APPENDIX X
MATES III

FINAL REPORT

Weekday/Weekend $PM_{2.5}$ Speciation Project

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X-1 Background

A major focus of MATES II and III is the estimation of ambient diesel particulate matter levels. Currently, diesel particulate matter is being estimated by quantifying the EC and other components of $PM_{2.5}$ samples. Although the MATES III Program assesses the annual South Coast Air Basin average risk associated with selected toxic air contaminants using monitoring data averaged over a year, emissions vary from day to day and especially from weekday to weekend, following variation of anthropogenic activity. Since this variation exists, additional weekend specific data on toxic air compounds could provide additional information on pollution sources. One of the most notable phenomena is the "ozone weekend effect" whereby concentrations of ozone are greater on the weekends than on the weekdays in the South Coast Basin. The weekend effect has become more pronounced over the last decade and is indicative of varying emissions sources as a function of the day of the week. Studies have also shown the reverse trend for VOCs, particulate matter (PM_{10} and $PM_{2.5}$), and carbon monoxide (CO) whereby high concentrations are observed during the weekdays and drop significantly (10 to 25%) on the weekends (ARB, 2004).

In an effort to investigate the weekday/weekend differences found, ARB initiated an emission source activity study characterized by day of the week which obtained data for on-road mobile sources, off-road mobile and area sources, and point sources which would include toxic air contaminant emissions (ARB, 2004). Through telephone and mail surveys, in-vehicle sensors checking driving activity, traffic volume observations on surface streets and freeways, continuous emissions monitoring, and on-site field surveys, it was shown that activity levels for on-road mobile sources, commercial off-road mobile sources, and commercial area sources declined on the weekends relative to weekdays, but activity levels for recreational off-road mobile sources and recreational sources increased on weekends relative to weekdays. The study included roadway loop sensor data which suggested that surface street traffic declined 20-27% on Saturdays and 27-33% on Sundays, but heavy-duty diesel traffic declined more, 67-83% (Figure X-1). Also, the study analyzed Caltrans Weigh-In-Motion (WIM) data for 2002 and observed that total freeway traffic declined 11% on Saturdays and 26% on Sundays (Figure X-2), but heavy-duty traffic declined 50-75% on weekends (Figure X-3). Different activity patterns exist for Friday, Saturday and Monday which is reflective of the transition from weekday to weekend activities and vice versa. According to ARB (Larsen, 2004), the preliminary observations for 2004 traffic patterns do not deviate significantly from those in 2002. Through surveys, activities such as boating, off-road driving, painting and barbecuing increased 25-165% from weekdays to weekends, but business activities declined 60-90% on the weekends, almost ceasing on Sunday (ARB, 2004).

X-2 Introduction

A special study was conducted in addition to the MATES III fixed site measurements to specifically compare weekday and weekend differences in elemental carbon, a marker for diesel exhaust, and later was expanded to include $PM_{2.5}$ mass and other compounds. Multiple-Channel Fine Particulate (MCFP) samplers from the PM Technical Enhancement Program (PTEP) were deployed to the Central Los Angeles, West Long Beach, and Rubidoux sites which were also selected for the PAH and the organic tracers measurements conducted as part of MATES III. The purpose of the extra samplers was to allow consistent Wednesday and Sunday sampling without interfering with the MATES III fixed-site sampling schedule and being able to acquire more day specific data than the fixed site sampling schedule. For the purpose of this study, Wednesday was chosen as the representative “weekday” because on-road vehicular activity was shown to be consistent from Tuesday through Thursday. Sunday was chosen as the representative “weekend” because it is the day with the lowest on-road vehicular activity within the South Coast Basin. Sampling by the MCFP samplers commenced in the high PM season starting in October 2004 and proceeded through March 2005 and then again from October 2005 through March 2006.

X-3 Methodology

The MCFP samplers collected a 24-hour integrated sample onto one Teflon filter and three quartz filters at the rate of 8 L min^{-1} (11,500 L per sample). Channel II of each MCFP sampler was equipped with a Teflon-coated cyclone for $PM_{2.5}$ size selective sampling. Information on the MCFP samplers can be found in Kim, et. al (2000). The sampler differs from the SASS samplers used in the routine sampling at the MATES III sites in the cyclone and flow rates. The MCFP sampler has been shown to produce comparable results to FRM samplers for mass and nitrates (Teffera,et. al, 1998). After mass was determined, metals were analyzed on the Teflon filters using X-ray Fluorescence Spectroscopy (XRF). EC/OC analysis duplicates were done on one of the quartz filters requiring two circular punches with a 5 mm diameter from the sample. After EC/OC analysis, the punched filters were stored with the collocated filters at 4^{o} C to await the organic tracer analysis. The two quartz filters with the most convergent EC concentrations on a given sampling day were selected to contribute to the monthly composite sample for the organic speciation analysis.

Volatile organic compound data and $PM_{2.5}$ filter data from the fixed site data were also used for day-of-week analysis and were measured using the methods described in Section 2.5; PAH measurement methods are depicted in Appendix IV; and $PM_{2.5}$ particulate-bound organic compound analysis is described in Appendix V.

X-4 Results and Discussion

In addition to normal quality control checks, the data from the MCFP samplers were compared to the data from the fixed sites for the days that there was overlap. The MCFP mass concentrations showed a positive bias from the SASS mass concentrations (Figure X-4). The bias was greater than 20% in all samplers. QC checks on the MCFP metals data indicated that there were unusually high concentrations of copper, zinc, nickel and other metals that were not seen in the

SASS metal data. A source of contamination was found in the brass fittings that were used upstream of the denuder tubes. Brass is an alloy consisting primarily of copper (~65%) and zinc (~35%) and other trace metals. When the total mass of the metals was compared to the overlapping samples, a positive bias was found in the MCFP sampler data. When that metal sum bias was subtracted from the MCFP $PM_{2.5}$ mass data, the adjusted mass MCFP concentration averages were comparable to the SASS mass data averages.

Because of the known metals contamination of the MCFP samples, the MCFP data was not used further for data analysis on $PM_{2.5}$ mass and metal content. Instead, the SASS sample data was used for the day-of-week comparisons for $PM_{2.5}$ filter data. The SASS data provides a complete data set over two years which provides around 35 data points for comparison for each day of the week for each site compared to the 24 data points originally conceived for the special project for one year with the MCFP. Also, it allows for seasonal comparisons as well as providing resolution to see Friday, Saturday, and Monday transition effects on the data.

The $PM_{2.5}$ EC and OC data from the MCFP samplers were relatively unaffected by the metals contamination as would be expected. The average EC and OC MCFP data was within 15%, the precision of the carbon analyzer at ambient concentrations, of the SASS averages with exception to the Rubidoux OC data which was within 25%. Thus, it can be inferred that the data for the $PM_{2.5}$ particle-bound speciated organic compound analysis is not significantly affected by the metals contamination.

Figure X-5 shows the day-of-week SASS $PM_{2.5}$ mass pattern for the seasonal data of West Long Beach, Los Angeles, and Rubidoux. The summer designation is for data collected in the months of April through September, and the winter designation is used for data collected in the months of October through March. The West Long Beach mass data shows that the annual weekend mass average (19.52 $\mu g\ m^{-3}$) is 10% higher than the weekday average (17.88 $\mu g\ m^{-3}$), but the average concentration is highest on Saturday (21.57 $\mu g\ m^{-3}$). This pattern was also observed in Rubidoux, Los Angeles, and also in the total regional average of all fixed station $PM_{2.5}$ mass data. When looking at the seasonal mass data, there is less of a change between weekend mass in the summer whereas there is a 30-50% increase in the winter between the three sites which accounts for most of the difference observed in the annual data. In the winter, the day-of-week trend indicates the maximum average mass concentrations on Saturday and the lowest on Monday with a 40 – 60% difference. Comparison of the stations confirms other observations that Rubidoux has higher average $PM_{2.5}$ concentrations relative to the western portions of the South Coast Air Basin.

This Saturday effect observed with the mass was also observed in the SASS $PM_{2.5}$ NO_3 and SO_4 data (Figure X-6 and Figure X-7) in all three sites with increases of 30% and 14% respectively for the annual average, but the larger differences (40 – 70%) were observed in the winter data. For comparison to other studies, average summer concentrations of NO_3 in this study were three to four times higher than the 0.54 to 0.82 $\mu g\ m^{-3}$ concentrations reported by the three-week summer time study by Lough, et al. (2003). The seasonal NO_3 and SO_4 trends are comparable to those reported by ARB, 2005. Concentrations of NO_3 were higher in the winter than in the summer and increase going from west to east which agrees with other studies which have shown secondary particulate formation downwind of NH_3 sources (Russell and Cass, 1986; Neuman, et al., 2003). NH_4 concentrations day-of-week patterns matched the NO_3 patterns for the three sites. Conversely, SO_4 concentrations were higher, especially during the weekdays, closer to the industrial and traffic sources in the western side of the Basin. MATES III SO_4 summer average concentration of 4.97 $\mu g\ m^{-3}$ agrees well with Los Angeles concentrations reported in the Lough, et al., Study (2003) which reported 4.4 ±1.8 $\mu g\ m^{-3}$. Also, 60 to 100% higher SO_4 concentrations were observed in the summer than in the winter at the three sites. The SO_4 average concentrations declined progressing eastward.

Average Wednesday to Sunday comparisons of selected organic speciated compounds from the MATES III Study were compared to PAH special study average data if the compounds were measured in both studies. Average concentrations of the fall PAH data to the organic speciated data for pyrene, indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene are within 95%, 14% and 30% respectively. The high discrepancy for pyrene would be expected as the particulate-bound heavier PAHs will retain to the filter while the more volatile pyrene would have less recovery on a filter compared to XAD-2, the absorbent used in the PAH study.

In the organic tracer data, pyrene, a stronger marker for diesel, shows a greater than 40% decrease on Sundays relative to Wednesdays for West Long Beach, Los Angeles and Rubidoux; benzo[g,h,i]perylene, a marker for light-duty vehicles, decreases from 40% in West Long Beach to 13% in Rubidoux; indeno[1,2,3-cd]pyrene, a tracer for older, higher polluting vehicles, decreases at West Long Beach and Los Angeles, but increase in Rubidoux; coronene, another tracer for light-duty vehicles decreases between 30 and 40%; and levoglucosan, a tracer for biomass combustion, increases at West Long Beach, Los Angeles and Rubidoux, with the largest increase at West Long Beach (Figure X-8). Pyrene, indeno[1,2,3-cd]pyrene, and indeno[1,2,3-cd]pyrene at West Long Beach have variable higher concentrations during Monday through Friday and decrease on the weekend. Other tracers of vehicle combustion such as benzene, toluene and m+p xylenes showed a similar pattern at West Long Beach (Figure X-9), but were different at Los Angeles (Figure X-10) and Rubidoux (Figure X-11). West Long Beach showed a 20 to 30% decrease between the average weekday to weekend concentrations and Rubidoux showed more modest changes (Figure X-12), whereas increases in concentrations of these volatile tracers increased during the weekend at Los Angeles, mostly attributed to a Saturday maximum.

OC average concentrations (Figure X-13) did not vary from weekend to weekday except at Rubidoux where both Saturday and Sunday concentrations were 20% higher than the weekday average. However, the seasonal pattern at West Long Beach and Los Angeles shows that fall/winter concentrations were 42% higher and 27% higher respectively. Rubidoux did not exhibit a seasonal difference.

EC average annual day-of-week concentration data showed concentrations drop 40 to 45% from Wednesdays to Sundays (Figure X-14). The day-of-week pattern shows an 18 to 30% drop from weekdays to weekends. The percentage differences were more enhanced in the summer. Also, over 50% differences between fall/winter and EC concentration were observed at the three sites. EC concentrations for the three sites were similar from Friday through Sunday, but showed variation Monday through Thursday whereby EC progressively decreases going eastward from West Long Beach to Rubidoux.

$PM_{2.5}$ metal concentration differences between Wednesdays and Sundays were observed in some of the metals (Figure X-15). Zinc (Zn) and Manganese (Mn) concentrations decreased at all three stations with the most significant decrease occurring at the Los Angeles station. Nickel (Ni) concentrations increased on Sundays. Other differences in concentrations from metals such as arsenic (AS), cadmium (CD), lead (Pb), and vanadium (V) were not consistent across all the stations. However, $PM_{2.5}$ V concentrations did exhibit a maximum concentration on Saturdays and showed a distinct presence in West Long Beach compared to the other two sites (Figure X-16).

X-5 Conclusions

The two years of fixed site data was substantial enough to perform a day-of-week comparison. The sampling that was originally designated for the weekday/weekend special study provided a good quality control check for EC, OC and also the mass, if corrected for the metals contamination. As hypothesized from the activity data, the MATES III $PM_{2.5}$ data evaluated from West Long Beach, Los Angeles and Rubidoux confirms that Wednesday data is reflective of concentrations observed on average with Tuesday through Thursday. However, Sunday average data did not always demonstrate to have the minimum concentrations in the week as shown with the $PM_{2.5}$ mass. This is added evidence that indicates that studies designed to consider weekday versus weekend effects in the South Coast Basin should require both Saturday and Sunday measurements. Also, for some of the $PM_{2.5}$ speciated components, the seasonality has a significant effect upon concentration and day-of-week patterns which should also be reflected in data sets, as many activity studies are based upon a time scale that would not capture seasonal effects.

Known compounds associated with vehicular traffic such as EC, benzene, toluene, and PAHs showed a reduction in concentrations from the weekdays to a minimum on Sunday average. $PM_{2.5}$ EC average concentrations decreased from weekday to weekend, with a greater than 40% decrease from the maximum on Wednesdays to the minimum on Sundays. This EC decrease corresponds with the reduction on the weekends from sources such as diesel exhaust and commercial stationary sources, especially on Sunday. The day-of-week difference was stronger than the observed seasonality effects, although the day-of-week differences were more enhanced in the fall/winter time periods. Also, the EC weekend decrease is similar to trends observed in benzene, toluene, and m+p xylene at West Long Beach, but was only observed slightly in Rubidoux and not consistent with the trend observed in Los Angeles.

Sunday average data did not always show the minimum concentrations in the week as shown with the $PM_{2.5}$ mass, OC and associated inorganic ions and metals. $PM_{2.5}$ mass average day-of-week patterns for Rubidoux, Los Angeles, and West Long Beach differed from earlier observations of enhanced concentrations on the weekends relative to weekdays (Motallebi et al., 2003), but only during the winter/fall time period. The decrease in mass of EC on the weekends is small compared to the large increase in the secondary pollutants, NO_3 and SO_4, contributing to the increased overall $PM_{2.5}$ mass. Nitrate contributed more $PM_{2.5}$ mass downwind of NH_3 sources and the SO_4 contributed to $PM_{2.5}$ mass closer to the commercial and traffic sources. The data shows a peak maximum on Saturdays for $PM_{2.5}$ mass, NO_3, SO_4 and a minimum on Mondays.

Vanadium exhibited weekday to weekend variability, which shared a similar trend with SO_4 in seasonal, day of week, and seasonally at the West Long Beach site. Although vanadium day-of-week trends were similar across the three stations, there were significant differences in concentration among the three stations, with the highest concentrations located in West Long Beach and the lowest in Rubidoux. If it can be inferred that vanadium concentrations can be connected to the cargo ship activity due to the ships' use of residual fuel containing vanadium; the vanadium data suggests that emissions due to these ships is highest on Saturdays which may correlate to the high Saturday $PM_{2.5}$ SO_4 and NO_3 formed by the oxidation of SO_2 and NO_x that may also be generated by the ships.

Further studies can be done to compare traffic data at a higher resolution using traffic counts from the WIM Program to better source apportion traffic activity by vehicle type to the chemical analysis which will improve the geographic correlation between the data and the traffic observed. The data was not obtainable in the time scale for this report, but data can be obtained for a future data analysis.

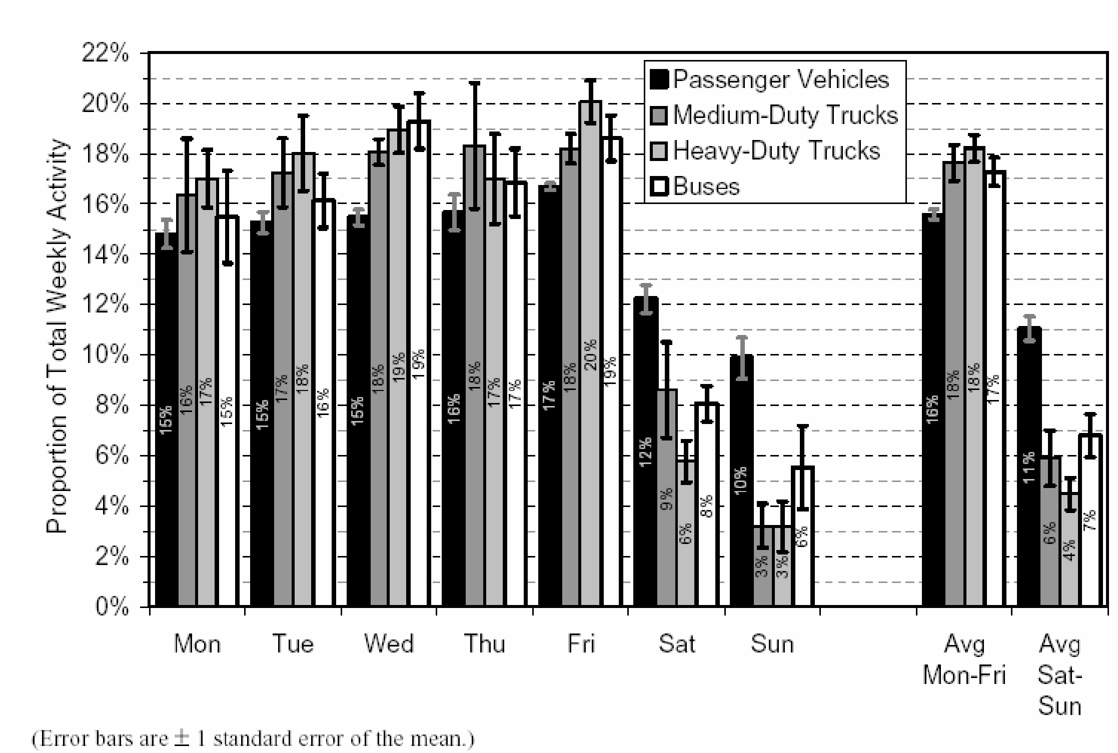


Figure X-1: Average day-of-week traffic patterns of differing vehicle classes observed for surface streets in 2002 (ARB, 2004).

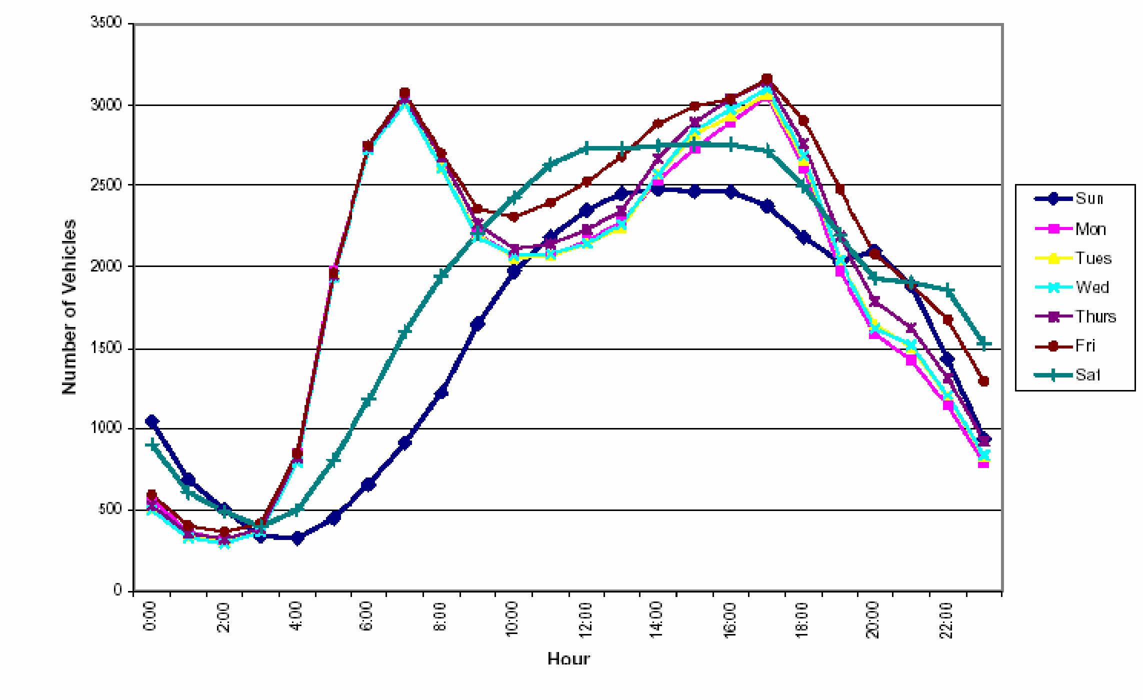


Figure X-2: Diurnal time series for light-duty vehicles by day of week.

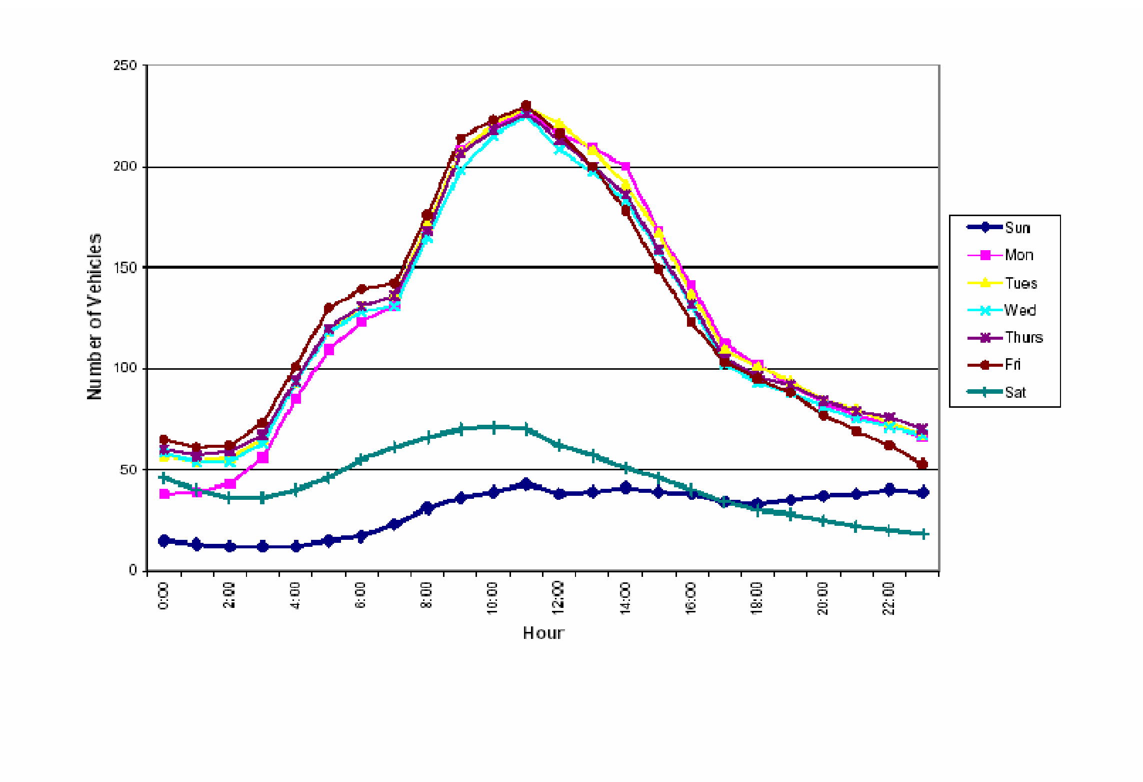


Figure X-3: Diurnal time series for heavy-duty vehicles by day of week.

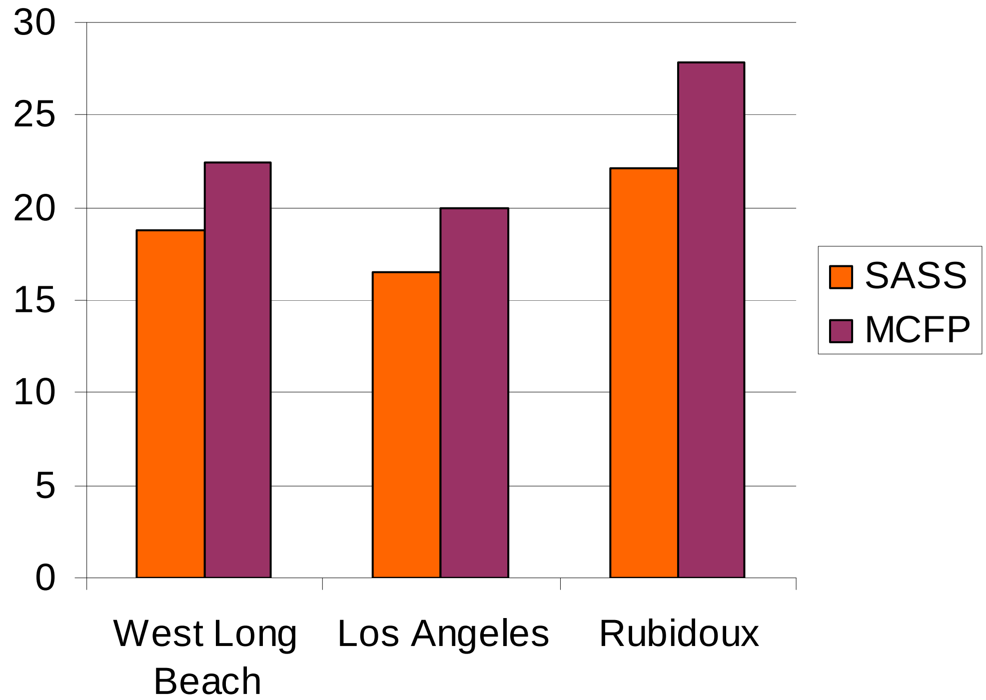


Figure X-4: Average of day-to-day comparisons (N= 17) of $PM_{2.5}$ mass data taken from SASS samplers from the fixed site data and the special purpose MCFP samplers.

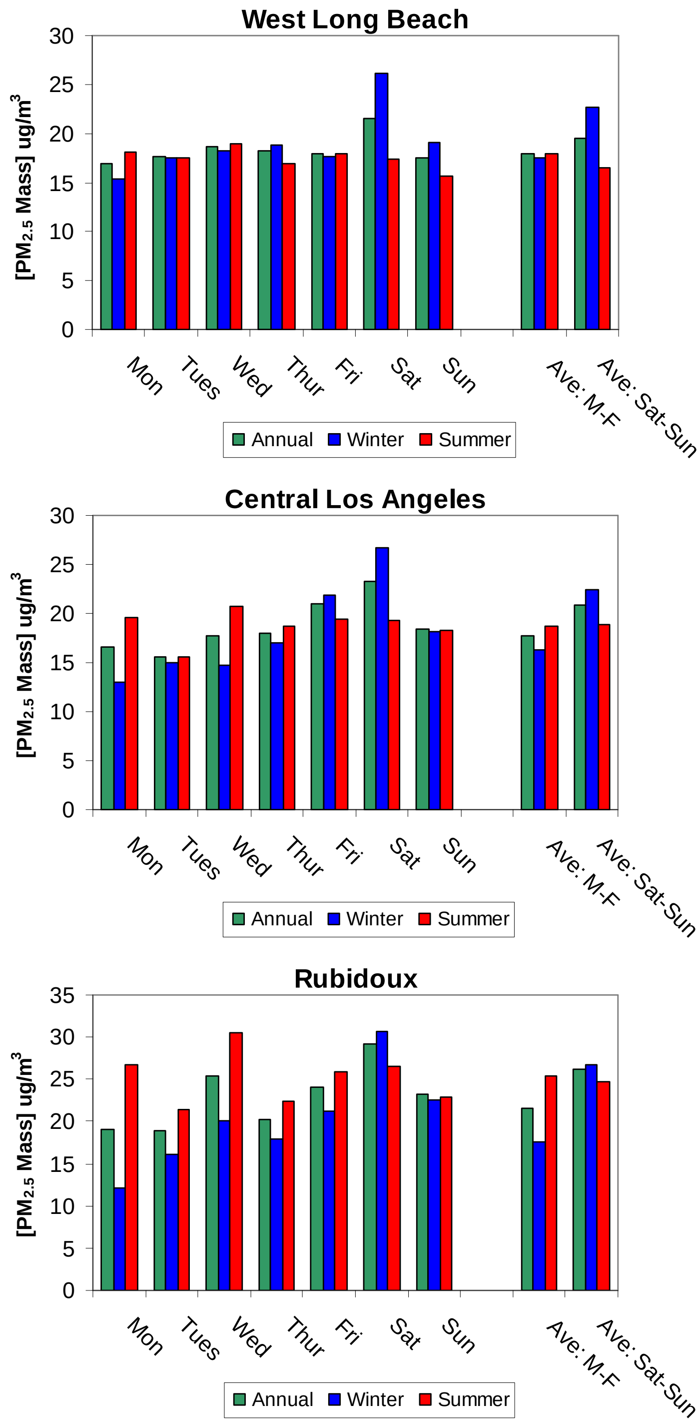


Figure X-5: Average day-of-week $PM_{2.5}$ mass concentrations by season for West Long Beach, Los Angeles and Rubidoux.

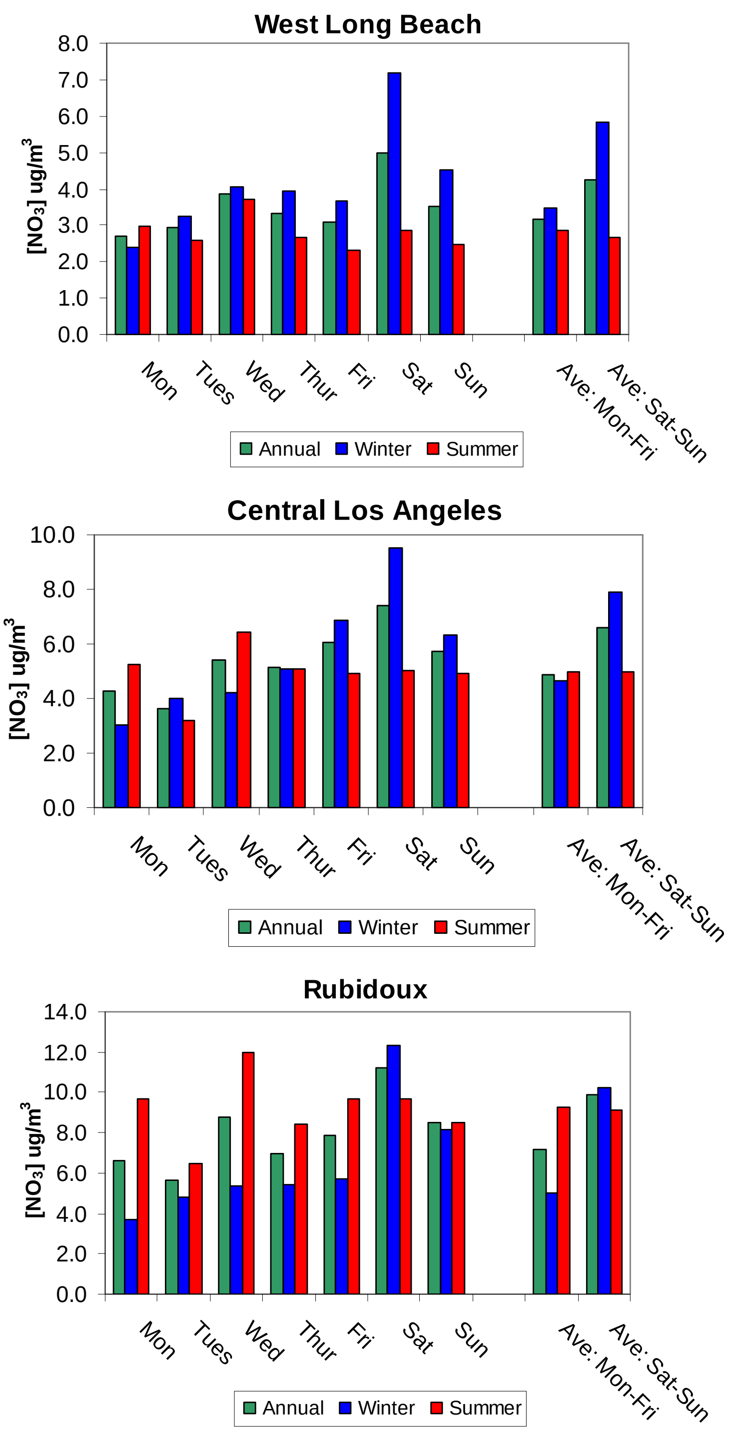


Figure X-6: Average day-of-week NO_3 concentrations by season for West Long Beach, Los Angeles and Rubidoux.

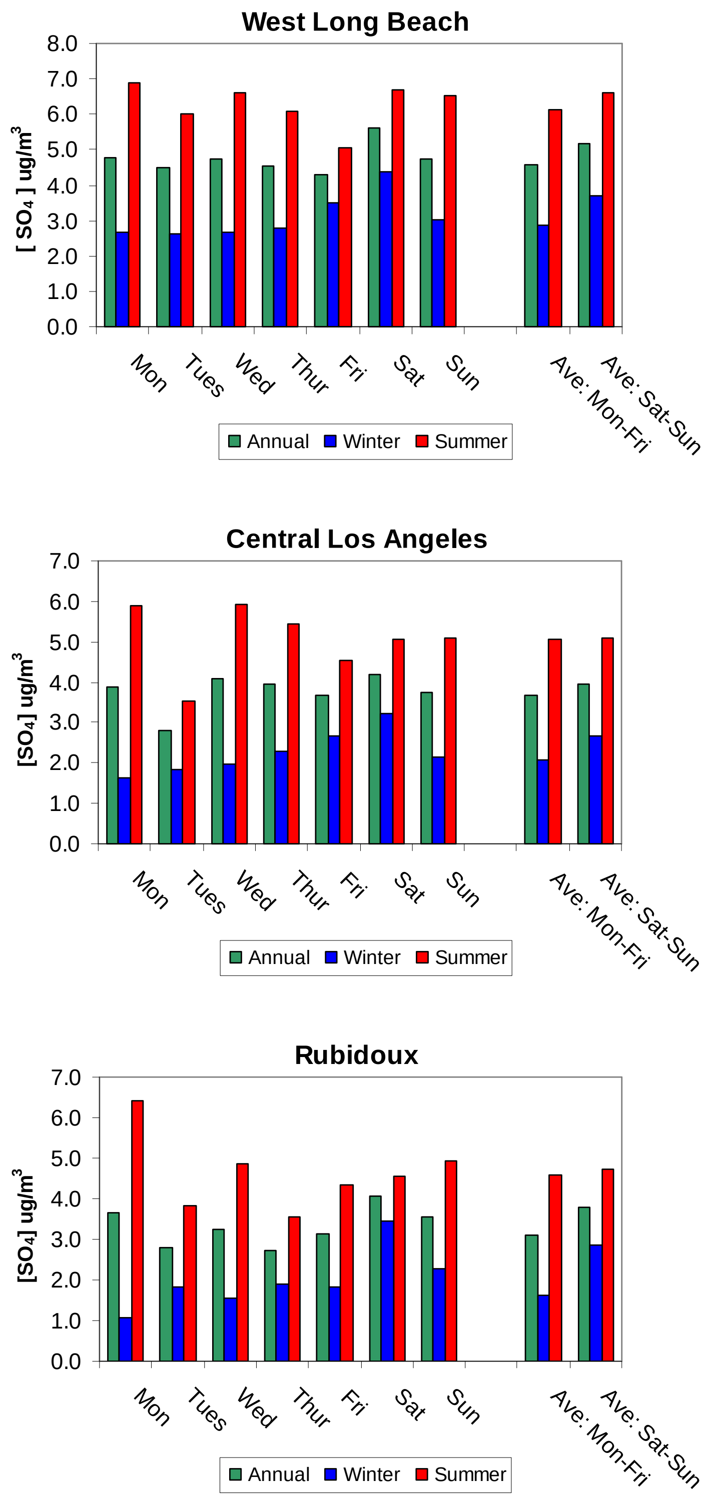


Figure X-7: Average day-of -week SO_4 concentrations by season for West Long Beach, Los Angeles and Rubidoux.

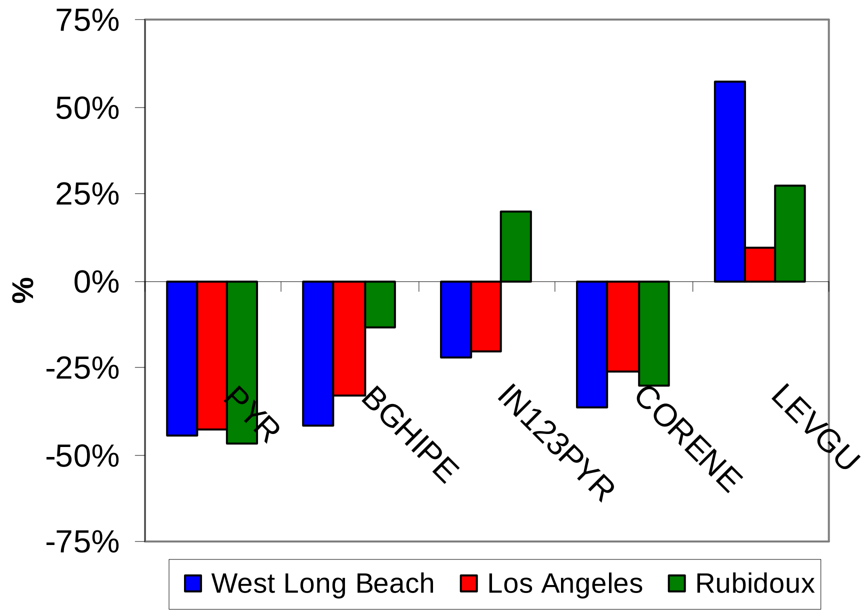


Figure X-8: Percentage change from Wednesday to Sunday of concentrations of selected organic tracer components at West Long Beach, Los Angeles, and Rubidoux during the fall and winter time.

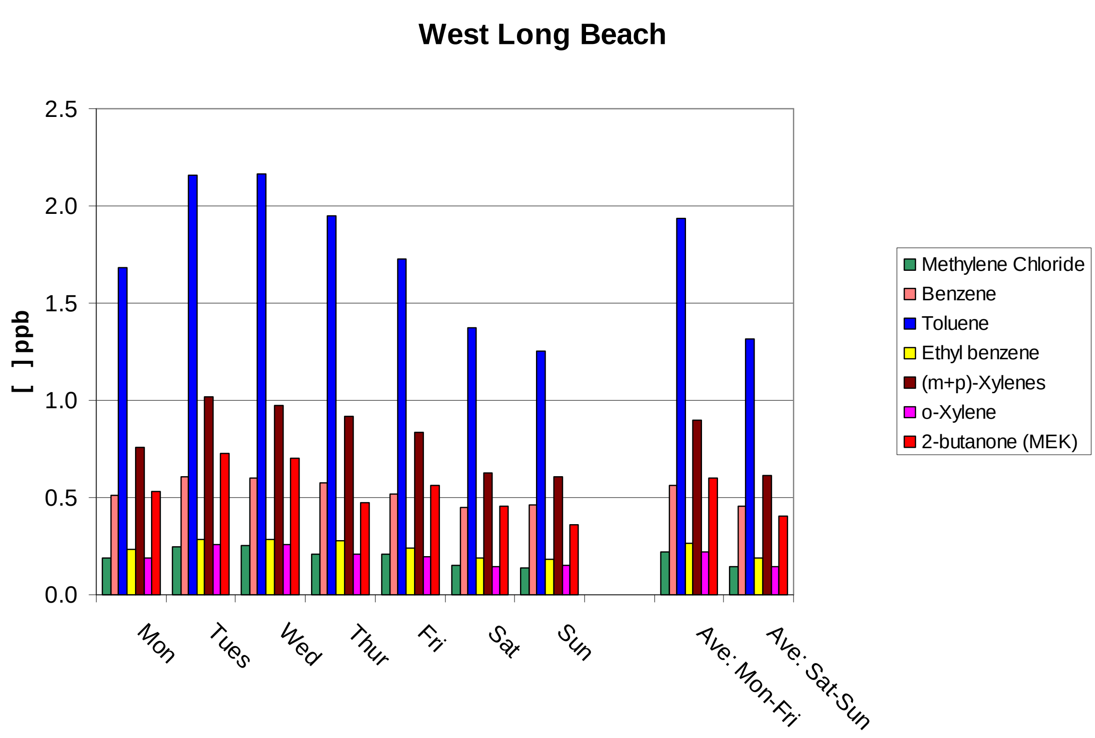


Figure X-9: Average selected VOC concentrations for West Long Beach by day.

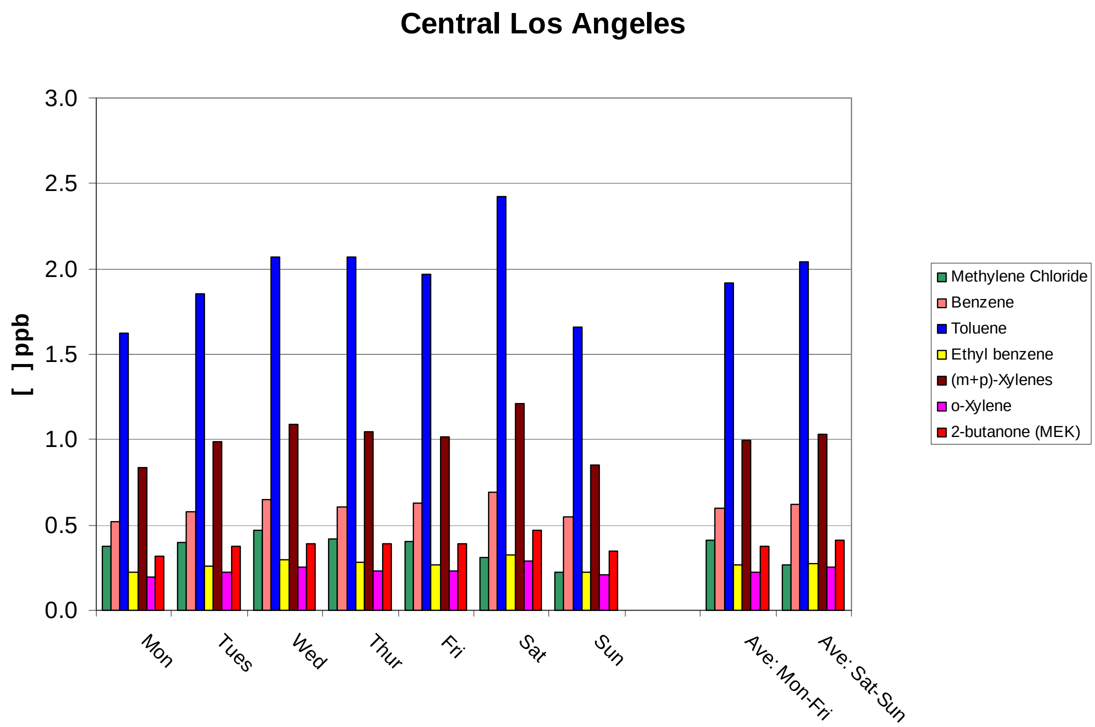


Figure X-10: Average selected VOC concentrations for Central Los Angeles by day.

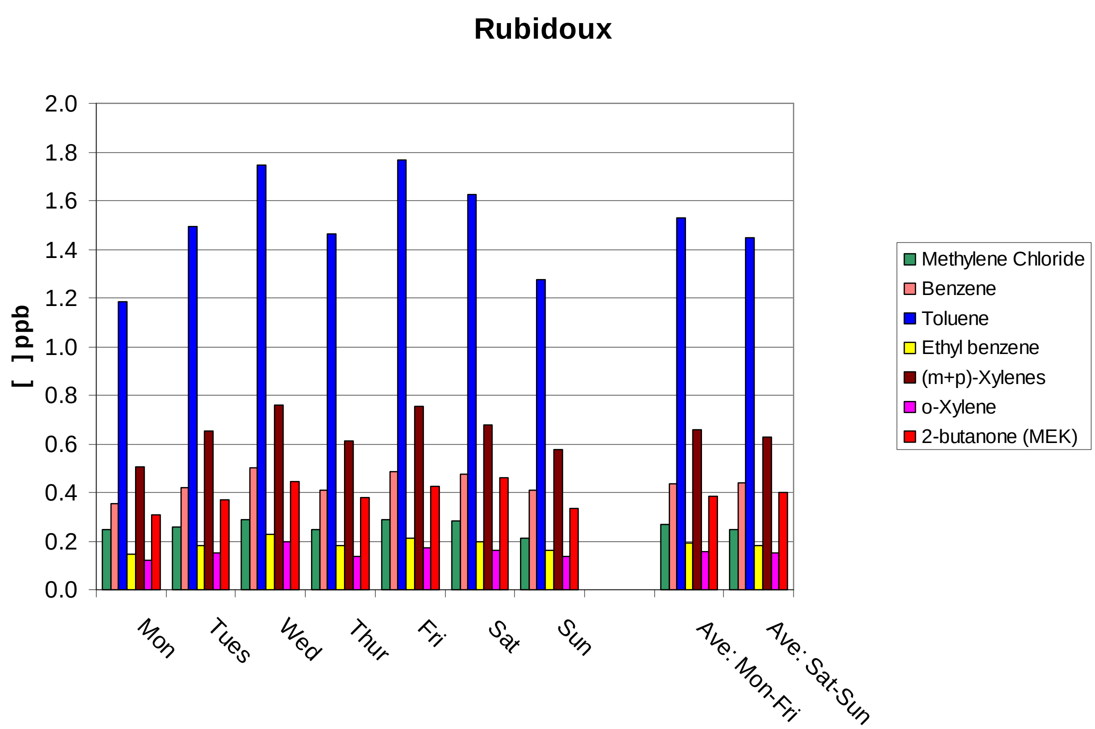


Figure X-11: Average selected VOC concentrations for Rubidoux by day.

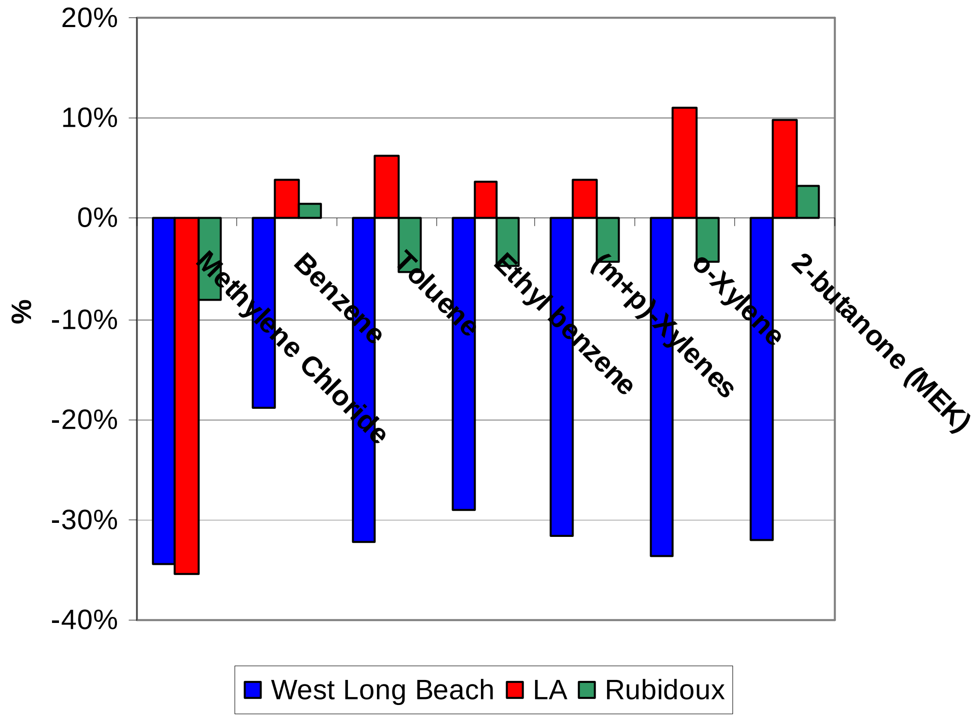
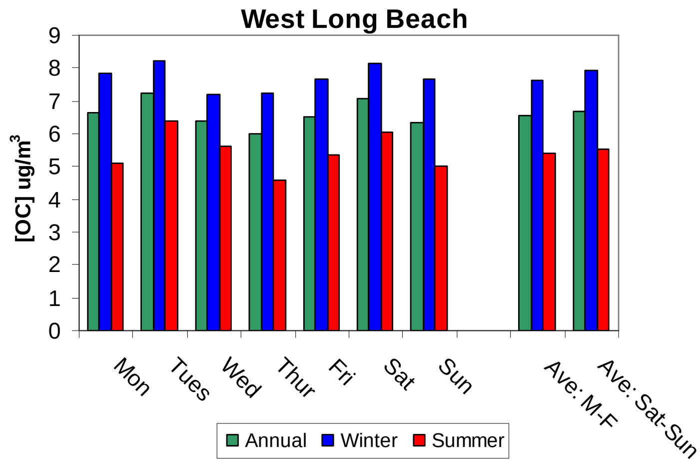
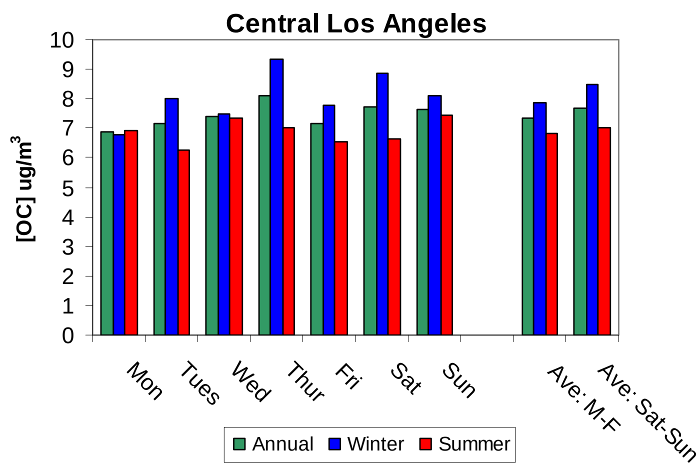


Figure X-12: Percentage difference of average weekday to weekend concentrations for select VOCs at West Long Beach, Los Angeles, and Rubidoux.





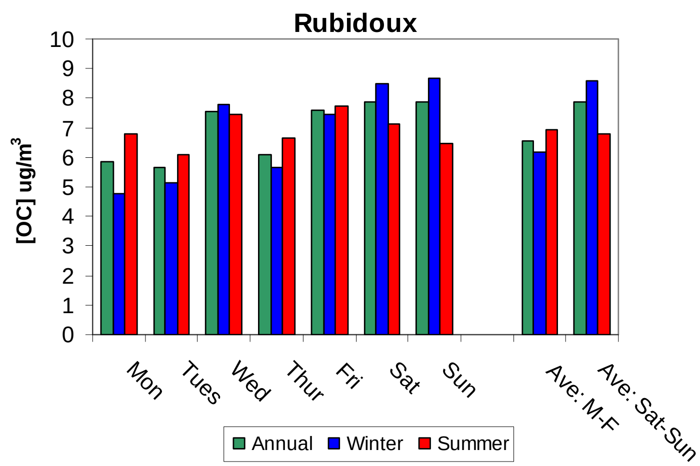


Figure X-13: Average day-of-week OC concentrations by season for West Long Beach, Los Angeles and Rubidoux.

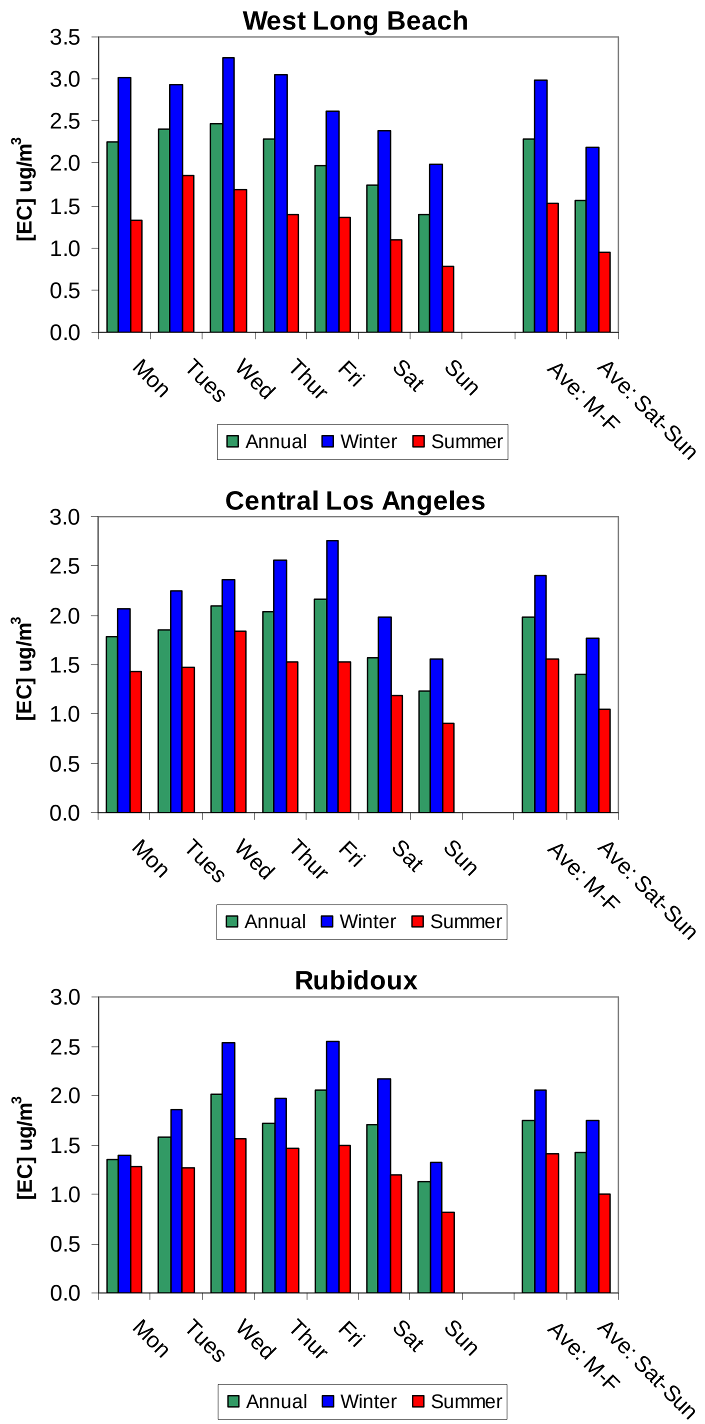


Figure X-14: Average day-of-week EC concentrations by season for West Long Beach, Los Angeles and Rubidoux.

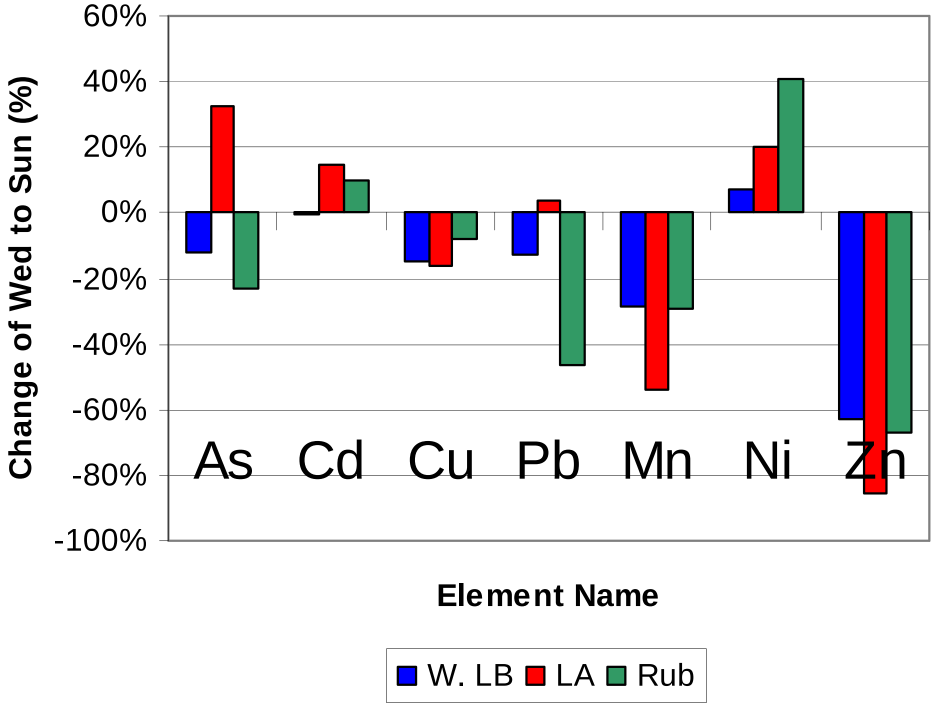
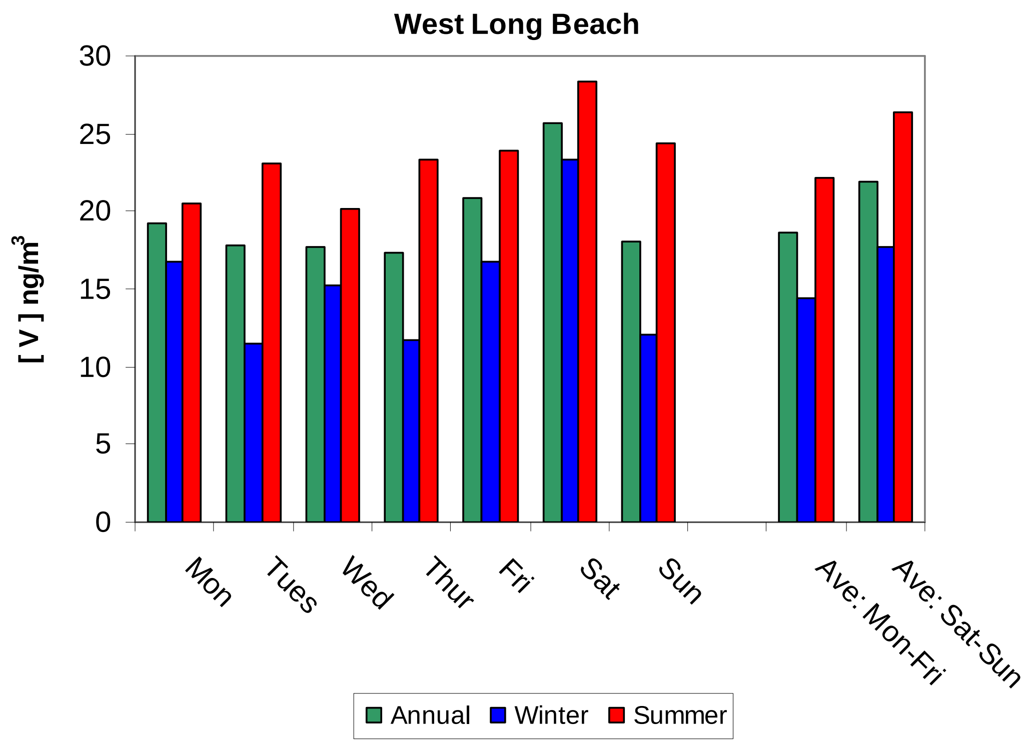


Figure X-15: Percentage differences from Wednesday to Sunday concentrations for $PM_{2.5}$ metals. A negative percentage indicates a drop in concentration on Sunday compared to the Wednesday concentration.



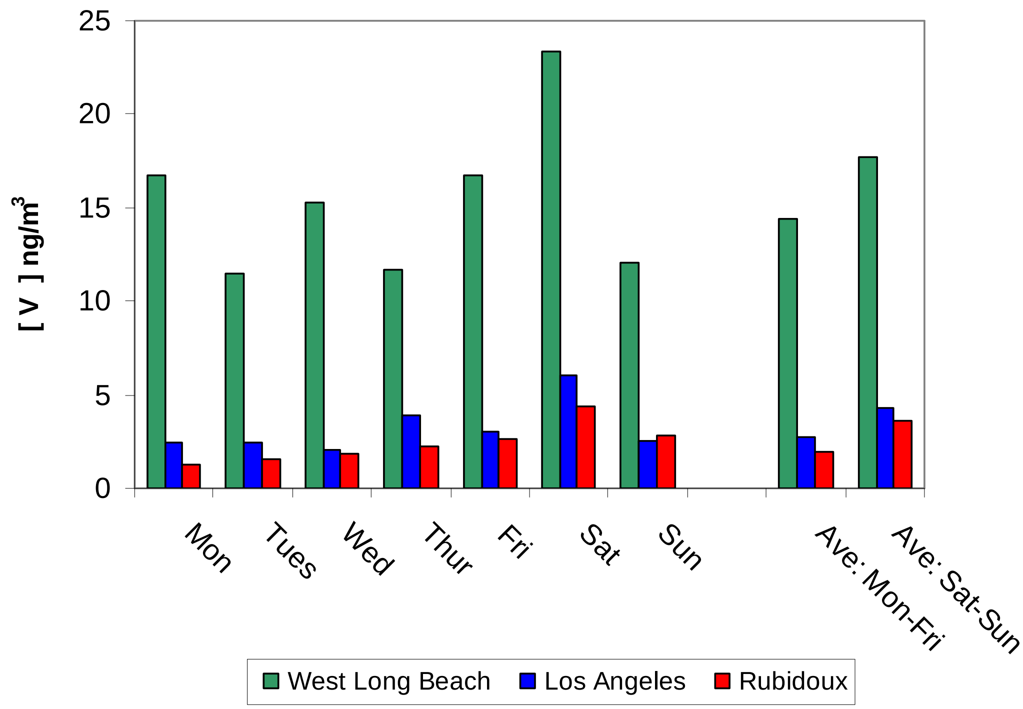


Figure X-16: Vanadium day-of-week average concentrations for West Long Beach by season and also in comparison to day-of-week trends with Los Angeles, and Rubidoux.

X-6 References

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