7. CONCLUSION

The specific objectives of this project were to:

- Characterize weekday and weekend variations of ambient particulate nitrate and precursor concentrations.
- Develop observational evidence supporting or contradicting the hypothesis that lower weekend emissions of NO_x lead to lower weekend concentrations of particulate nitrate.
- Complement modeling studies and provide information of use for further research on relations among particulate nitrate and its precursors, as well as on the possible side effects of nitrate control strategies on ozone formation.

The ambient measurements revealed significantly lower concentrations of some primary pollutants on weekends compared with weekdays (CO, NO_x, $PM_{2.5}$ and PM_{10} mass). No significant differences between mean weekday and weekend particulate nitrate or nitric acid (HNO_3, the precursor of particulate nitrate) concentrations were observed. The weekend levels of nitrate and HNO_3 were not significantly lower than weekday levels, despite statistically significant decreases in ambient NO_x levels. These comparisons indicate a general lack of responsiveness of HNO_3 and particulate nitrate to changes in NO_x levels occurring from weekdays to weekends. The lack of response of both HNO_3 and particulate nitrate to lower weekend NO_x levels is consistent with gas-phase reactions in which HNO_3 formation is limited by the availability of radicals, and would therefore be responsive to changes in VOC emissions.

The similarity of mean weekday and weekend levels of nitrate did not result from limitations on the formation of particulate nitrate from its precursor, HNO_3. The reaction of gas-phase HNO_3 and ammonia (NH_3) is a principal pathway for the formation of fine particulate nitrate. For nearly all samples examined, particulate nitrate formation was not limited by the availability of ammonia. Emission changes that lower the rates of formation of HNO_3 are therefore predicted to lower particulate nitrate concentrations as well.

In contrast to the absence of differences between mean weekday and weekend nitrate concentrations, declining levels of particulate nitrate were observed at some sites from 1980 through 1999. Statistically significant declines in monthly average concentrations occurred for PM_{10} mass at 70 percent of the sites, for NO_x at 52 percent of the sites, for PM_{10} nitrate at 48 percent of the sites, and for TSP nitrate at 34 percent of the sites. The magnitudes of emission changes that have occurred over time are different from those that occur from weekdays to

weekends (with greater VOC than NO_x reductions having occurred over time). This study did not find evidence causally linking trends in nitrate to specific trends in either NO_x or VOC levels. Further investigation of the response of ambient particulate nitrate concentrations to VOC emission changes is recommended.

As is the case for ozone, particulate nitrate forms by means of a series of atmospheric chemical reactions, which are highly nonlinear. Gas-phase oxidation of NO_2 yields nitric acid (HNO_3); aqueous-phase reactions are by comparison unimportant. The rate of nitric acid production is a nonlinear function of NO_x concentration, and may be limited by either hydroxyl (OH) radical or NO_2 concentrations. Nitric acid reacts with ammonia (NH_3) to produce particulate nitrate, which establishes a temperature- and humidity-dependent equilibrium with its gas-phase precursors. Sodium nitrate may also be generated via reaction of nitric acid with sodium chloride in marine aerosol. The ambient concentrations of particulate nitrate also depend upon sulfate concentrations, as particulate H_2SO_4 reacts preferentially with ammonia. During seasons with lower temperatures and higher relative humidities, when equilibrium favors particulate nitrate over nitric acid and ammonia, the concentrations of particulate nitrate may be limited by the availability of either ammonia or nitric acid (specific situtations must be studied to identify the limiting precursor).

Previous applications of thermodynamic equilibrium models to data collected in the 1987 Southern California Air Quality Study (SCAQS) and the 1988-94 California Acid Deposition Monitoring Program (CADMP) have indicated that the majority of samples collected in southern California had excess ammonia and predicted that particulate nitrate concentrations would typically decrease in nearly the same proportion as ambient concentrations of HNO_3 decreased. In the present work, these results were extended using data from the 1995-96 PM_{10} Enhancement Program (PTEP). These measurements were taken at five locations in the South Coast Air Basin: Anaheim, downtown Los Angeles, Diamond Bar, Fontana, and Riverside-Rubidoux. Nearly all samples showed that particulate nitrate decreased in response to a 20 percent reduction of total nitrate; in many cases, the predicted decrease was close to twenty percent. In contrast, predicted particulate nitrate concentrations decreased by much smaller amounts in response to a twenty percent decrease in ammonia concentrations, and decreases in sulfate concentrations left the particulate nitrate concentrations essentially unchanged. Thus, few samples showed any evidence of ammonia limitation. Emission changes that lower the rates of formation of HNO_3 are therefore predicted to lower particulate nitrate concentrations as well.

Data from the 1986 Carbon Species Measurement Comparison Study (CSMCS), the SCAQS, the CADMP, and the 1997 Southern California Ozone Study (SCOS) were examined to characterize differences between weekday and weekend concentrations of HNO_3, PAN, NO_y and ozone. The data from these special studies indicate that mean weekend levels of HNO_3 were not significantly different than weekday concentrations (averaged over 12 or 24 hour periods). This result is a different response than was shown by PAN or ozone, both of which had higher mean weekend than weekday concentrations.

The PM measurements made during the 1995-96 PTEP Study showed no statistically significant differences between mean weekday and weekend nitrate concentrations at any of the five monitoring sites for either the $PM_{2.5}$ or PM_{10} size fractions. The 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 compared the weekday and weekend values without testing for statistical significance. At seven of the eight SCOS weekday/weekend pairs, morning NMOC concentrations decreased from weekday to weekend. 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. 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.

Measurements from compliance monitoring sites were examined for the period 1980 through 1999. Hourly data were compiled into 24-hour averages and matched with the sampling schedules for PM_{10} and TSP measurements. During the cool/wet season (October through April), 24-hour mean weekday and weekend concentration differences were statistically significant ($p<0.01$) for some species. 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 significantly higher ($p<0.01$) than weekday concentrations at:

- 14 out of 23 sites for ozone and
- 17 out of 27 sites for the ratio of CO to NO_x.

There were no statistically significant changes in weekend particulate nitrate concentrations--some sites showed a decrease and some sites showed an increase between weekends and weekdays. The ratios of nitrate to NO_x or PM_{10} mass were higher on weekends, though most differences were not statistically significant.

Average nitrate levels were typically a small fraction of the mean NO_x concentrations. Thus, ambient NO_x concentrations provide an extensive reservoir for nitrate, so that nitrate production is not limited by the availability of its precursor, NO_2.

Mean nitrate levels at some sites were lower during the period 1995-1999 than during earlier years. However, the differences over time were generally less than the magnitudes of the seasonal variations. Trends were examined using linear regressions of log-transformed mean concentrations against time. Statistically significant declines in monthly average concentrations occurred for PM_{10} mass at 70 percent of the sites, for NO_x at 52 percent of the sites, for PM_{10} nitrate at 48 percent of the sites, and for TSP nitrate at 34 percent of the sites. Therefore, nitrate levels have responded over time to changes in precursor emissions. These temporal changes contrast with the lack of nitrate change occurring between weekdays and weekends. However, the type of precursor changes that have occurred over time are different from those that occur from weekdays to weekends (with greater VOC than NO_x reductions having occurred over time). The co-existence of NO_x and nitrate trends is inadequate for inferring causality, as other emission changes have also occurred over time.

Since PM nitrate concentrations showed so little variation from weekdays to weekends, few or no clear linkages to the ambient concentrations of other species, and weak temporal trends, we attempted to relate nitrate concentrations to other variables using a multivariate statistical approach. The specific method used was principal component analysis (PCA), applied to combined CADMP and routine CARB data collected at downtown Los Angeles, Long Beach, Azusa, and Santa Barbara. The correlations among species were generally consistent among the four sites. All four sites showed high correlations among the primary pollutants: CO, NO, NO_2 (technically, this measurement of NO_2 includes interferants such as PAN), NO_x, the CADMP measurement of NO_2, and, to a lesser degree, NH_3 and SO_2. Ozone and nitric acid were associated at all four sites, and higher concentrations of these species correlated with higher temperatures and radiation at all three of the SoCAB sites. At the three SoCAB sites, $PM_{2.5}$ NH_4, $PM_{2.5}$ NO_3, and $PM_{2.5}$ SO_4 were associated with each other. Thus, higher PM nitrate concentrations varied with sulfate and ammonium concentrations, rather than with ozone and nitric

acid (reflecting the opposing temperature dependencies of nitrate and nitric acid). In all cases, the secondary species were grouped separately from the primary species, indicating that higher concentrations of secondary species did not correlate directly with higher concentrations of primary species. All sites showed correlations between PM_{10} Cl and PM_{10} Na, which are usually linked to sea salt aerosol, and the sites showed varying associations of coarse nitrate (PM_{10} nitrate minus $PM_{2.5}$ nitrate) with this last factor. The PCA results indicate that PM nitrate concentrations vary in complex ways with meteorological factors and the concentrations of other secondary species. PM nitrate concentrations cannot be directly linked to primary species concentrations in a simple cause-effect relation.