

Day-of-Week Patterns of Particulate Matter and its Species at Selected Sites in the SoCAB

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Introduction

The purpose of this study is to analyze the concentrations of particulate matter by day of week in the SoCAB and to describe or characterize any weekday/weekend effect on particulate matter (PM). Given the contribution of NO_x and VOC ozone precursors to secondary PM formation, it would be useful to know whether the variations by day of week in these precursors are evident in PM data. Analyses of the day-of-week effects of the 1995 PM₁₀ Technical Enhancement Program (PTEP) conducted by Dr. Bong Kim of SCAQMD are also summarized.

PM Data

The particulate data used in this study were available from routine particulate matter monitoring program and the California Acid Deposition Monitoring Program (CADMP). For the routine monitoring program, particulate matter-10 micron samples (PM₁₀) are collected over a 24-hour period using a high volume sampler equipped with a size selective inlet (SSI) or a dichotomous (Dichot) sampler. Samples are usually collected from midnight to midnight every sixth day. Composition analysis currently provides measurements of nitrate, sulfate, ammonium, chloride, and potassium for selected sites. The dichotomous sampler, or virtual impactor, uses a low volume PM₁₀ inlet followed by a split in the flow stream that separates particles in two separate fractions: fine particles (PM_{2.5}, i.e., particles with diameters less than 2.5 μm) and coarse particles (those having diameters 2.5-10 μm). The sum of the fine and coarse fractions provides a measure of total PM₁₀ from the Dichot sampler.

Initially, the CADMP sampler had two units designed for collection of particulate species in two size fractions and for collection of acidic gases. The PM₁₀ unit collected particles less than 10 μm aerodynamic diameter on a Teflon filter, and had impregnated back filters for collection of ammonia and sulfur dioxide. The Teflon filter was analyzed for sulfate, nitrate, chloride, ammonium, sodium, magnesium, calcium, and potassium ions. The PM_{2.5} unit collects two samples of particles less than 2.5 μm aerodynamic diameter, one on a Teflon-nylon filter pack without a nitric acid denuder, and the other on a nylon filter after a denuder (consisting of anodized aluminum tubes). The Teflon filter is analyzed for the same species as the PM₁₀ Teflon filter while the nylon back filter is analyzed for nitrate ions. Concentrations of dry-deposition particles and gases were measured by collecting consecutive 12-hour daytime and nighttime samples (day: 0600 to 1800 PST; night: 18:00 to 0600 PST), once every sixth day. In September 1995, the CADMP network reduced to five monitoring sites (Azusa, Bakersfield, Long Beach, Los Angeles, and Sacramento), primarily in urban areas. The sample collection was changed from two 12-hour samples to one 24-hour sample commencing at midnight like the routine particulate matter monitoring network, and the sampling was reduced to PM_{2.5} monitoring only.

PTEP monitoring was established at six sites including: downtown Los Angeles, Anaheim, Diamond Bar, Rubidoux, Fontana, and San Nicolas Island. At each location, sampling equipment was deployed to collect fine and coarse particulate fractions for speciation as well as nitric acid, elemental carbon, ammonium and metals. Total mass was determined gravimetrically as collected on Teflon filters and the concentrations of 36 trace elements were determined by energy dispersive x-ray fluorescence. Quartz fiber filters were used to collect samples to be analyzed for organic carbon and elemental carbon using an optical thermal carbon analyzer. Water soluble ionic species, such as nitrate, sulfate, ammonium, chloride, and sodium were extracted from the quartz filters and analyzed by ion chromatography. Two gaseous species, nitric acid and ammonia, were determined by the denuder difference method. PTEP sampling was conducted on a one in six-day schedule (except for Rubidoux, which was sampled once every three days) from January to March of 1995. The sampling frequency was increased to once every three days from April to June, and then to every day from July to December 1995 (except for San Nicolas Island which remained on a one in six-day schedule for the entire year). During the second half of 1995, although sampling was scheduled every day except at San Nicolas Island, PM10 and PM2.5 chemical speciation were conducted only every third day. However, PM10 and PM2.5 mass was determined for each daily sample. During the PM episodes, chemical speciation was conducted every day.

We examined day-of-week differences in particular matter and its species in the South Coast Air Basin (SoCAB). From 1989 through 1998, the SSI sampling network includes 21 sampling sites in SoCAB. Of these, Avalon and Los Alamitos had very limited data. Hence, the data from these two sites were not analyzed. SSI-PM10 species used in this study include only nitrate and sulfate ions. Three of the 19 sites have parallel dichotomous samplers: Azusa, North Long Beach, and Riverside-Rubidoux. To compare SSI data with data from the Dichot sampler, PM10 data from the SSI monitors are plotted against matched Dichot measurements.

For information on the SSI, Dichot, and CADMP data sets, and for data requests, please see the ARB Air Quality web site: <http://www.arb.ca.gov/aqd/aqd.htm>. For the PTEP data set, please contact Dr. Bong Kim (bkim@aqmd.gov) of SCAQMD

Methodology

The general approach is to first analyze day-of-week patterns of PM10. We performed statistical tests to provide an indication of the magnitude of the systematic differences between days of the week relative to random day-to-day variation. Where significant differences exist, we would then determine which species contribute to the differences.

- (1) Since the ambient air quality standards for PM are based on geometric means, we first calculated the geometric means of SSI-PM10 for each day of the week for each site for the period 1989-1998. The pattern showed Sunday being generally lower than other days of the week. However, to determine statistical significance of the differences between days of the week, we performed a rigorous analyses as follows.
- (2) We adjusted for seasonality and trend by taking residuals (differences between actual and fitted values) from a smoothing spline. Splines have an advantage over other smoothing methods when applied to complex data sets in that their degree of smoothness is locally

adaptive, rather than being uniform over the range of the data. The degree of smoothness was selected by generalized cross validation to yield a curve which followed the seasonal pattern and trend without excessive roughness. The residuals from the spline fit, henceforth referred to as the adjusted concentrations, were largely uncorrelated and symmetrically distributed.

- (3) Treating the adjusted concentrations for different days of week as independent, we computed group means and standard errors. The assumption of independence is reasonable because PM samples are collected 6 days apart, long compared to the time scale of daily meteorological events which strongly impact atmospheric concentrations.
- (4) We compared days of the week by examining error bar charts of adjusted concentration (see attached charts). The width of the error bars was set to a 97.5% confidence interval to yield an approximate 95% confidence level for pairwise comparisons between days.
- (5) To ensure that the seasonal adjustment procedure did not introduce artifacts, we compared results against geometric means. While there were minor differences between the geometric means of the raw and the arithmetic means of the residual concentrations, it made no difference to the overall conclusions.
- (6) The above test of significant differences between days of the week was performed for SSI-PM10 at all 19 sites and various PM species at the 3 dichotomous and CADMP sites.
- (7) To confirm the statistical results, we used the SAS GLM (general linear model) procedure to perform analysis of variance on day-of-week means, including fixed effects for month crossed with year. In order to stabilize the error variance and reduce the effect of extreme observations, we transformed the data according to the relationship $y = \log(x)$, rendering the transformed data as normally distributed since the original data is lognormally distributed. We compared the GLM significance levels for pairwise comparisons of days of week against the error bar charts. GLM tends to report slightly higher significance levels than the charts, which is expected since the confidence bounds used to generate the charts are conservative.
- (8) For the 3 dichotomous, SSI, and CADMP sites, we calculated geometric means of PM10, PM2.5 mass and species.
- (9) For the 3 dichotomous and CADMP sites, we also calculated geometric means for separate seasons (winter, spring, summer, and fall) and separate time periods (1989-1991, 1992-1994, and 1996-1998), avoiding the introduction of reformulated gasoline regulations in 1995.
- (10) The statistical significance of the PTEP database has not been established. Rather, the arithmetic means of PTEP data are presented in charts.

Discussion of Results

The following graphs present the results of the PM weekday/weekend effect data analyses. From these graphs several preliminary conclusions can be determined.

- The most abundant components of PM10 and PM2.5 in the Basin are ammonium, nitrate, sulfate, and elemental carbon. Aluminum, silicon, calcium, manganese, and iron are abundant only in coarse PM10. Concentration of crustal components is low at urban areas, where most of the road surfaces are paved. Nitrate is the largest chemical component of both PM10 (23-26% of the PM10 mass) and PM2.5 (28-40% of the PM2.5 mass) in the Basin.
- The major components of the “others” (unexplained portion of the measured PM mass) in the PTEP database are water and trace metals, and in the CADMP database are organic

compounds, water, and trace metals.

- Analyses of PM₁₀ mass from the SSI and CADMP samplers show that Sunday is the lowest day of the week at many sites, often significantly different from mid-week. This might be because of lower road dust related to lower car and truck traffic. The Saturday mean concentration is comparable to weekdays, but generally slightly lower than Friday. Roughly half of the sites show a slight dip on Wednesday. Some sites show Thursday as being the highest day during the week.
- Dichot-PM₁₀ (the sum of coarse and fine fractions) tracks the same pattern as SSI-PM₁₀ at all 3 sites. The coarse fraction is significantly lower on Sunday and Saturday at Azusa, but not at North Long Beach and Riverside-Rubidoux.
- Significance testing of CADMP data shows PM₁₀-daytime adjusted concentrations being significantly lower on Saturday and Sunday than weekdays at Azusa. For other sites and individual species, results for daytime, nighttime, and 24-hour samples do not show significant day-of-week differences at 95% level.
- Examination of results at each of PTEP sites indicates a weekly pattern very similar to one another with the maximum occurring on Thursday or Friday and the minimum occurring on Saturday at all five sites for PM₁₀ and PM_{2.5} mass. PM₁₀ and PM_{2.5} concentrations on Wednesday are lower than on the other weekdays at Rubidoux, Fontana, and Anaheim. Average PM₁₀ and PM_{2.5} concentrations showed strong spatial variations with low concentrations at coastal areas and high concentrations at inland areas.
- Ammonium and nitrate show a strong spatial variation with low concentrations at coastal locations and high concentrations at inland locations. This is partly due to transported precursor emissions having more time to react with nitric acid. Sulfate concentrations do not show strong spatial variations. Although elemental carbon concentrations do not show a strong spatial variation, Downtown Los Angeles has the highest elemental carbon concentration because it is in the most dense traffic area in the Basin. Dichot-PM_{2.5}, SSI-nitrate, and SSI-sulfate are virtually the “same” for all days of week.
- Across periods, PM has decreased considerably. Because of the limited amount of data for each season and period, no significance testing was performed on day-of-week differences. No results are shown.
- The formation of secondary particles, which are a major contributor to PM levels in the SoCAB, from precursors is a complex, nonlinear process, and we should not expect to see one-to-one relationship between precursor emissions and ambient secondary PM concentrations. For example, there are several factors influencing the relationship between NO_x emissions and particulate nitrate concentrations, which might act to reduce the impact of decreases in weekend NO_x emissions on ambient 24-hour average nitrate concentrations. For example, photochemical conditions that lead to higher ozone on weekends may also increase the fraction of NO_x that is converted to nitric acid and particulate nitrate.

Conclusion

Given the wide variety of sources contributing to PM (e.g., primary particles and secondary particles from combustion sources) and the factors listed above, interpretation of these results in terms of weekday/weekend emissions differences is complex and should be done with caution.

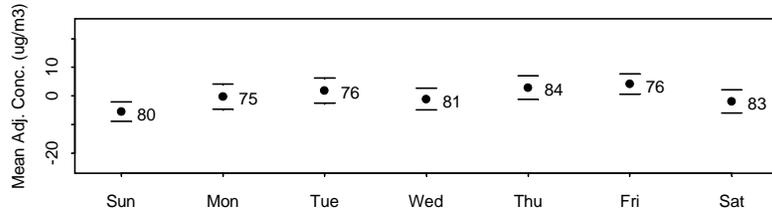
Explanation of Charts

The attached charts show the mean adjusted concentrations by day of week, with error bars showing 97.5% confidence intervals for individual means. If the error bars for two days do not overlap, the means are significantly different at the 95% level of confidence. Numbers next to the means indicate sample sizes.

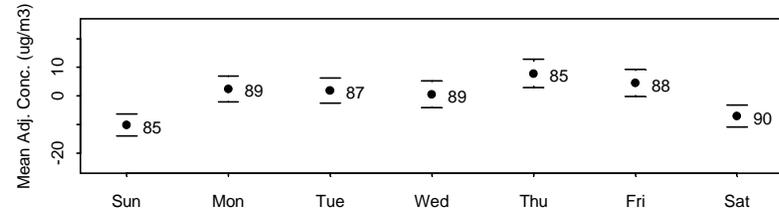
The next group of charts shows the geometric means of PM10 and PM2.5 mass and various species collected from the criteria network, the CADMP monitoring program, and the PTEP program. For the PTEP database, the arithmetic means of PM10 and PM2.5 mass and its species are calculated for each day of the week at all five sites.

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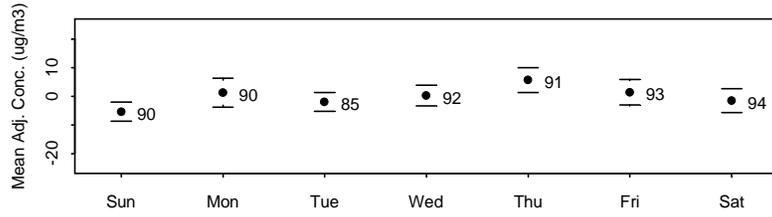
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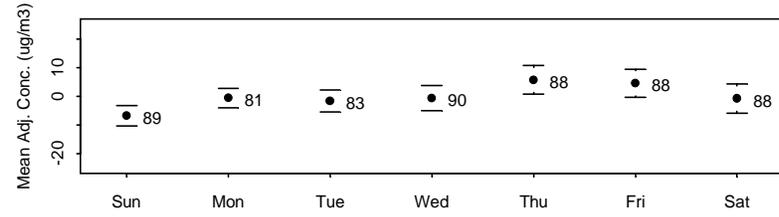
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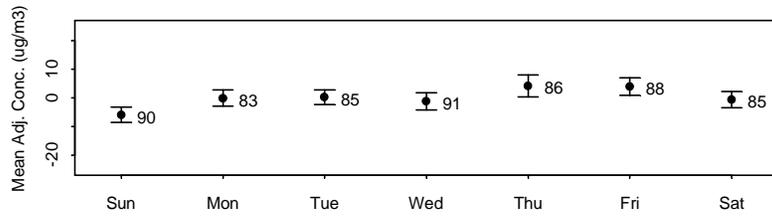
SSI-PM10, Banning



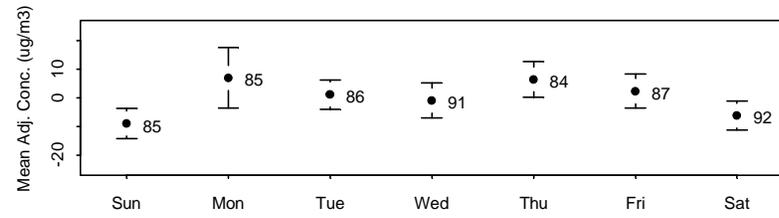
SSI-PM10, Burbank



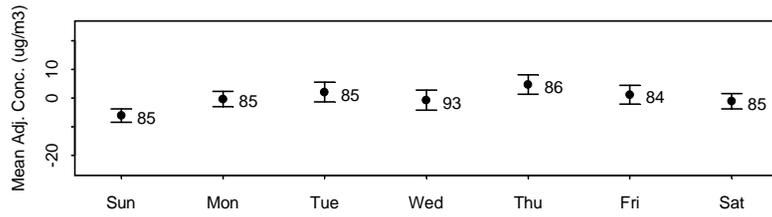
SSI-PM10, El Toro



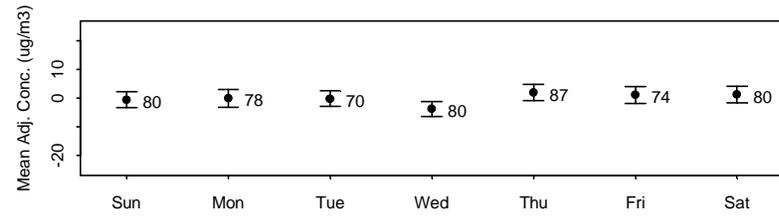
SSI-PM10, Fontana



SSI-PM10, Hawthorne

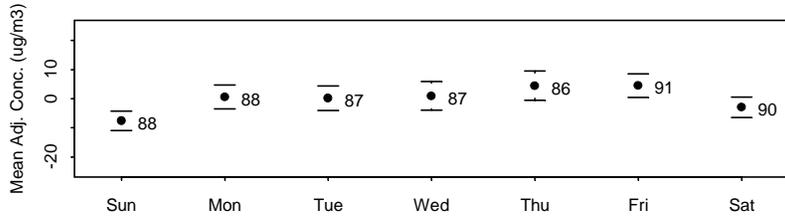


SSI-PM10, Lake Gregory

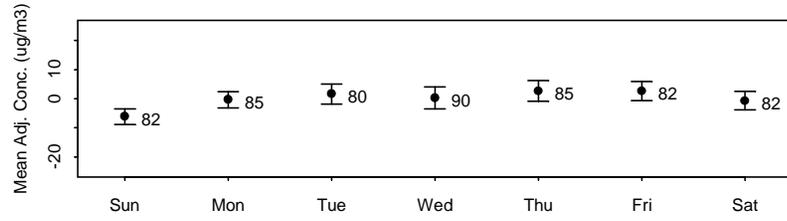


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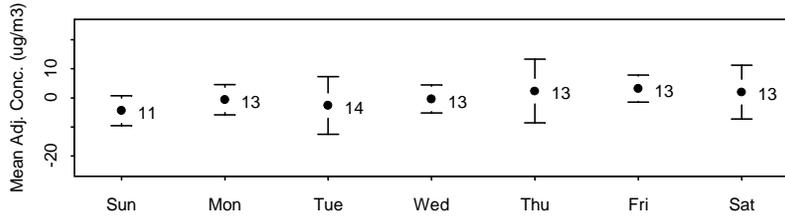
SSI-PM10, Los Angeles



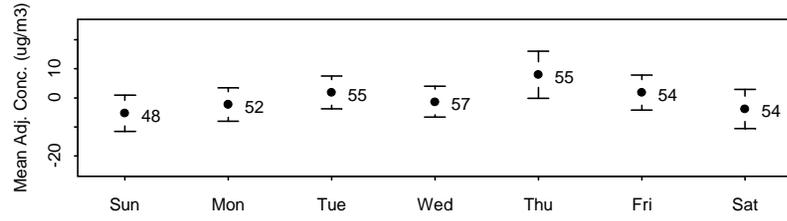
SSI-PM10, N. Long Beach



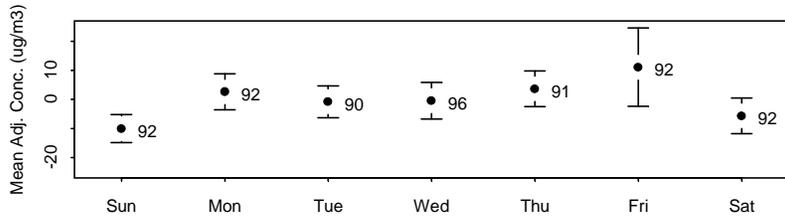
SSI-PM10, Newport Beach



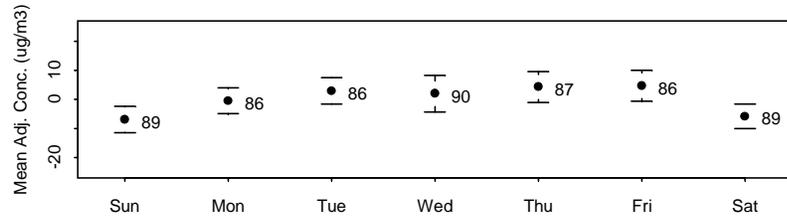
SSI-PM10, Norco



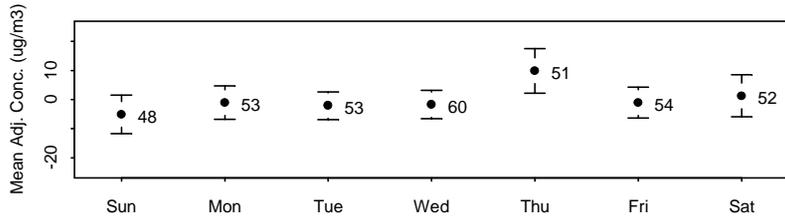
SSI-PM10, Ontario



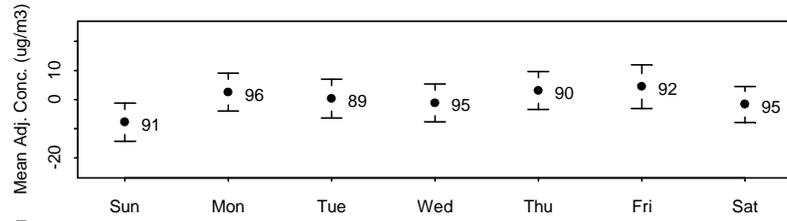
SSI-PM10, Perris



SSI-PM10, Redlands

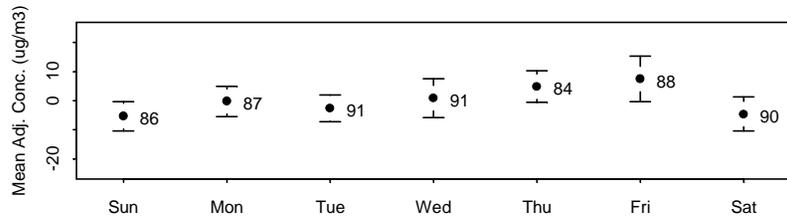


SSI-PM10, Riverside

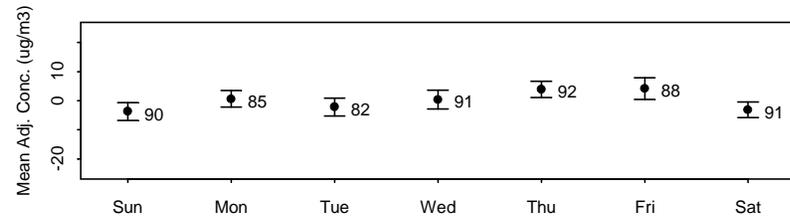


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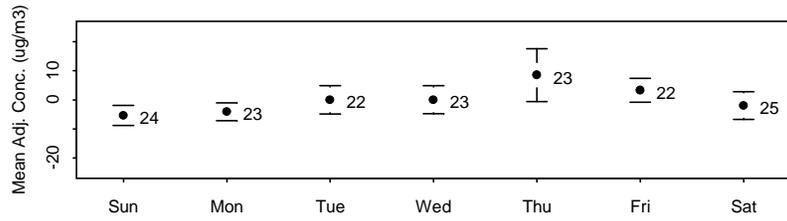
SSI-PM10, S. Bernardino



SSI-PM10, Santa Clarita

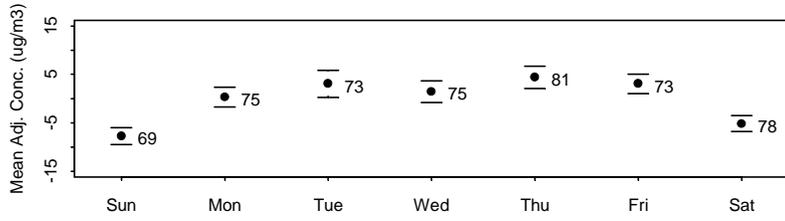


SSI-PM10, Temecula

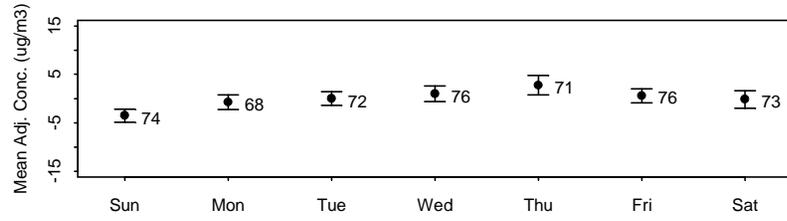


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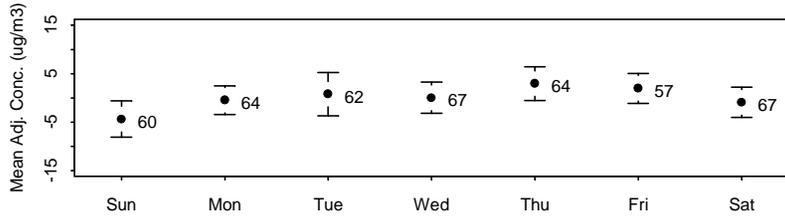
Dichot-CRS, Azusa



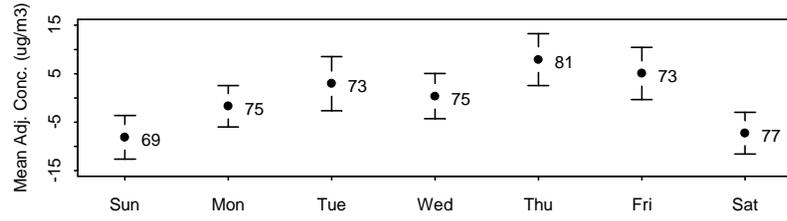
Dichot-CRS, N. Long Beach



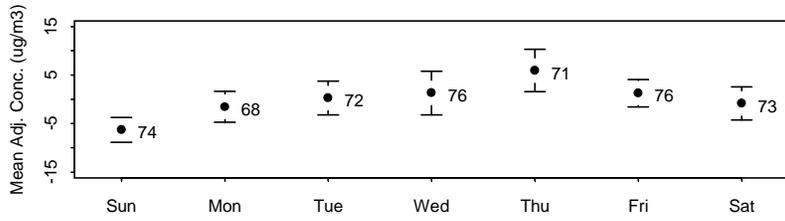
Dichot-CRS, Riverside



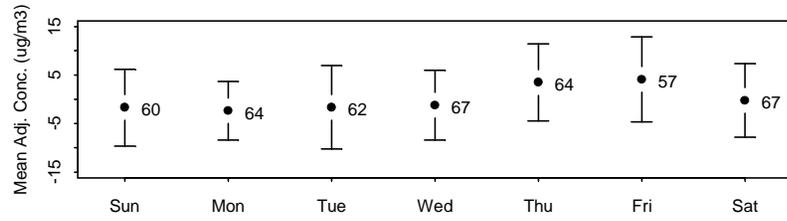
Dichot-PM10, Azusa



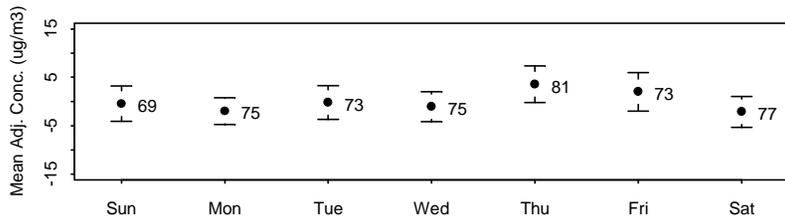
Dichot-PM10, N. Long Beach



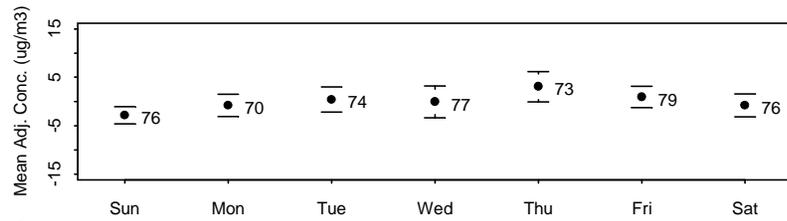
Dichot-PM10, Riverside



Dichot-PM2.5, Azusa

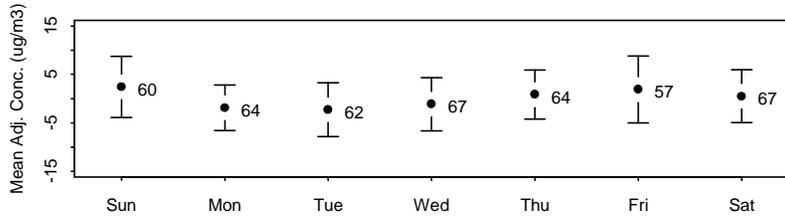


Dichot-PM2.5, N. Long Beach

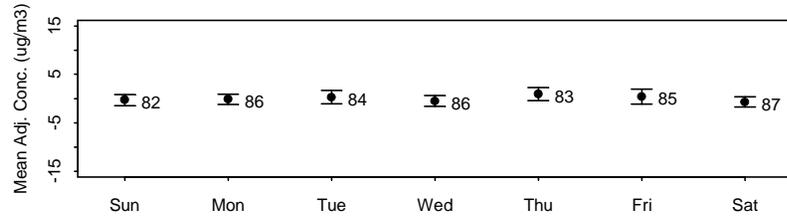


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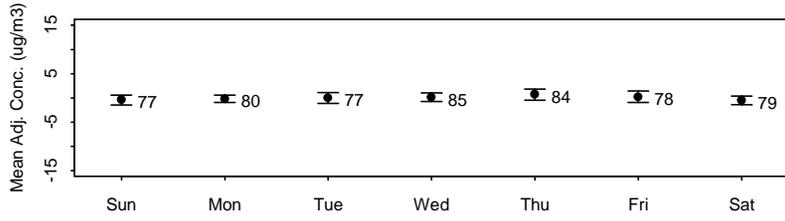
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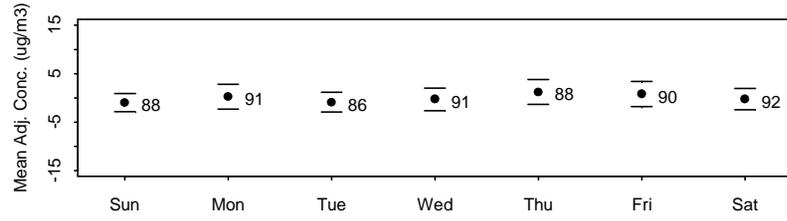
SSI-NO3, Azusa



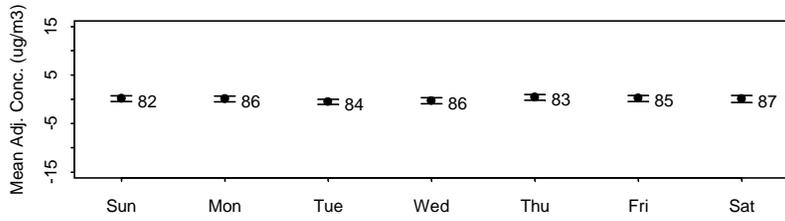
SSI-NO3, N. Long Beach



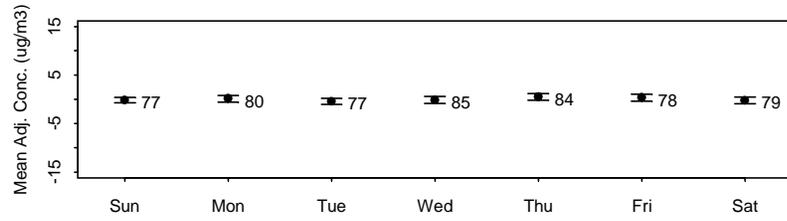
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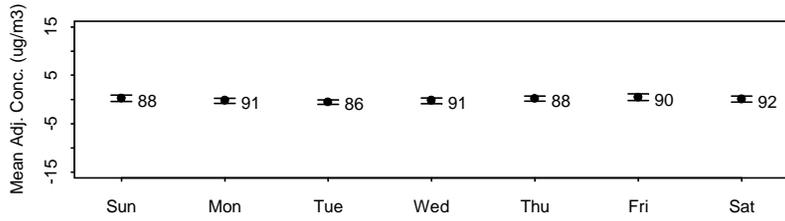
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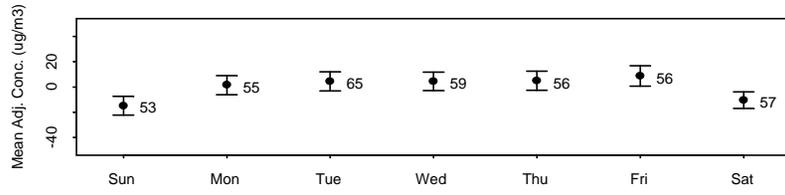


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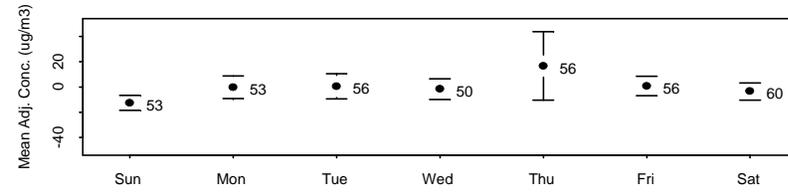


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PM10-Daytime-CADMP, Azusa



PM10-Daytime-CADMP, LA North Main



PM10-Daytime-CADMP, N. Long Beach

