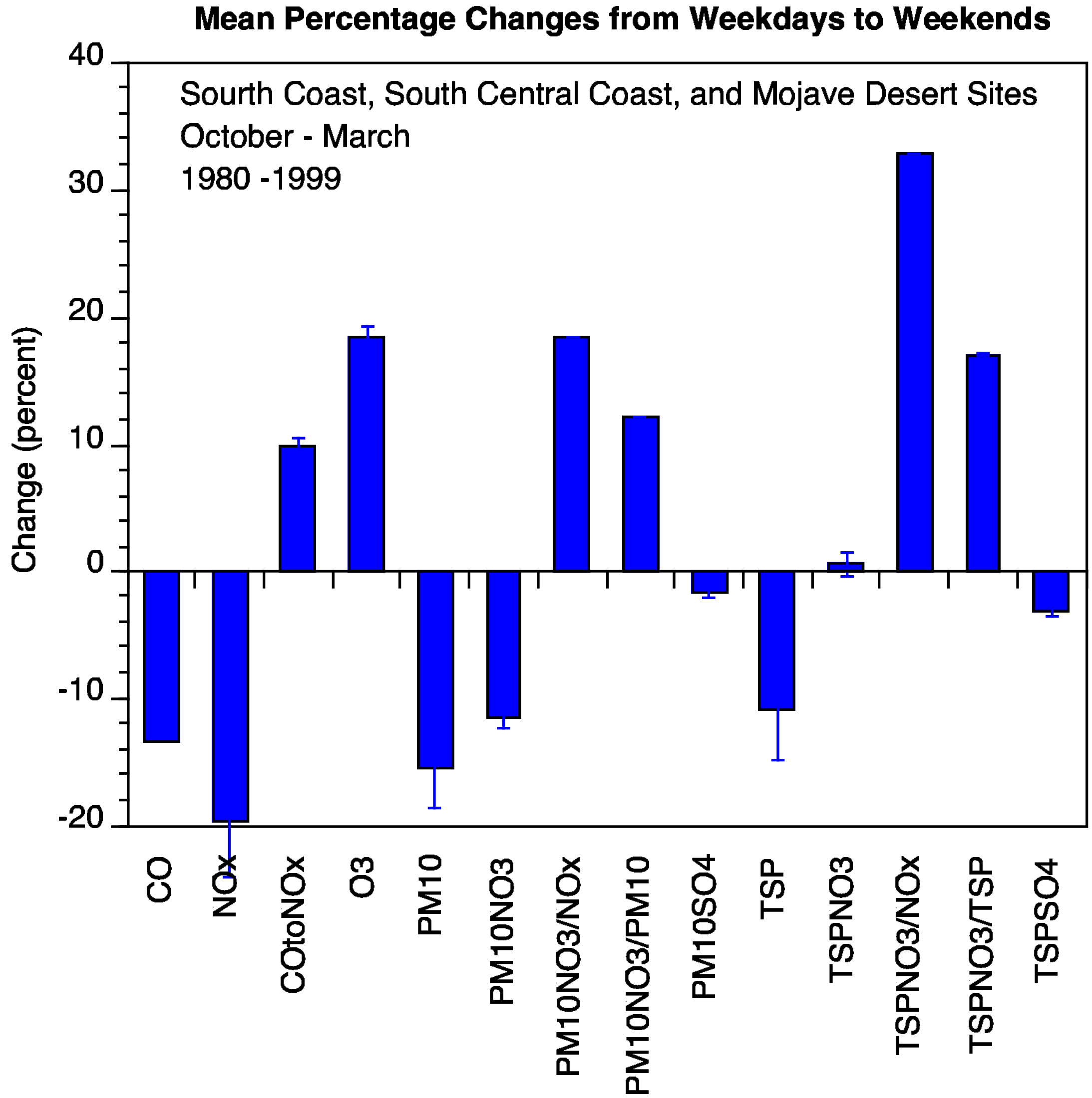

Figure 30. Mean weekday-weekend percentage changes in 24-hour species concentrations at sites in the South Coast, South Central Coast, and Mojave Desert air basins during the cool/wet season, 1980-1999. Negative values denote lower weekend than weekday concentrations. Percentage changes were determined for each site. The graph shows the averages of sites' percentage changes. Error bars are averages of sites' one standard error of the mean.

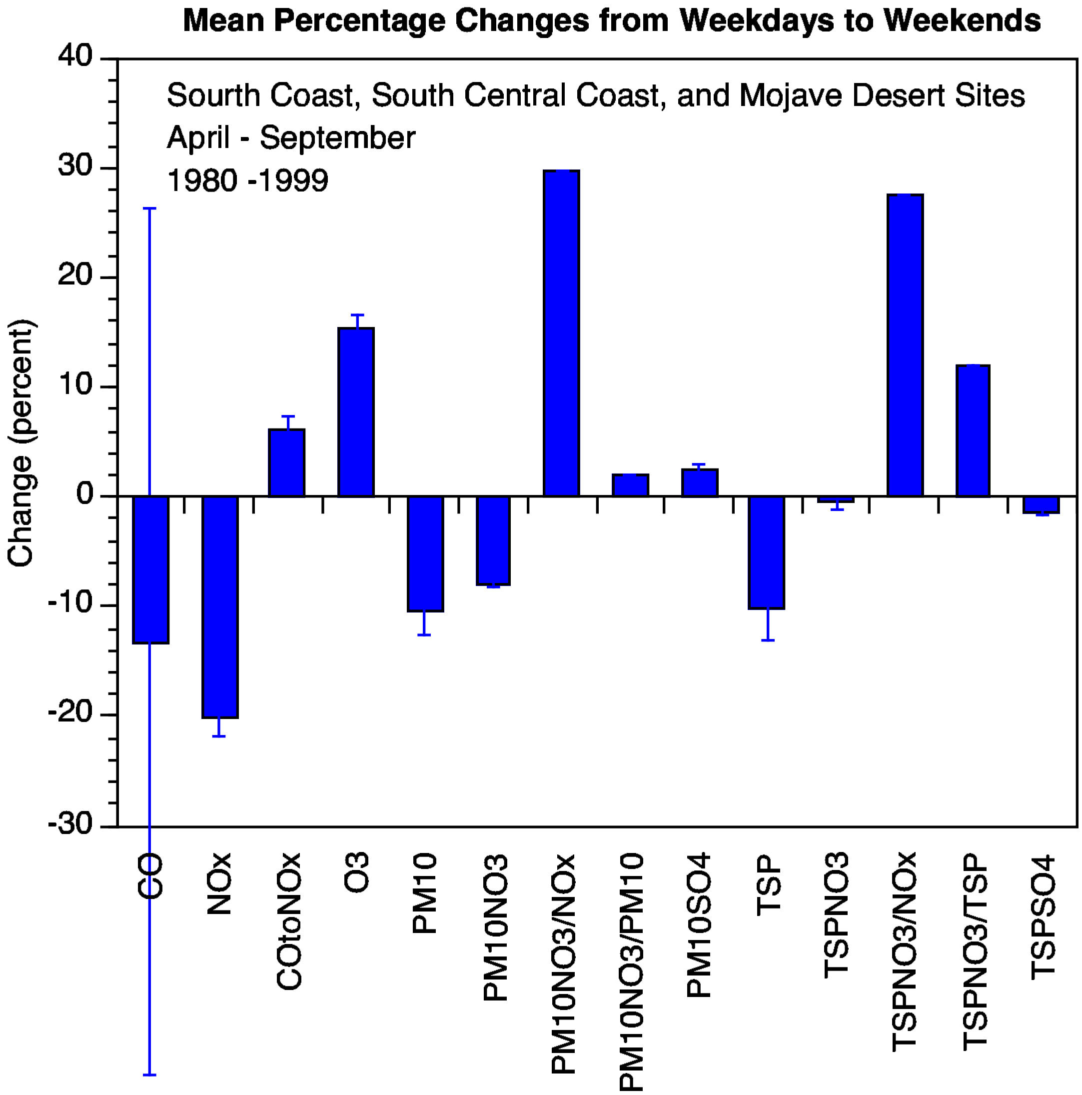

Figure 31. Mean weekday-weekend percentage changes in 24-hour species concentrations at sites in the South Coast, South Central Coast, and Mojave Desert air basins during the warm/dry season, 1980-1999. Negative values denote lower weekend than weekday concentrations. Percentage changes were determined for each site. The graph shows the averages of sites' percentage changes. Error bars are averages of sites' one standard error of the mean.

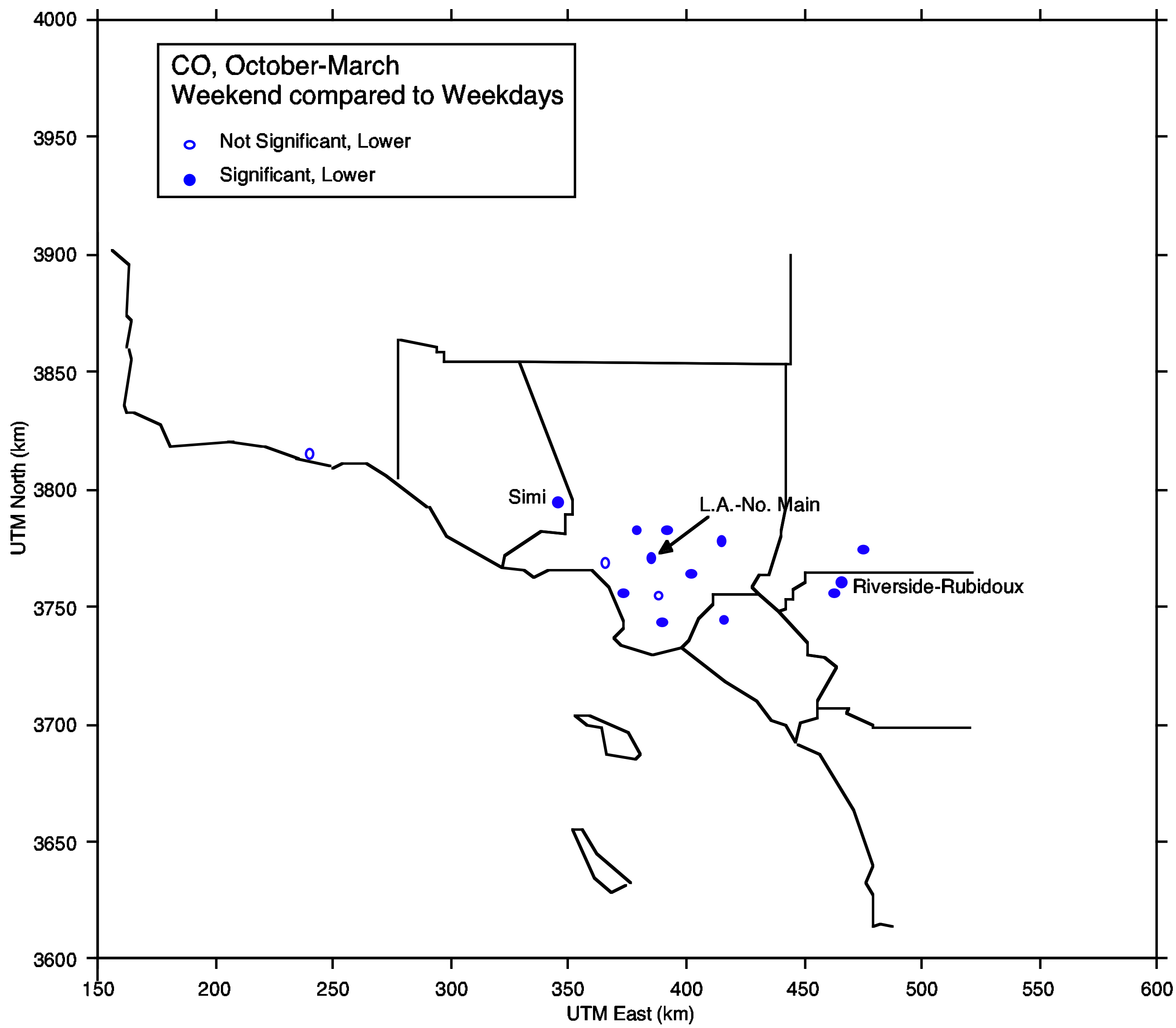

Figure 32. Geographic pattern of changes in CO concentration from weekdays to weekends during the cool/wet season (Oct-March) for all sites in the South Coast, South Central Coast, and Mojave Desert air basins. Open symbols represent changes that are not significant; closed symbols are significant ($p<0.01$). Circles represent decreasing values from weekdays to weekends; squares represent increasing values.

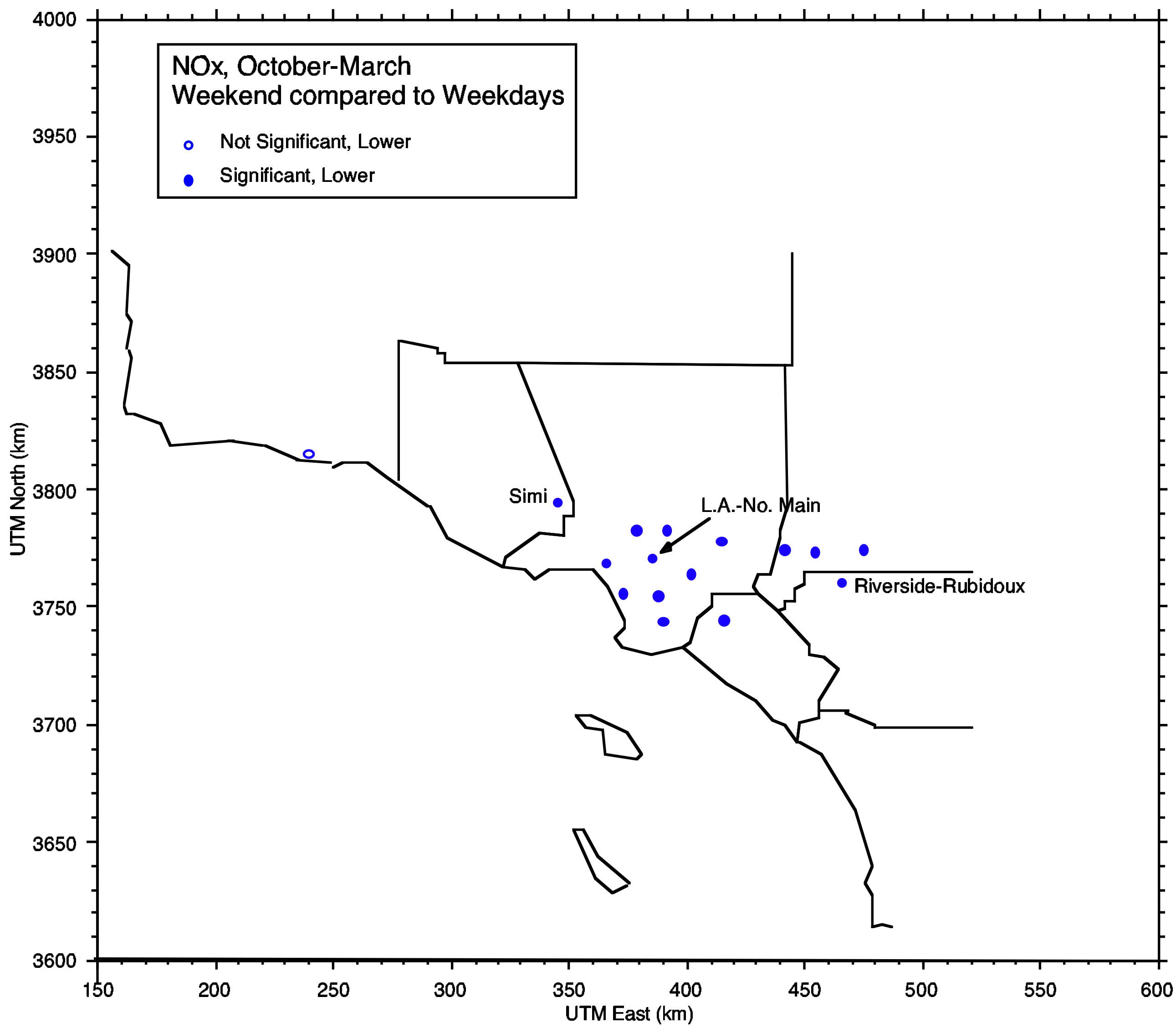

Figure 33. Geographic pattern of changes in NO_x concentration from weekdays to weekends during the cool/wet season (Oct-March) for all sites in the South Coast, South Central Coast, and Mojave Desert air basins. Open symbols represent changes that are not significant; closed symbols are significant (p<0.01). Circles represent decreasing values from weekdays to weekends; squares represent increasing values.

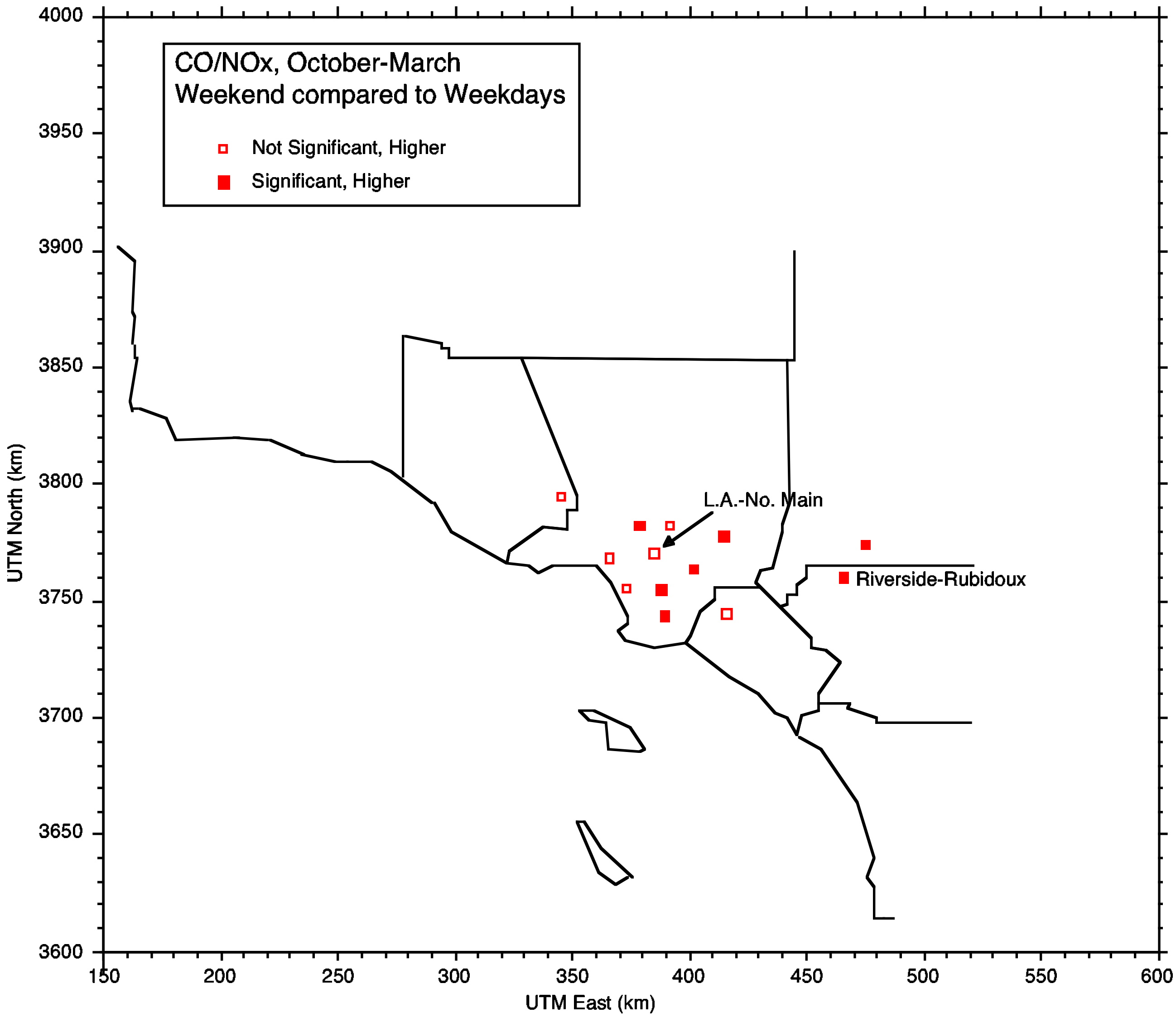

Figure 34. Geographic pattern of changes in CO/NO_x concentration from weekdays to weekends during the cool/wet season (Oct-March) for all sites in the South Coast, South Central Coast, and Mojave Desert air basins. Open symbols represent changes that are not significant; closed symbols are significant ($p<0.01$). Circles represent decreasing values from weekdays to weekends; squares represent increasing values.

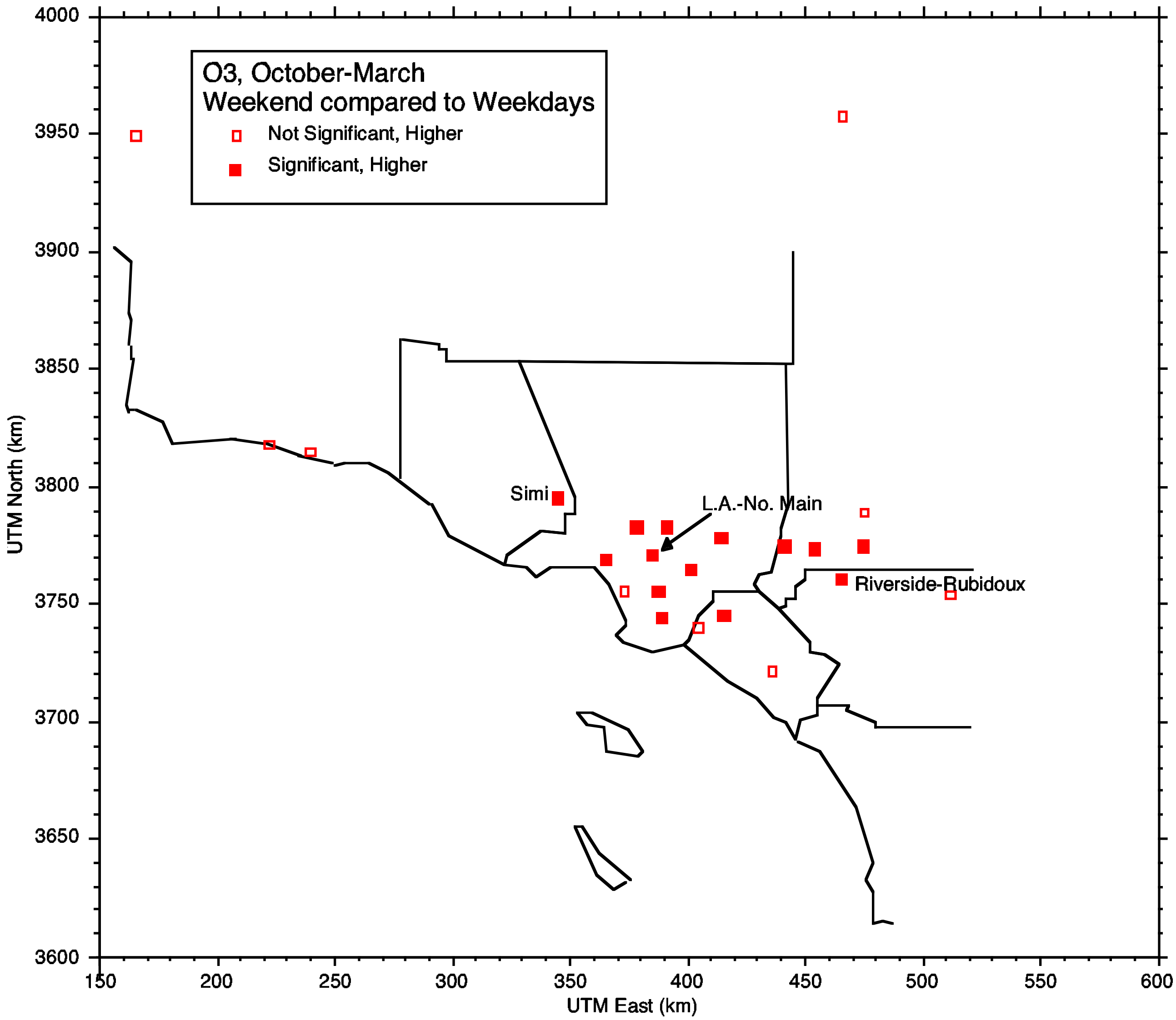

Figure 35. Geographic pattern of changes in ozone concentration from weekdays to weekends during the cool/wet season (Oct-March) for all sites in the South Coast, South Central Coast, and Mojave Desert air basins. Open symbols represent changes that are not significant; closed symbols are significant ($p<0.01$). Circles represent decreasing values from weekdays to weekends; squares represent increasing values.

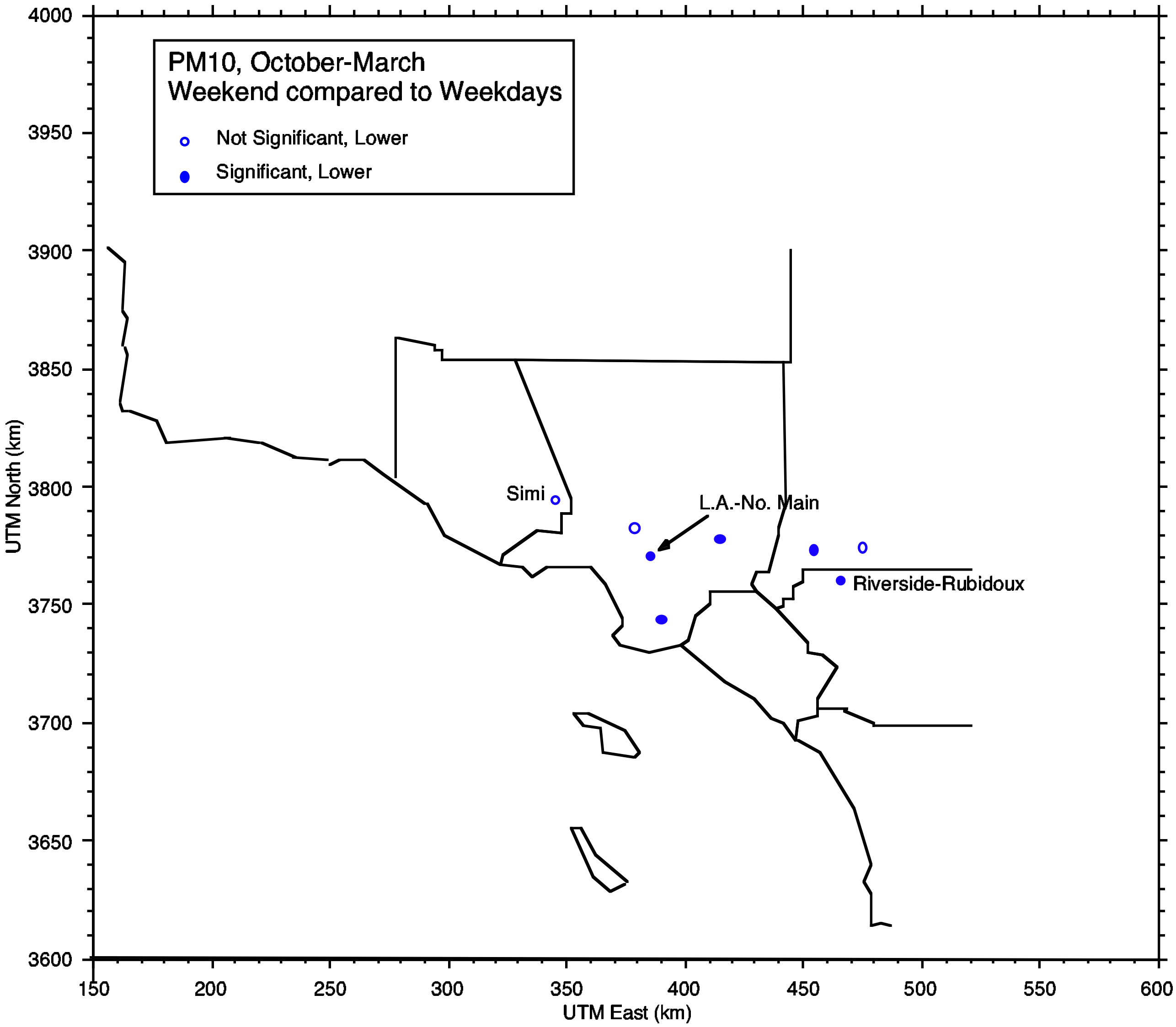

Figure 36. Geographic pattern of changes in PM_{10} concentration from weekdays to weekends during the cool/wet season (Oct-March) for all sites in the South Coast, South Central Coast, and Mojave Desert air basins. Open symbols represent changes that are not significant; closed symbols are significant ($p<0.01$). Circles represent decreasing values from weekdays to weekends; squares represent increasing values.

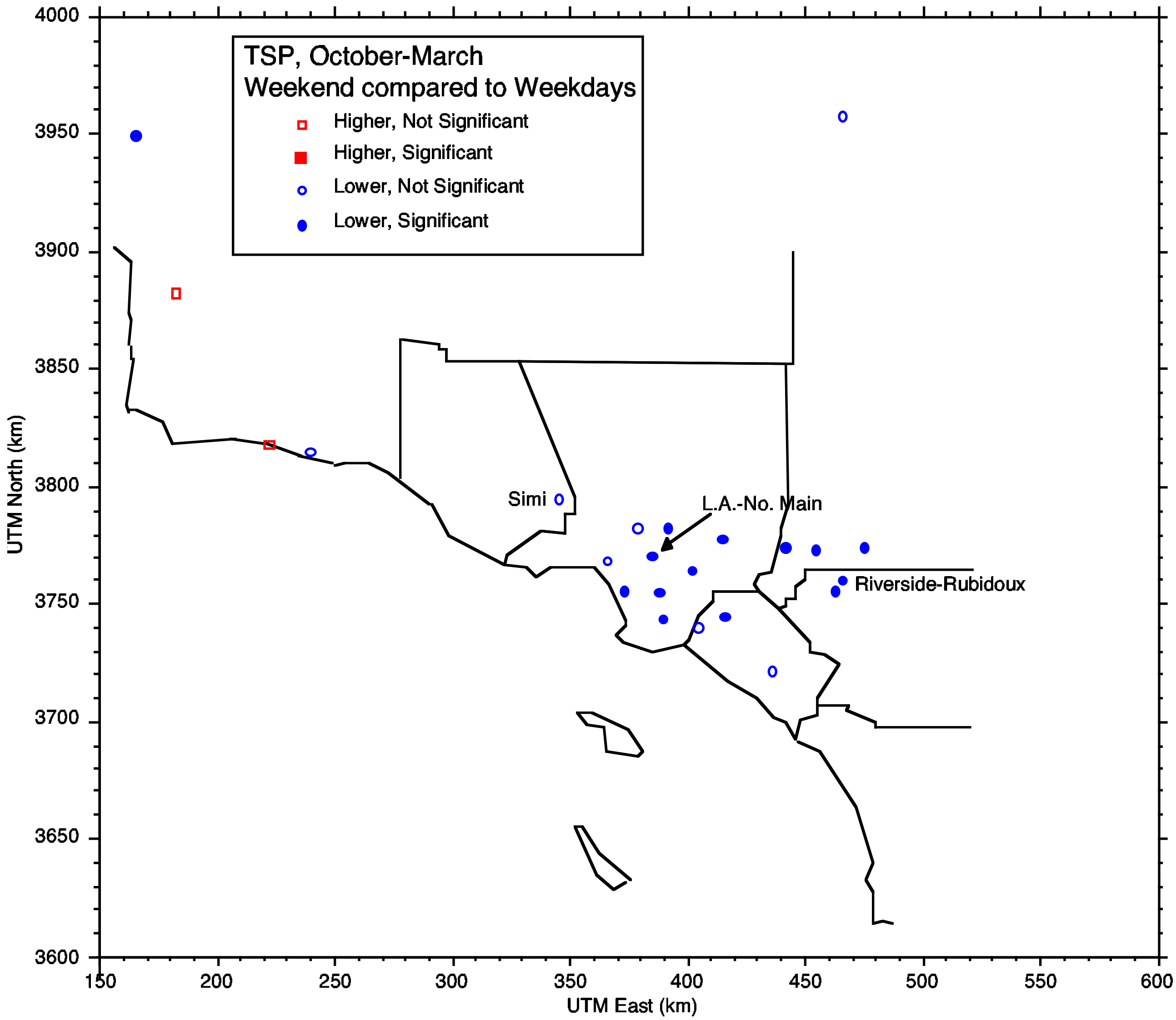

Figure 37. Geographic pattern of changes in TSP concentration from weekdays to weekends during the cool/wet season (Oct-March) for all sites in the South Coast, South Central Coast, and Mojave Desert air basins. Open symbols represent changes that are not significant; closed symbols are significant (p<0.01). Circles represent decreasing values from weekdays to weekends; squares represent increasing values.

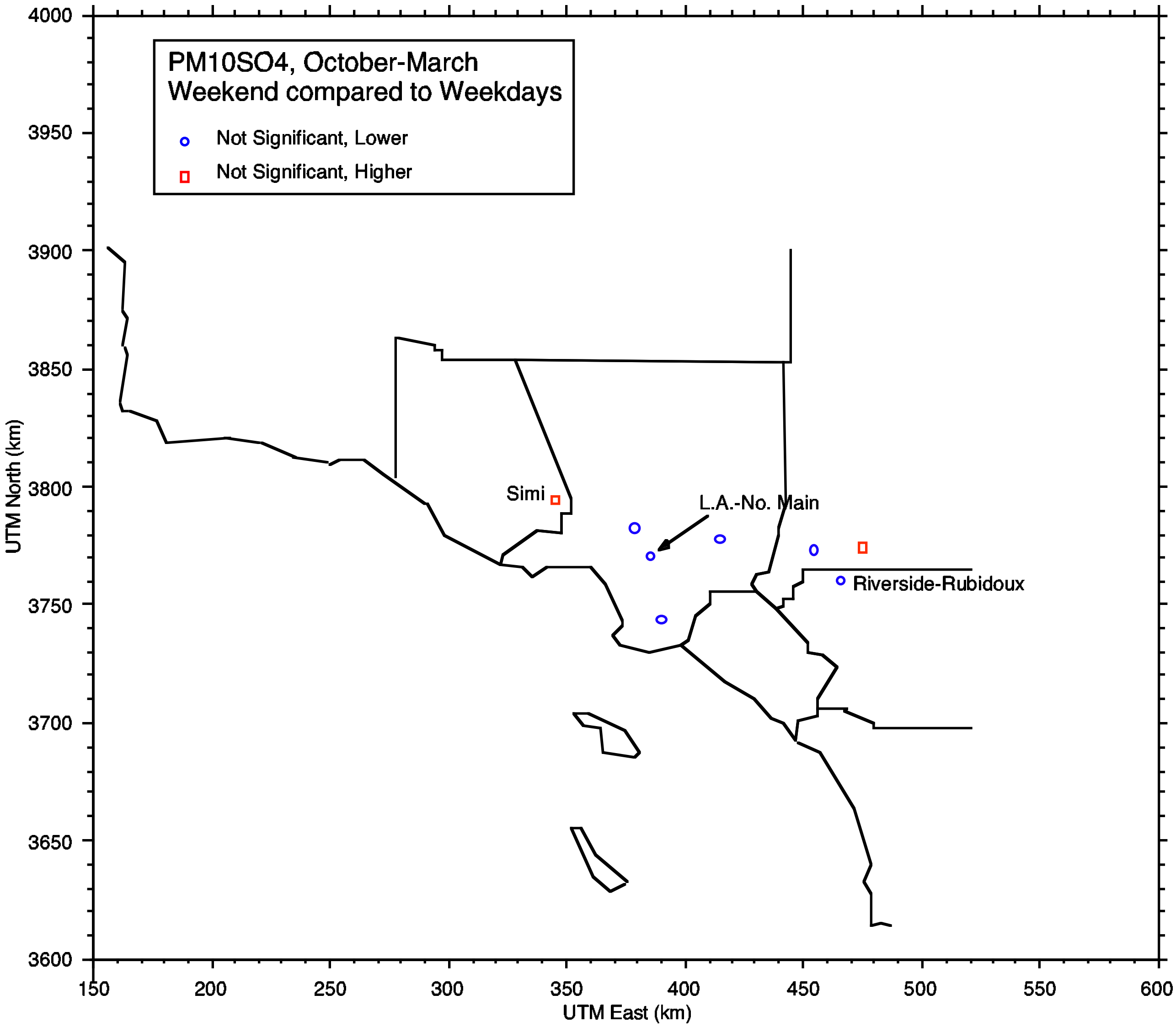

Figure 38. Geographic pattern of changes in PM_{10} SO_4 concentration from weekdays to weekends during the cool/wet season (Oct-March) for all sites in the South Coast, South Central Coast, and Mojave Desert air basins. Open symbols represent changes that are not significant; closed symbols are significant ($p<0.01$). Circles represent decreasing values from weekdays to weekends; squares represent increasing values.

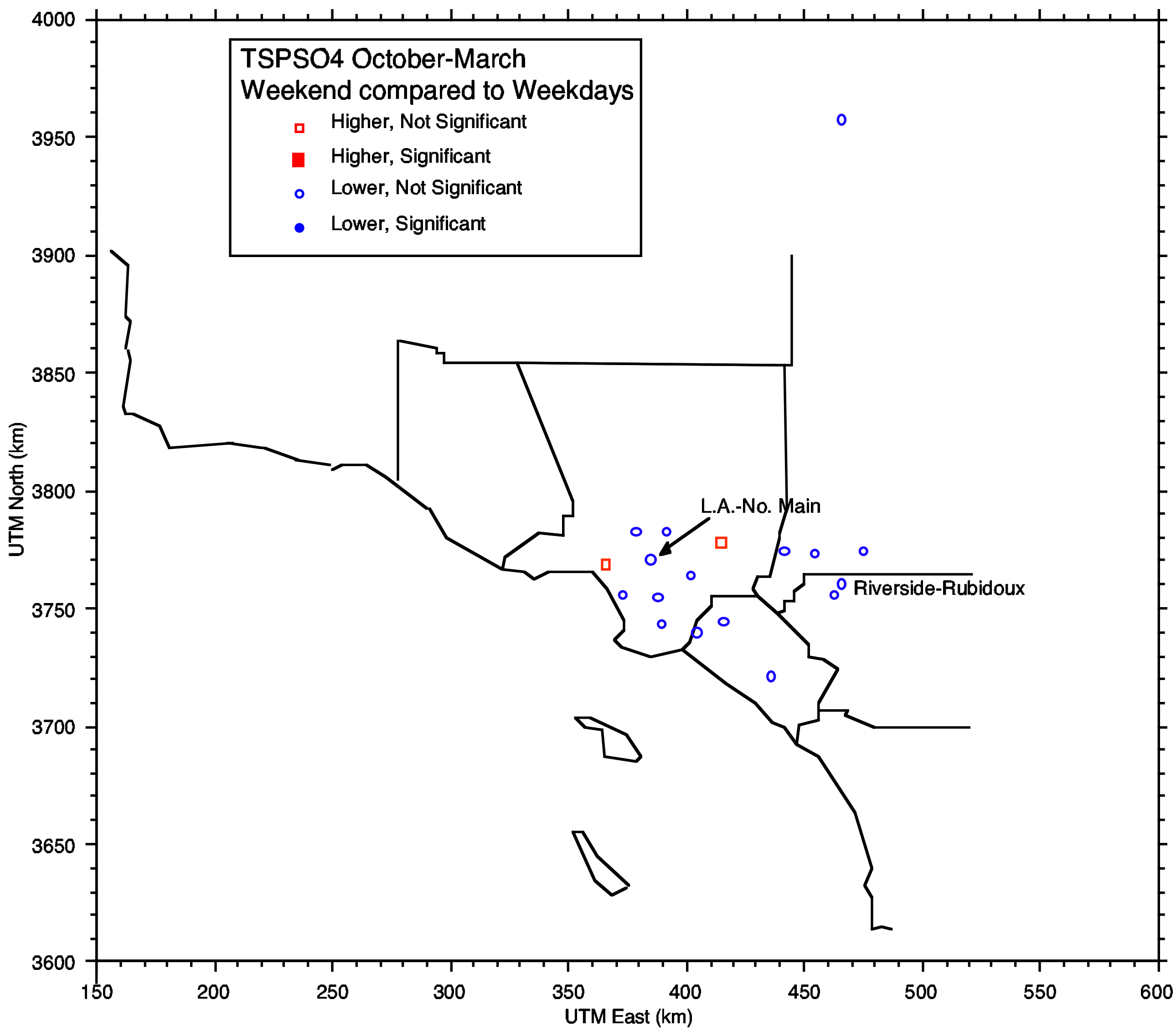

Figure 39. Geographic pattern of changes in TSP SO_4 concentration from weekdays to weekends during the cool/wet season (Oct-March) for all sites in the South Coast, South Central Coast, and Mojave Desert air basins. Open symbols represent changes that are not significant; closed symbols are significant ($p<0.01$). Circles represent decreasing values from weekdays to weekends; squares represent increasing values.

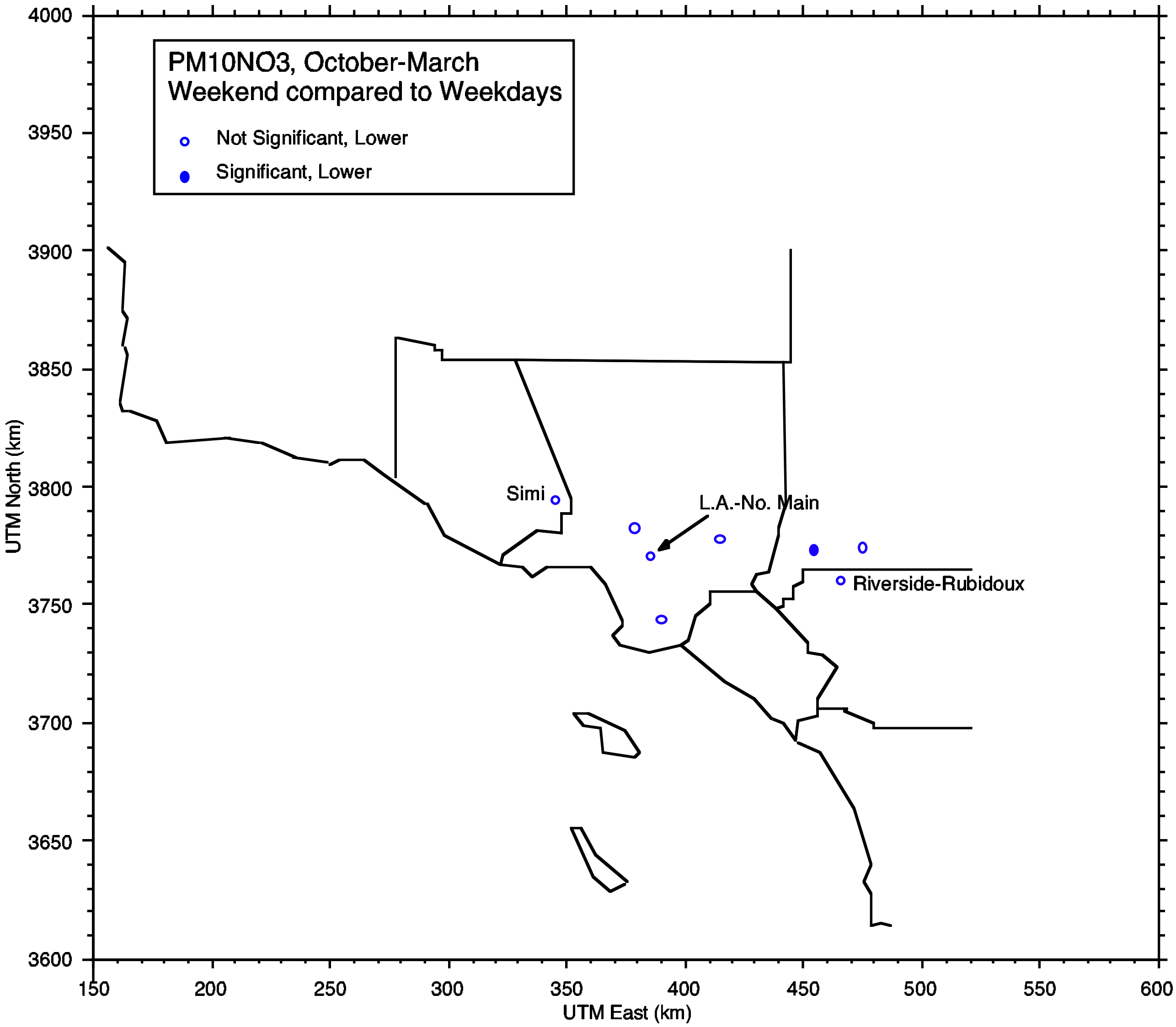

Figure 40. Geographic pattern of changes in PM_{10} NO_3 concentration from weekdays to weekends during the cool/wet season (Oct-March) for all sites in the South Coast, South Central Coast, and Mojave Desert air basins. Open symbols represent changes that are not significant; closed symbols are significant ($p<0.01$). Circles represent decreasing values from weekdays to weekends; squares represent increasing values.

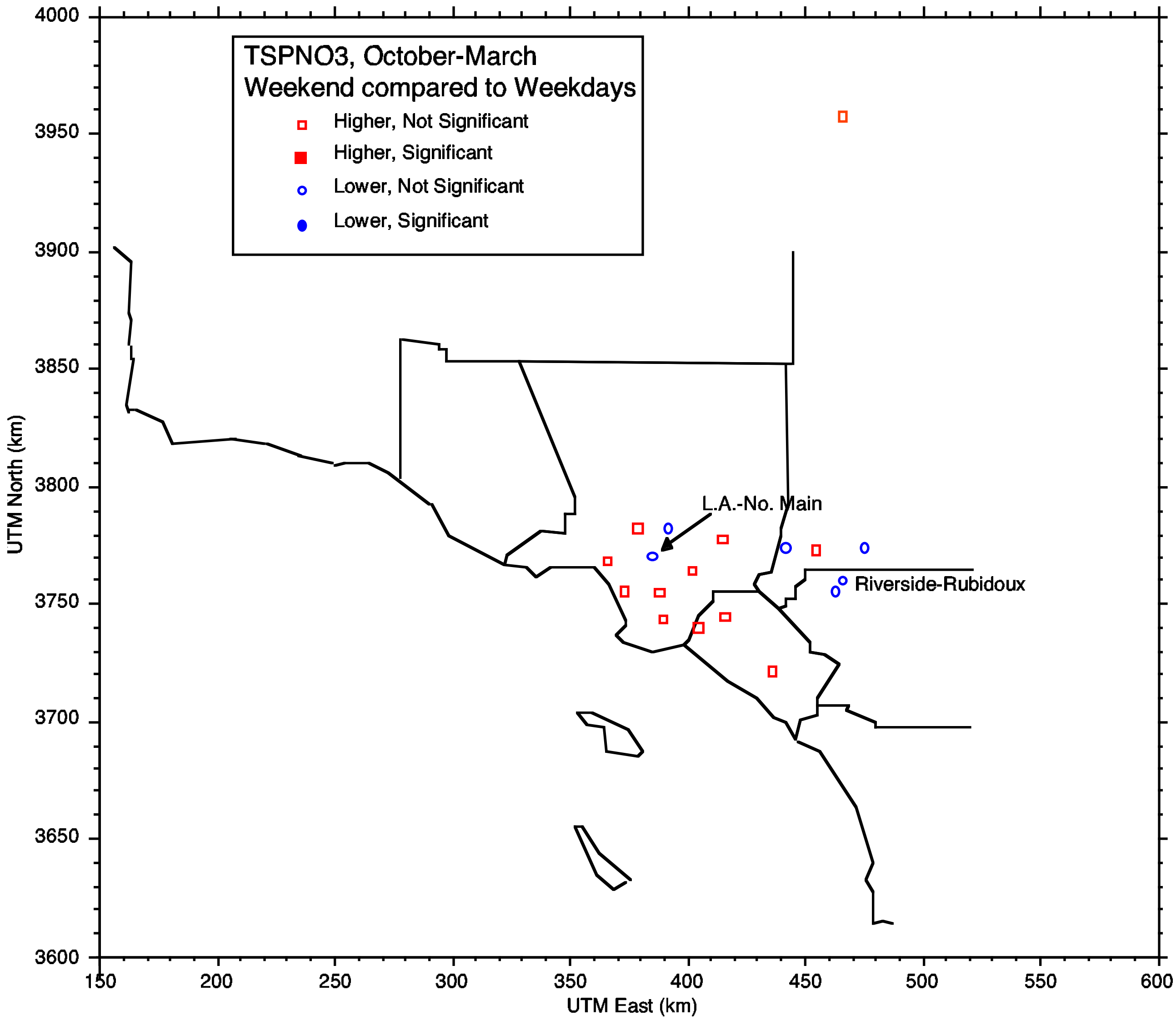

Figure 41. Geographic pattern of changes in TSP NO_3 concentration from weekdays to weekends during the cool/wet season (Oct-March) for all sites in the South Coast, South Central Coast, and Mojave Desert air basins. Open symbols represent changes that are not significant; closed symbols are significant ($p<0.01$). Circles represent decreasing values from weekdays to weekends; squares represent increasing values.

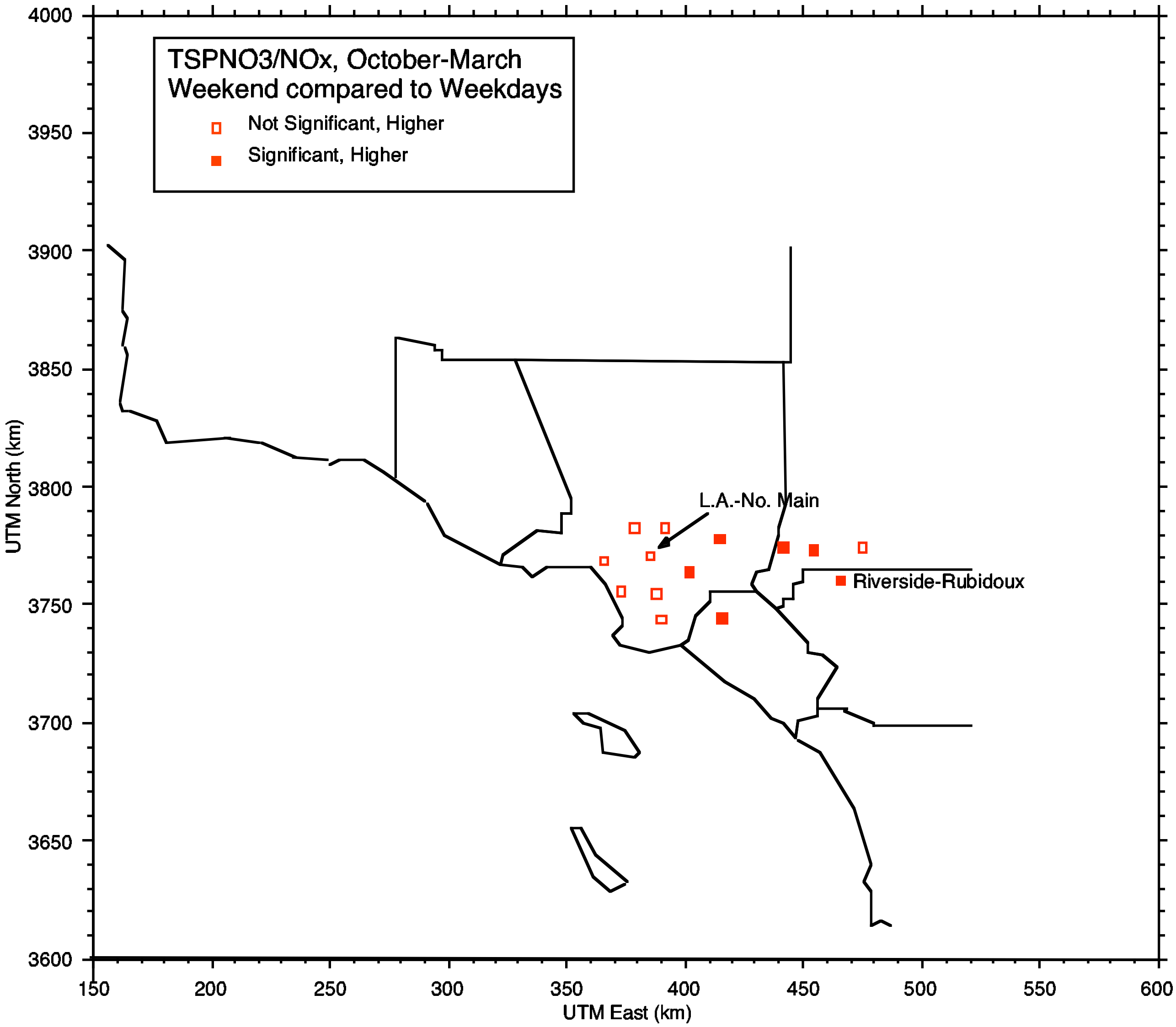

Figure 42. Geographic pattern of changes in TSP NO_3/NO_x concentration from weekdays to weekends during the cool/wet season (Oct-March) for all sites in the South Coast, South Central Coast, and Mojave Desert air basins. Open symbols represent changes that are not significant; closed symbols are significant ($p<0.01$). Circles represent decreasing values from weekdays to weekends; squares represent increasing values.

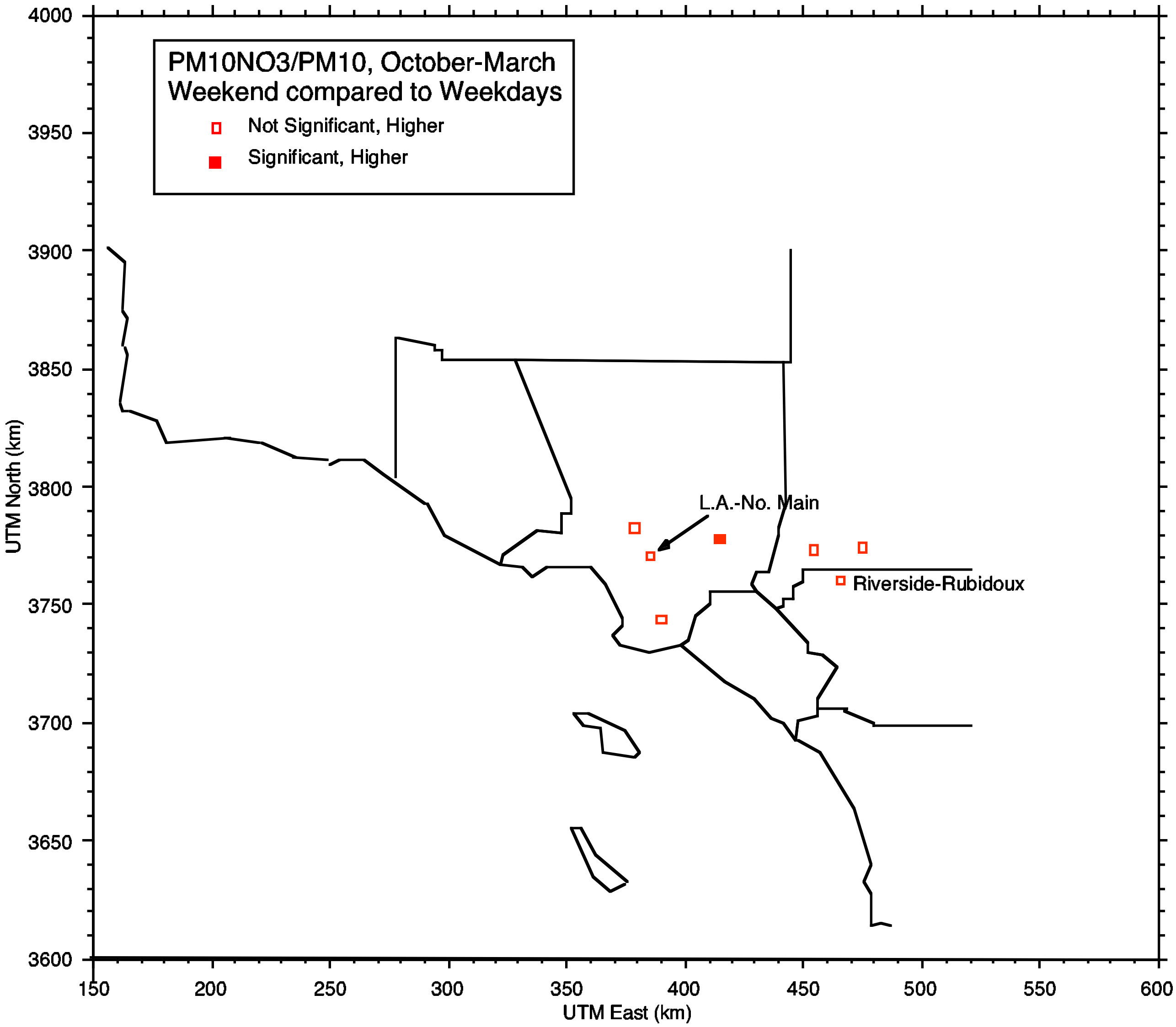

Figure 43. Geographic pattern of changes in PM_{10} NO_3/PM_{10} concentration from weekdays to weekends during the cool/wet season (Oct-March) for all sites in the South Coast, South Central Coast, and Mojave Desert air basins. Open symbols represent changes that are not significant; closed symbols are significant ($p<0.01$). Circles represent decreasing values from weekdays to weekends; squares represent increasing values.

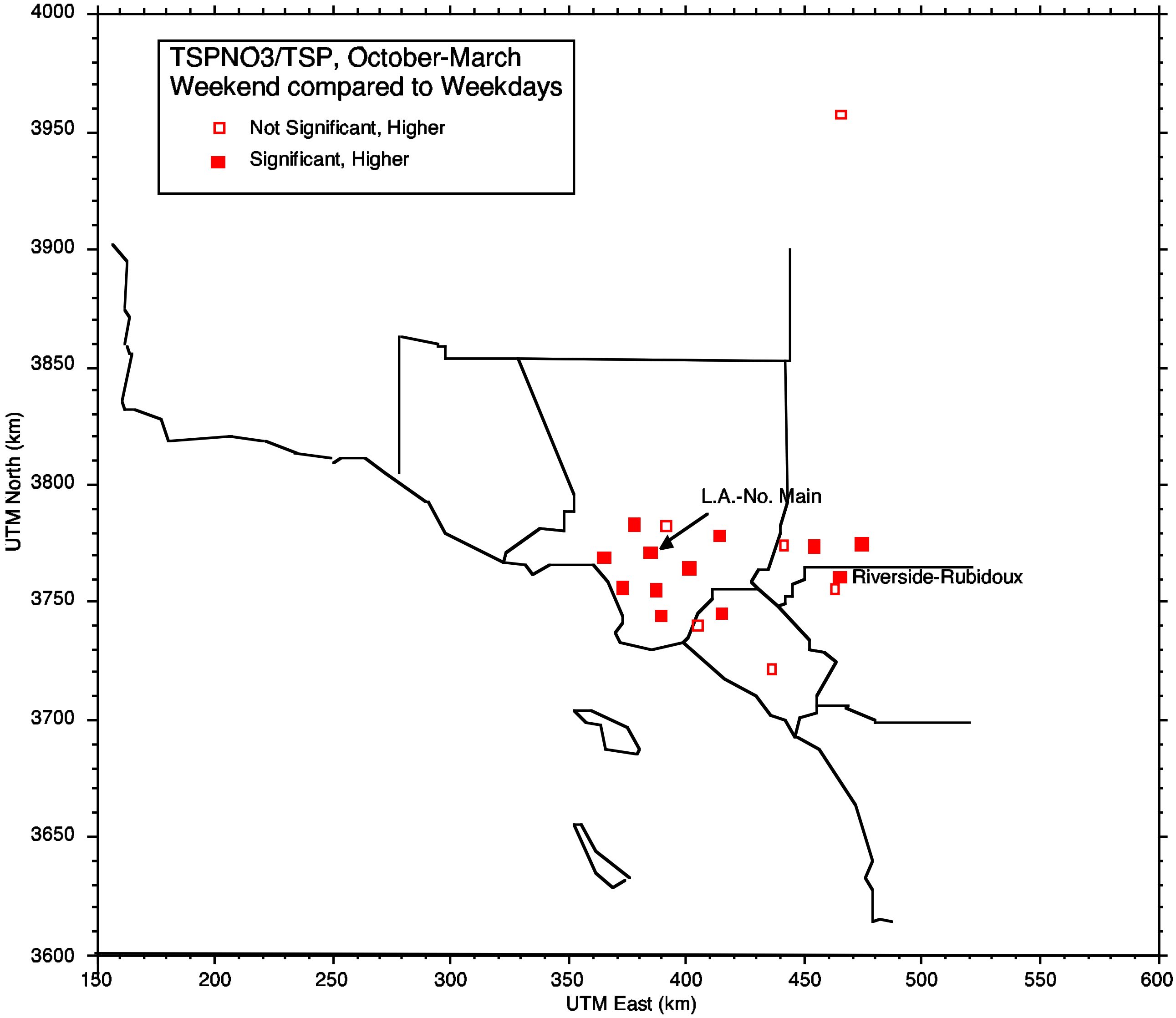

Figure 44. Geographic pattern of changes in TSP NO_3/TSP concentration from weekdays to weekends during the cool/wet season (Oct-March) for all sites in the South Coast, South Central Coast, and Mojave Desert air basins. Open symbols represent changes that are not significant; closed symbols are significant ($p<0.01$). Circles represent decreasing values from weekdays to weekends; squares represent increasing values.