

# Wintertime Vertical Variations in Particulate Matter (PM) and Precursor Concentrations in the San Joaquin Valley during the California Regional Coarse PM/Fine PM Air Quality Study

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## ABSTRACT

Air quality monitoring was conducted at a rural site with a tower in the middle of California's San Joaquin Valley (SJV) and at elevated sites in the foothills and mountains surrounding the SJV for the California Regional PM<sub>10</sub>/PM<sub>2.5</sub> Air Quality Study. Measurements at the surface and on a tower at 90 m were collected in Angiola, CA, from December 2000 through February 2001 and included hourly black carbon (BC), particle counts from optical particle counters, nitric oxide, ozone, temperature, relative humidity, wind speed, and direction. Boundary site measurements were made primarily using 24-hr integrated particulate matter (PM) samples. These measurements were used to understand the vertical variations of PM and PM precursors, the effect of stratification in the winter on concentrations and chemistry aloft and at the surface, and the impact of aloft-versus-surface transport on PM concentrations. Vertical variations of concentrations differed among individual species. The stratification may be important to atmospheric chemistry processes, particularly nighttime nitrate formation aloft, because NO<sub>2</sub> appeared to be oxidized by ozone in the stratified aloft layer. Additionally, increases in accumulation-mode particle concentrations in the aloft layer during a fine PM (PM<sub>2.5</sub>) episode corresponded with increases in aloft nitrate, demonstrating the likelihood of an aloft nighttime nitrate formation mechanism. Evidence of local transport at the surface and regional transport aloft was found; transport processes also varied among the species. The distribution of BC appeared to be regional, and BC was often uniformly mixed vertically. Overall, the combination of time-resolved tower and surface measurements provided important insight into PM stratification, formation, and transport.

## IMPLICATIONS

This study demonstrated the use of continuous vertically resolved measurements to better understand the atmospheric formation, transport, and emissions of PM<sub>2.5</sub> in the SJV. Nighttime aloft nitrate formation appeared to be a source of accumulation-mode particles; this observation is important for future modeling and analysis.

## INTRODUCTION

The California Regional PM<sub>10</sub>/PM<sub>2.5</sub> Air Quality Study (CRPAQS) was a multiyear program of meteorological and air quality monitoring, emission inventory development, data analysis, and air quality simulation modeling. CRPAQS was designed to elucidate the nature and causes of particle concentrations and visibility impairment in and around central California, with a focus on the San Joaquin Valley (SJV).

The Integrated Monitoring Study of 1995 (IMS95) laid much of the groundwork for CRPAQS. IMS95 resulted in a better conceptual model for particulate matter (PM) formation in the SJV. Some key findings were that: (1) stagnation was the single most important factor in the accumulation of PM within the SJV; (2) on winter nights, a shallow surface inversion of only 30–50 m above ground level (agl) formed; (3) pollutants isolated in the aloft layer could be transported over distances of 50–300 km on a nightly basis; and (4) fog droplets served as both aqueous reactors for the production of secondary sulfate and nitrate and facilitated the wet removal of PM ammonium, sulfate, and nitrate.<sup>1,2</sup> According to this model, on winter nights, concentrations of species subject to deposition, such as ozone and PM<sub>2.5</sub>, should decrease at ground level and remain fairly constant in the aloft layer. The IMS95 trace-gas measurements at the Candelabra tower in the central SJV revealed that, during a time when the top of the fog moved up and down past the trace gas instruments at 427 m, sharp gradients in concentrations of nitric oxide (NO), reactive oxides of nitrogen (NO<sub>y</sub>), and ozone existed across the top boundary of the fog. The ozone concentrations were much higher, and the NO and NO<sub>y</sub> concentrations much lower, in the clear air above the fog.<sup>3</sup>

The conceptual model of PM formation in the SJV has since been improved by measurements at the Fresno Supersite.<sup>4</sup> Two mechanisms are possible for the production of nitric acid and, thereby, ammonium nitrate.<sup>5,6</sup> The first mechanism involves the daytime hydroxyl radical reaction with nitrogen dioxide (NO<sub>2</sub>) forming nitric acid.<sup>7</sup> The second mechanism involves ozone reaction with NO<sub>2</sub> at night and subsequent formation of nitric acid.<sup>8</sup> One or both reactions may occur in the aloft environment. Solar intensity is normally sufficient to drive photochemical

reactions immediately after sunrise and before sunset. With low NO concentrations aloft at night, the ozone reaction with NO<sub>2</sub> will form nitric acid. Any nitric acid formed will quickly combine with ammonia to form particulate nitrate in the aloft layer.<sup>9,10</sup> Abrupt morning increases in the particulate nitrate concentrations at the Fresno Supersite provided evidence to support this hypothesis.<sup>4,11</sup>

Inversion layers during CRPAQS were often <100 m during the night; this stratification allowed for investigation of potentially different chemical and transport regimes in the surface and aloft layers. These different regimes can result in different rates of PM formation, particularly ammonium nitrate formation. From mid-November 2000 through mid-February 2001, ammonium nitrate often constituted >50% of the fine PM (PM<sub>2.5</sub>) mass and, during CRPAQS episodes, constituted on average >70% of the PM<sub>2.5</sub> mass.<sup>4,12</sup> As such, it is vital to understand ammonium nitrate formation and transport mechanisms in the SJV.

Although measurements of the vertical distribution of various species have been widely conducted using balloon,<sup>13–15</sup> lidar,<sup>16,17</sup> aircraft,<sup>18–21</sup> and satellite measurements,<sup>22</sup> few studies have focused on the first few hundred meters above ground. Some studies were conducted on tall buildings<sup>15,23–26</sup> in urban environments. The Angiola site in the central SJV differs from previously studied environments, because it is a rural location that is occasionally influenced by high vehicle traffic volume on a freeway located 8 miles away, urban emissions from several dense population areas in the SJV, and a variety of area sources. In addition to the Angiola monitoring, ambient air monitoring was conducted in locations representative of boundary and/or background conditions where air flows into or out of the SJV. Background conditions are described in further detail in MacDonald et al.,<sup>27</sup> and boundary conditions are examined for their vertical profile implications in this work.

With vertically resolved measurements in the current study, the ideas posited in the conceptual model can be further investigated. Specifically, the vertical and temporal variation in PM precursors, such as ozone and NO, were investigated for evidence of nighttime NO titration and NO<sub>2</sub> + ozone reactions, which would lead to the formation of nitric acid and, subsequently, ammonium nitrate. Differences in particle concentrations were investigated for evidence of aloft transport of particles and the degree of regional influences in the accumulation and coarse particle modes. Black carbon (BC) concentrations are controlled by different mechanisms than ammonium nitrate concentrations; thus, the vertical variations of BC were investigated to understand the distribution of particles resulting from transport and deposition. BC in the SJV is primarily emitted by diesel engines (both mobile and stationary) and wood combustion.<sup>28</sup> Patterns in BC concentrations are useful for investigating whether local concentrations are dominated by regional emissions or by local transport from nearby highways and agricultural activity.

## EXPERIMENTAL WORK

The Angiola monitoring site is located in a flat, remote, agricultural field between U.S. Interstate 5 and U.S.

Highway 99, ~60 miles south of Fresno, CA, and at an elevation of 345 m (Figure 1). Air quality measurements were performed at three elevations in Angiola: on top of a trailer at 7 m agl, in the middle of a tower at 45 m agl, and on top of the tower at 90 m agl. The trailer housed an extensive array of instruments, but this analysis focused on the most robust measurements from instruments operated at the 7-m and 90-m elevations. NO was measured with a Thermo Environmental 42CY NO/NO<sub>y</sub> instrument. Ozone measurements were obtained from an Advance Pollution Instrumentation 400A. A Climet Spectro CI-500 optical particle counter (OPC) with a 10- $\mu$ m cyclone collected particle number concentrations in 15 size bins with diameters between 0.343 and 10  $\mu$ m. Lastly, continuous PM<sub>2.5</sub> nitrate data were collected using a Rupprecht and Patashnick 8400N and BC data using an Anderson AE3X Aethalometer with a cyclone size cut of 2.5  $\mu$ m. The database included hourly average values for those parameters listed above for the period from December 1, 2000, through February 5, 2001, and wind speed and direction measurements made at 7 and 100 m agl.

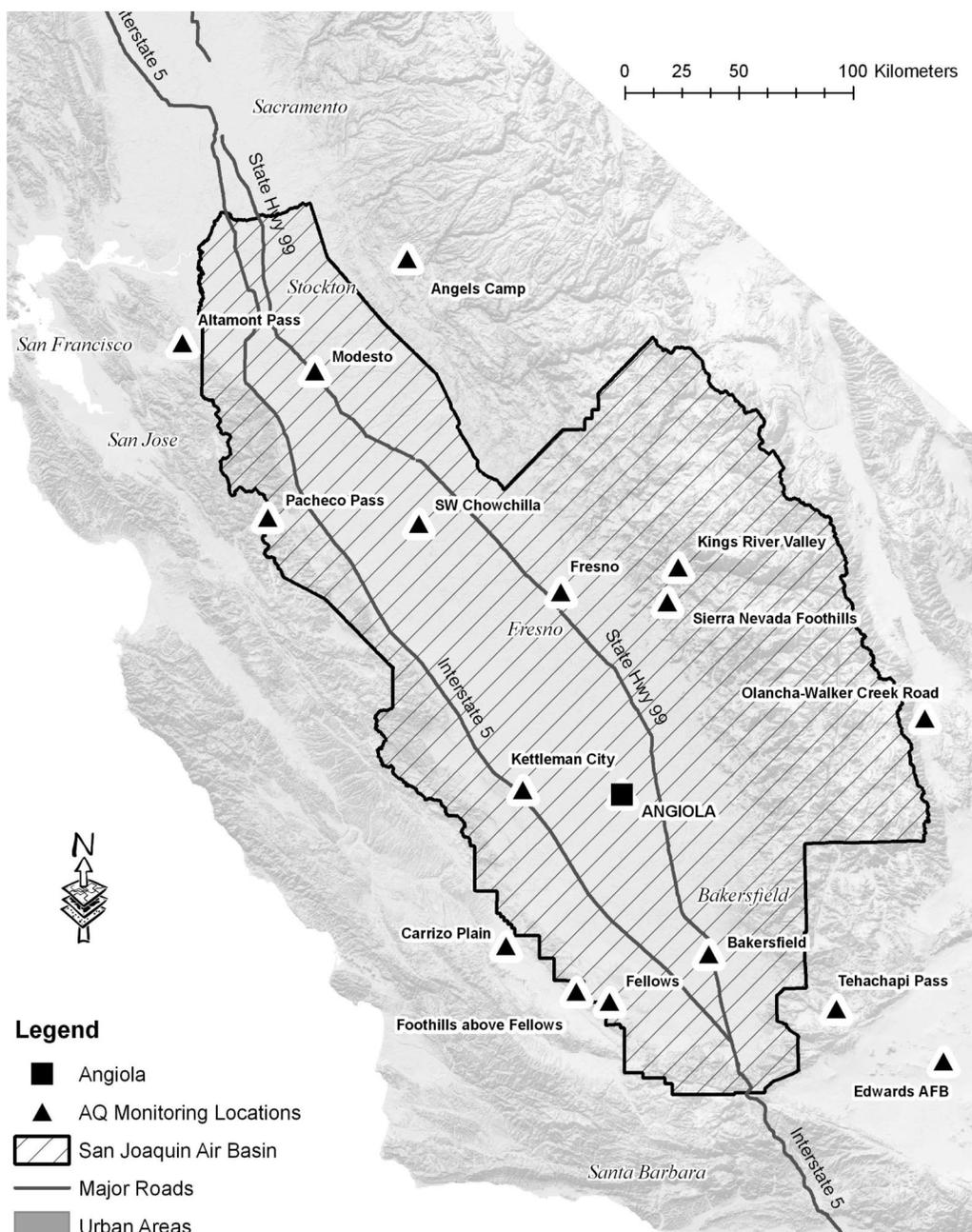
In addition to the tower measurements at Angiola, elevated sites likely to represent boundary conditions are also shown in Figure 1. These elevated sites include Altamont Pass, Pacheco Pass, Carrizo Plain, and Foothills above Fellows (two sites at 510 and 360 m) in the west and Angels Camp, Sierra Nevada Foothills, and Kings River Valley in the Sierra Nevada Mountains; Tehachapi Pass in the south represented the most likely boundary site in the southern passes. Many of these sites are at elevations greater than a few hundred meters above the valley floor, and as such can provide insight into the nature of PM<sub>2.5</sub> at elevated levels at the boundary of the SJV.

## RESULTS AND DISCUSSION

### Elevated Boundary Site Conditions

PM<sub>2.5</sub> concentrations at the elevated boundary sites (sites with elevations >200 m above the valley floor) were usually substantially cleaner than concentrations in the SJV. Typical PM concentrations at the elevated sites were less than half those at the rural sites on the valley floor. Moreover, boundary sites like Altamont Pass, Pacheco Pass, Sierra Nevada Foothills, and Kings River Valley exhibited higher concentrations when impacted by air originating from the SJV than from elsewhere.

Average PM<sub>2.5</sub> concentrations during the winter episode by site are shown in Figure 2. The two Fellows sites (Foothills above Fellows at 510-m elevation and Fellows at 360-m elevation) located in the southwestern SJV experienced the highest PM<sub>2.5</sub> concentrations for elevated sites, which may indicate that mixing heights at these sites were high enough to have a substantial impact on their concentrations. However, the average PM<sub>2.5</sub> concentration at the nearby Carrizo Plain site (at elevation 600 m), located west of the first coastal ridge in the coastal range, were a factor of three lower than those at the Fellows sites. The PM<sub>2.5</sub> concentrations at Edwards Air Force Base and Tehachapi Pass were also very low. It is suspected that the mixing heights were not sufficiently high to impact these latter sites. Therefore, the topography of the central SJV border appears to be an effective boundary for high PM<sub>2.5</sub> concentrations.



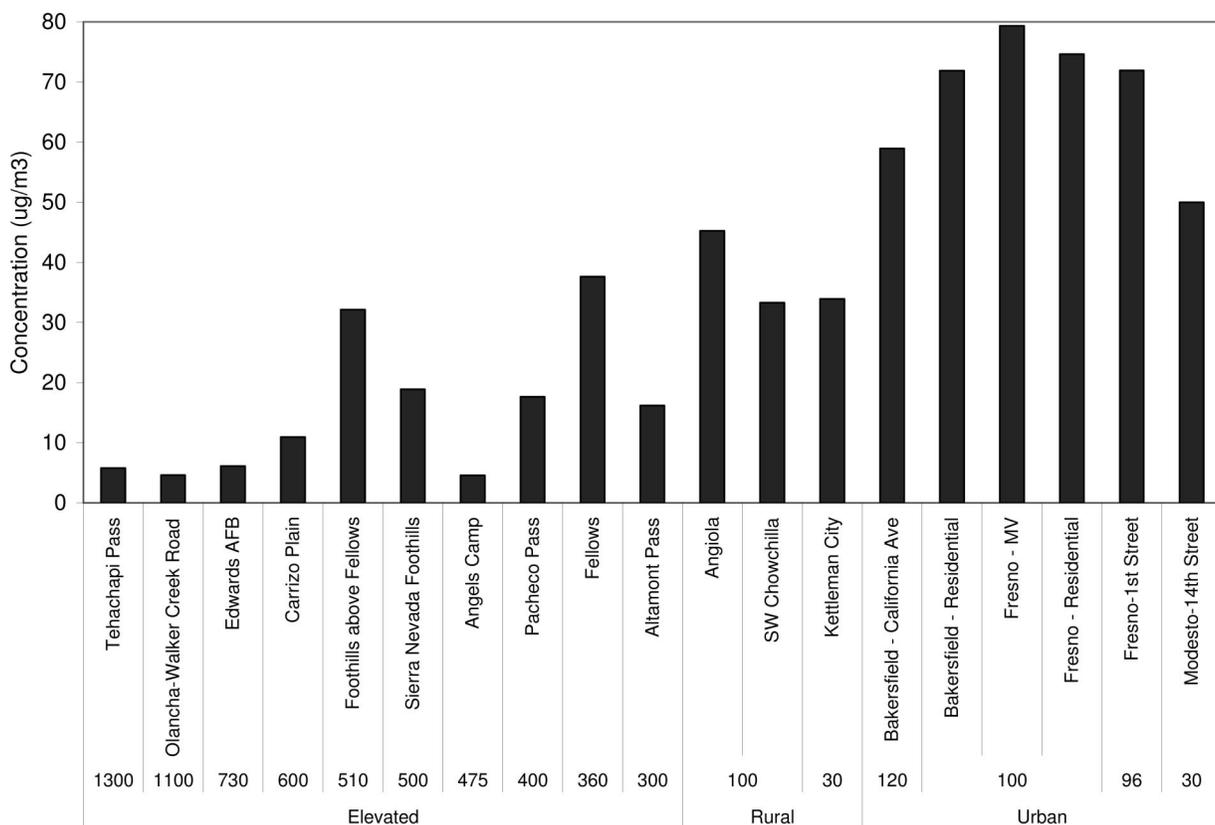
**Figure 1.** The locations of selected CRPAQS air quality and meteorological monitoring sites in and near the SJV Air Basin.

Additionally, concentrations were lower at elevated sites on the sides of the SJV (e.g., at Angel's Camp and Sierra Nevada Foothills in the Sierra and at Pacheco Pass in the coastal range) than in the SJV itself. Elevated sites on the eastern, southern, and western borders had  $PM_{2.5}$  concentrations significantly lower than those in the SJV; this difference suggests that the high  $PM_{2.5}$  concentrations were limited to the first 300–500 m above sea level for most of the episode and that the  $PM_{2.5}$  concentrations in air potentially flowing into the SJV were much lower than those within the SJV. Overall, transport of material from aloft or the Sierra Nevada Mountains is not likely to contribute to the high  $PM_{2.5}$  concentrations experienced in the SJV during the winter, because concentrations of PM and its precursors were typically lower at the elevated sites surrounding the SJV than at monitoring sites located

on the valley floor.  $PM_{2.5}$  is typically confined to a layer of a few hundred meters above the valley floor; analysis of the Angiola tower measurements provides further insight into the nature of this shallow vertical layer that dominates during the winter.

#### **PM Precursors at Angiola: Ozone and NO**

Figure 3 shows box whisker plots of the diurnal variability of ozone concentrations aloft and at the surface in Angiola. In these plots, the box defines the interquartile range (IQR, 25th to 75th percentile); the boxes are notched (narrowed) at the median and return to full width at the 95% lower and upper confidence interval values, and the whiskers extend to data within 1.5\*IQR. Data beyond the interquartile range are shown as asterisks if they are within three times the interquartile range, and

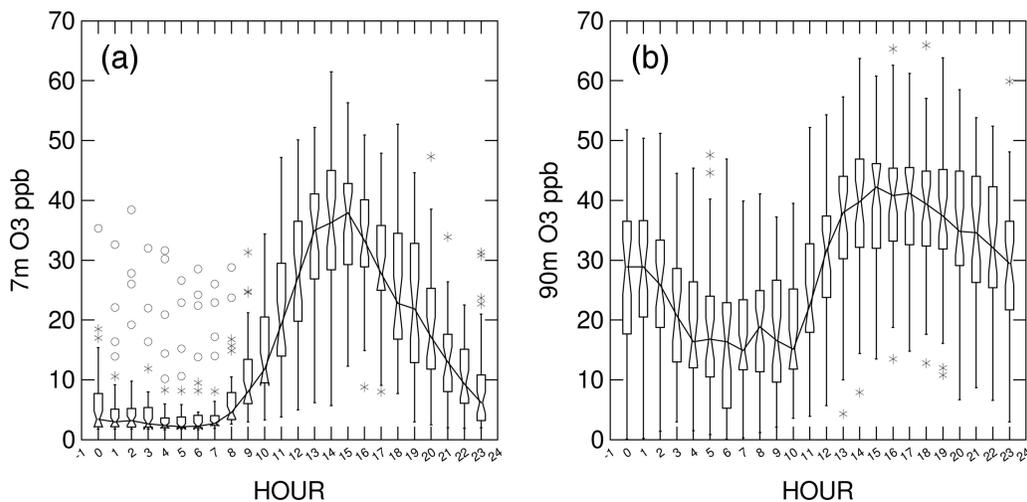


**Figure 2.** Average PM<sub>2.5</sub> concentrations (μg/m<sup>3</sup>) from December 2, 2000, through February 3, 2001, at selected elevated, rural, and urban sites. Site elevations (shown below the site names) within each category decreases from left to right.

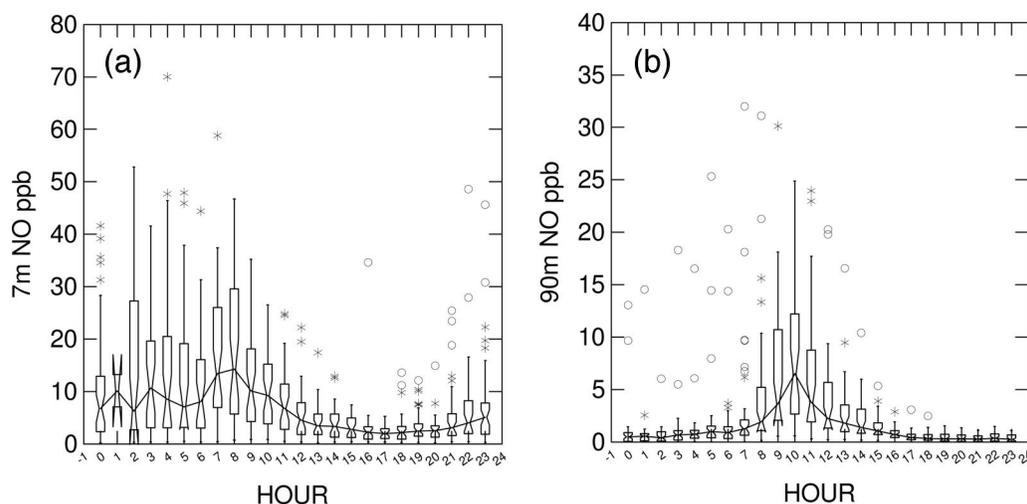
beyond this range as circles. The median is highlighted as a line. Surface measurements showed low median concentrations (generally <10 ppb) during the nighttime and early morning reflecting nighttime ozone titration and deposition. Peak concentrations occurred in the late afternoon and averaged 35 ppb, which is comparable to the average background concentration.<sup>29</sup> Outliers (concentrations >10 ppb) during the early morning are mostly because of mixing down from aloft and/or decreased ozone titration in conjunction with a shift in wind direction away from the east where U.S. Highway 99

is located (and, therefore, no fresh NO emissions from the freeway). Concentrations aloft showed more variability (i.e., larger boxes), especially at night, with a minimum in the early morning and a peak in the afternoon (at ~40 ppb). This pattern aloft is likely because of nighttime titration of ozone with NO and NO<sub>2</sub>, after which concentrations return to background levels at midday.

NO concentrations ranged from 0 to 70 ppb at the surface and to 90 ppb aloft (see Figure 4) at Angiola. The diurnal patterns of NO aloft and at the surface were inversely related to those of ozone, with peaks in the early



**Figure 3.** Box whisker plots of hourly (PST, begin hour) ozone (ppb) at (a) 7 and (b) 90 m.

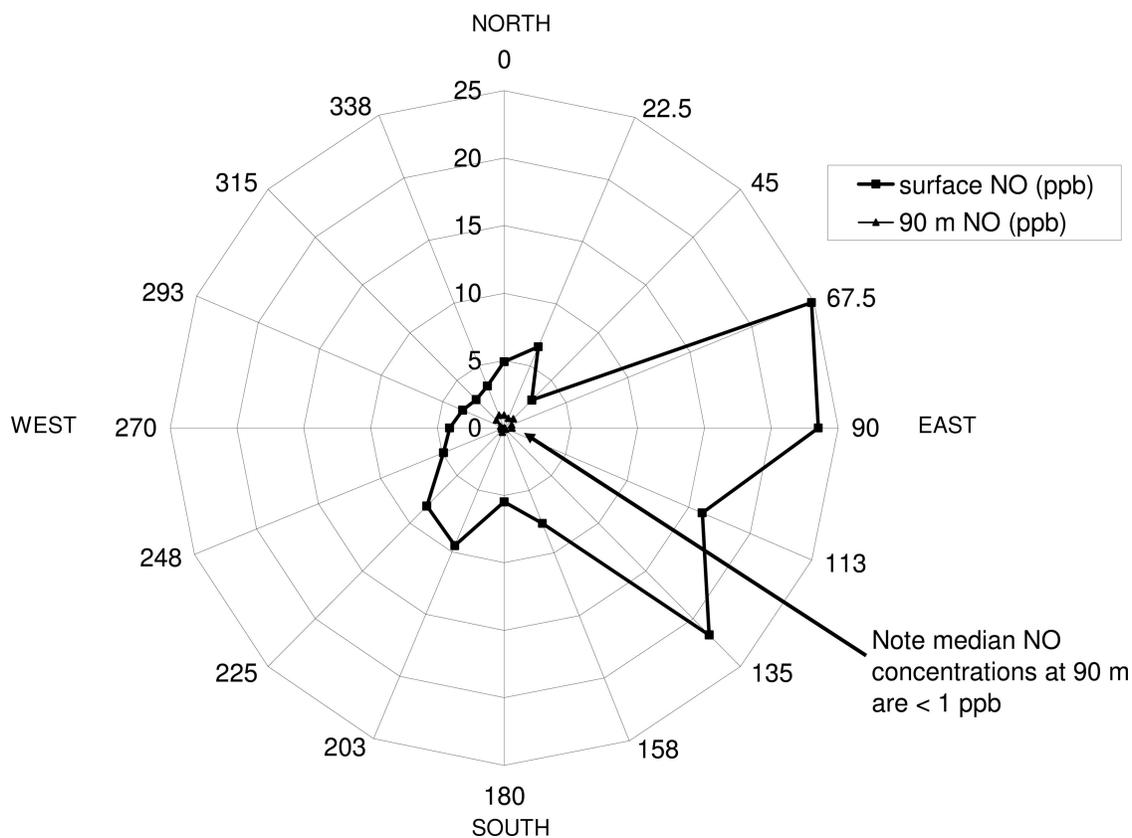


**Figure 4.** Box whisker plots of hourly (PST, begin hour) NO (ppb) at (a) 7 and (b) 90 m.

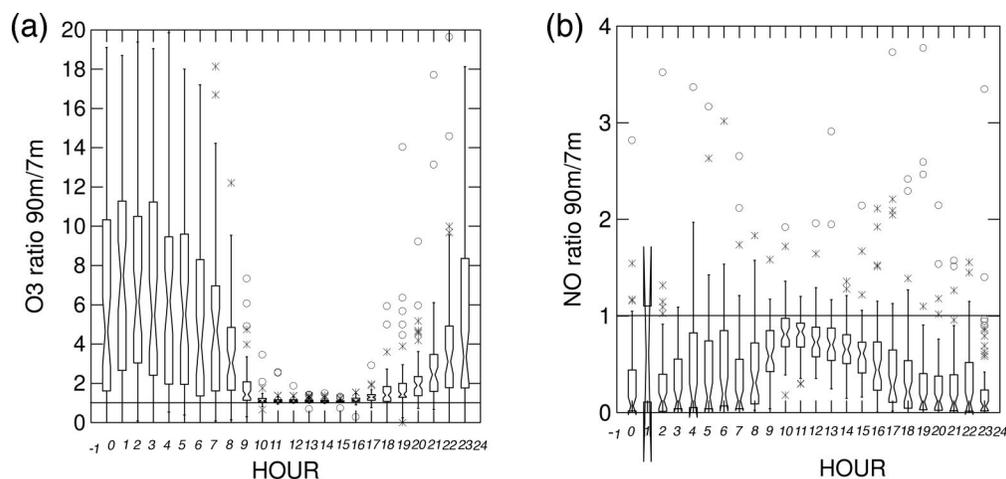
morning at the surface and later in the morning aloft, consistent with primary emissions of NO in the morning from mobile sources. Local influence is further corroborated by the relationship of concentrations to wind direction (shown in Figure 5). Nighttime surface NO concentrations were highest on average with winds from the east that carry emissions from U.S. Highway 99, a major freeway and diesel truck route, located 8 mi east of Angiola. During most nights, the inversion layer was present, and emissions from the freeway only impacted the NO concentrations at the surface and not in the aloft layer. NO concentrations aloft began to increase around 8:00 a.m.

Pacific Standard Time (PST), when surface concentrations began to decrease, which likely indicates the start of mixing between the two layers.

The ratios of the aloft and surface concentration of ozone and NO were calculated for each hour; the resulting distributions are shown in Figures 6. Concentration ratios close to 1 indicate good mixing between the surface and 90 m and an absence of bias in the instruments. The aloft-to-surface ratios for ozone and NO show complementary diurnal trends. Both ratios were close to 1 at midday and during the afternoon, indicating that the boundary layer was well mixed at this time. The ratios



**Figure 5.** Median NO concentration (ppb) at 90 and 7 m at night (10:00 p.m. to 5:00 a.m. PST) by 100- and 7-m wind direction, respectively.



**Figure 6.** Box whisker plots of the ratios of (a) ozone and (b) NO concentrations at 90 m to those at 7 m by hour (PST, begin hour).

departed from 1 during the night and morning, demonstrating stratification between the surface and 90 m.

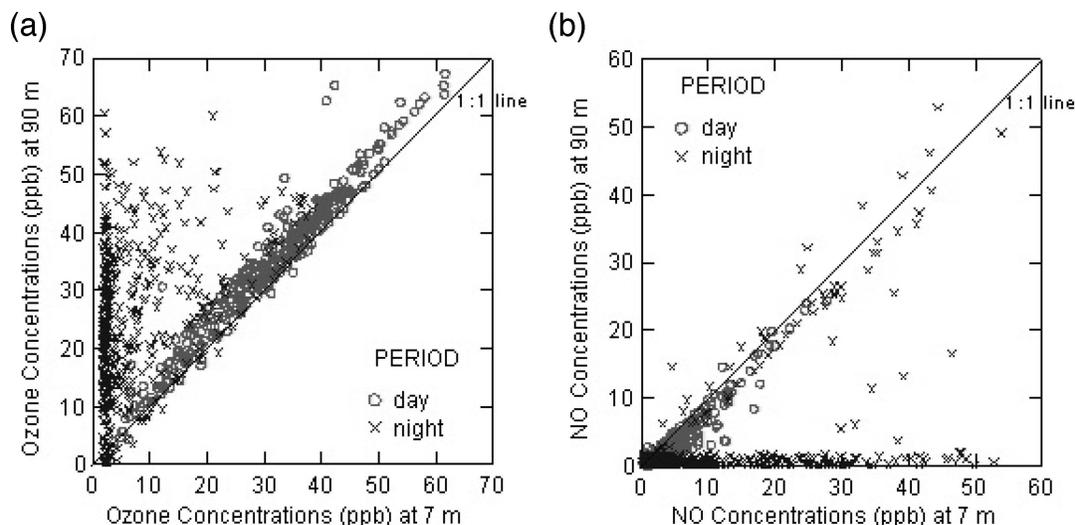
The high ratio during the nighttime shows that ozone was depleted at the surface relative to the aloft layer. This is likely because of a combination of deposition<sup>30,31</sup> and titration by fresh NO emissions at the surface. No fresh source of NO was apparent in the aloft layer; and once this layer became separated from the surface by an inversion, the NO was depleted by reaction with ozone. Nighttime chemistry effects can be seen by examining the relationship between the surface and aloft concentrations segregated by day (11:00 a.m. to 4:00 p.m. PST) and night (10:00 p.m. to 5:00 a.m. PST) in Figure 7. As seen by the fairly tight 1:1 relationship between surface and aloft concentrations, ozone and NO are well mixed during the daytime. Conversely, at night, ozone concentrations aloft are consistently at or higher than surface concentrations, whereas NO concentrations aloft are usually near zero. This NO depletion at night is required for the nighttime oxidation of NO<sub>2</sub> by ozone and other species to form nitric acid and, subsequently, ammonium nitrate aloft.<sup>8</sup> The nighttime NO<sub>2</sub> oxidation by ozone and

other species is not likely to lead to significant ammonium nitrate production in the surface layer, because higher NO concentrations at the surface impede the reaction cycle.

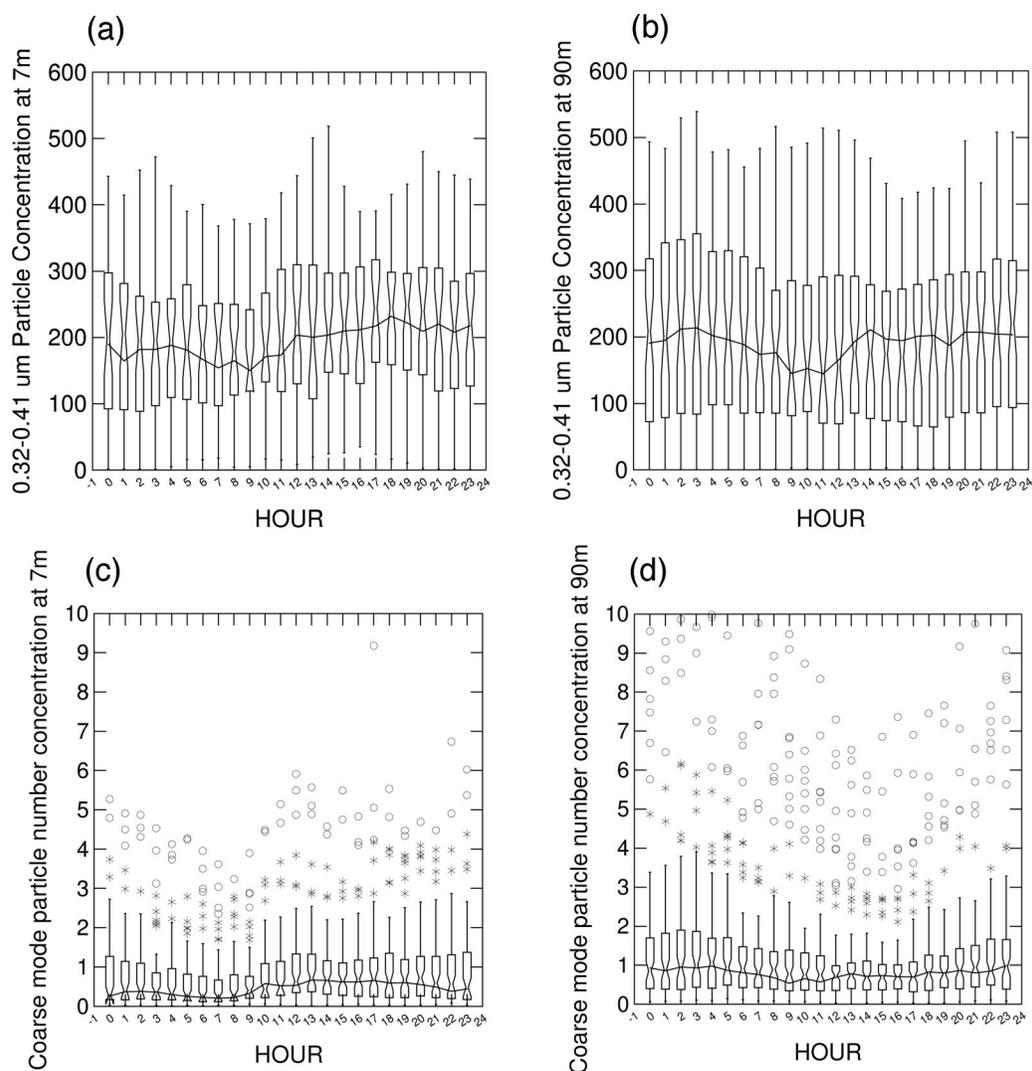
#### Angiola Aerosol Size Distribution

Hourly particle number concentrations in 16 size bins from 0.32 to 10  $\mu\text{m}$  were measured at 7 and 90 m using OPCs. The aerosol size distribution can help identify potential sources and transformations of aerosols. As expected, particle number concentrations in the accumulation mode (i.e., <2  $\mu\text{m}$  in diameter) were an order of magnitude higher than those in the coarse mode.

Figure 8 shows hourly particle number concentrations in the 0.32–0.41  $\mu\text{m}$  range, representative of the accumulation mode, and in the coarse particle range (1.72–10  $\mu\text{m}$ ) at the surface. At the surface, median particle counts in both modes showed little hour-to-hour differences, which suggests that the aerosol at this rural site is regional. Figure 8 also shows hourly particle number concentrations of the same two size ranges aloft.



**Figure 7.** Concentrations (ppb) of (a) ozone and (b) NO at 90 m and 7 m during the day (11:00 a.m. to 4:00 p.m. PST) and night (10:00 p.m. to 5:00 a.m. PST).



**Figure 8.** Box whisker plots of number concentrations (per  $\text{cm}^3$ ) for (a and b) particles with diameters between 0.32 and 0.41  $\mu\text{m}$  and (c and d) coarse mode particles at 7 and 90 m by hour (PST, begin hour).

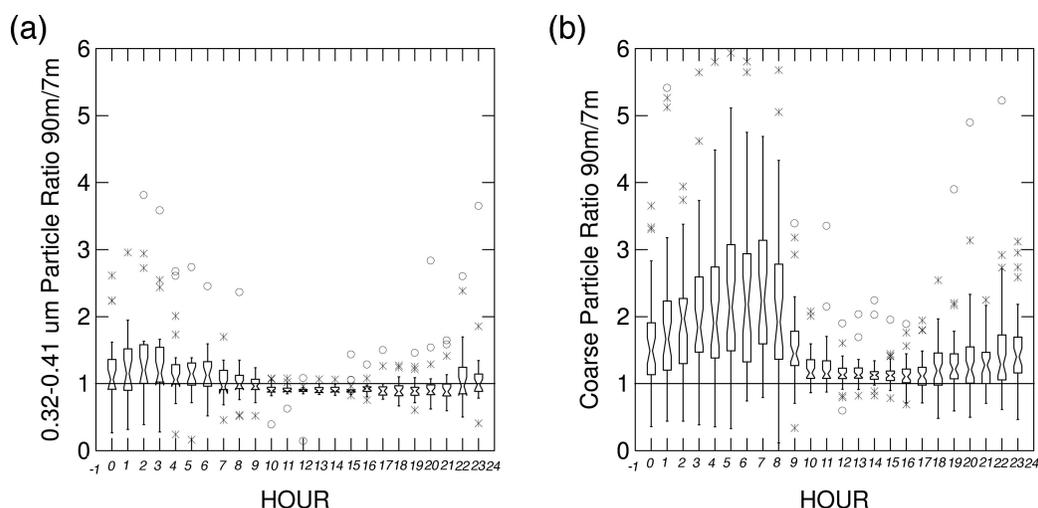
These measurements showed a smaller hour-to-hour variation in both modes than at the surface. The coarse-mode results demonstrate the potential for significant transport of coarse PM aloft, as well as at the surface, although deposition effects will impact transport near the surface. Similar to what was observed with the NO and ozone data, different formation mechanisms at the surface and aloft may be affecting the accumulation mode.

The diurnal aloft/surface ratios differed significantly within the various size fractions as shown in Figure 9. The ratio in the accumulation mode was  $\sim 1$  throughout the day and night. At midday, when the inversion layers were much higher than 90 m, this ratio showed little variability and was consistently just below 1. The slight difference from a ratio of 1 at midday may result from minor differences in the bin size cuts for the two instruments, so the analysis focuses on changes in the ratio. The accumulation mode aloft-to-surface ratio was slightly above 1 during the early morning, possibly indicating particle losses by deposition at the surface or particle formation aloft. The lack of diurnal variation in the ratio and the preponderance of values near unity further support the supposition that accumulation

mode particles are aged and regional in nature in the central SJV. This is different than what is observed with the NO data, as expected, because of their different atmospheric lifetimes.

The aloft/surface ratio for the coarse mode was  $>1$  during the nighttime and early morning and approached 1 during the afternoon when the layers were well mixed. The ratios  $>1$  are most likely a result of depletion of particles in the surface layer and/or an increase in particle concentrations aloft. With physical decoupling of aloft and surface layers, it may be more likely that coarse particles are removed in the surface layer via deposition and gravitational settling than are coarse particles in the aloft layer.

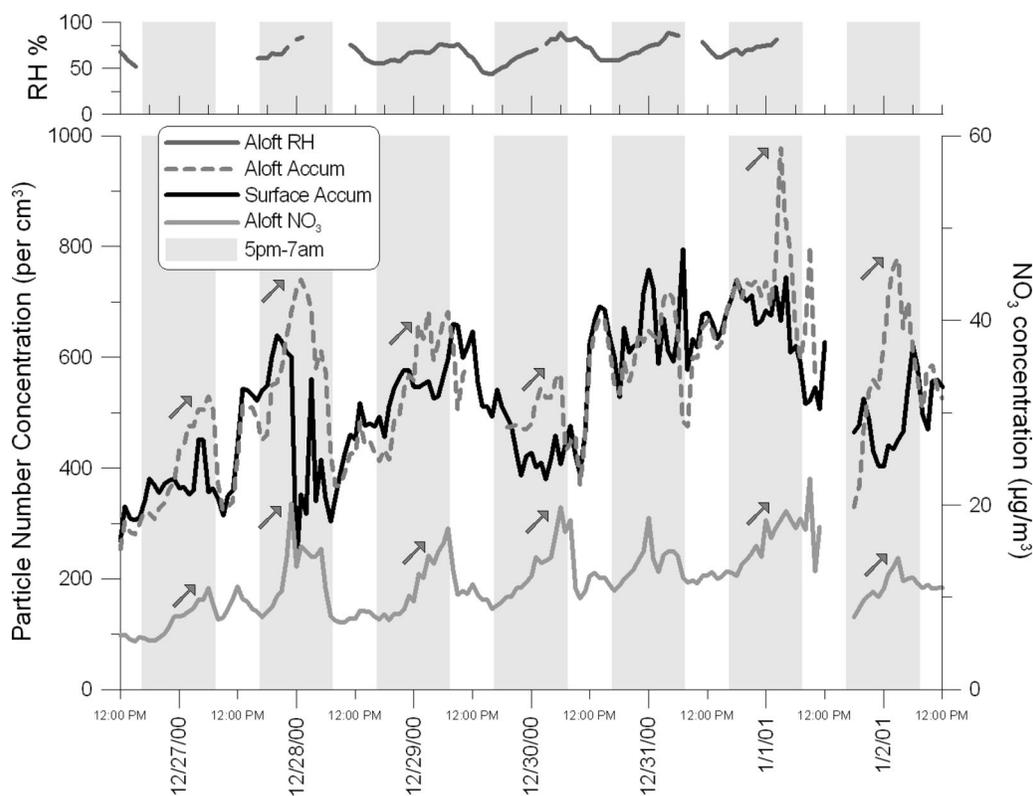
*Implication for Aloft Nighttime Nitrate Formation.* Although the surface and aloft particle number concentrations are usually similar for particles in the 0.32–0.41  $\mu\text{m}$  diameter range, Angiola tower OPC data for a broader particle size range extending from 0.32 to 1.07  $\mu\text{m}$  diameter occasionally show noticeable divergence of surface and aloft number concentrations at night. Figure 10 shows a time series



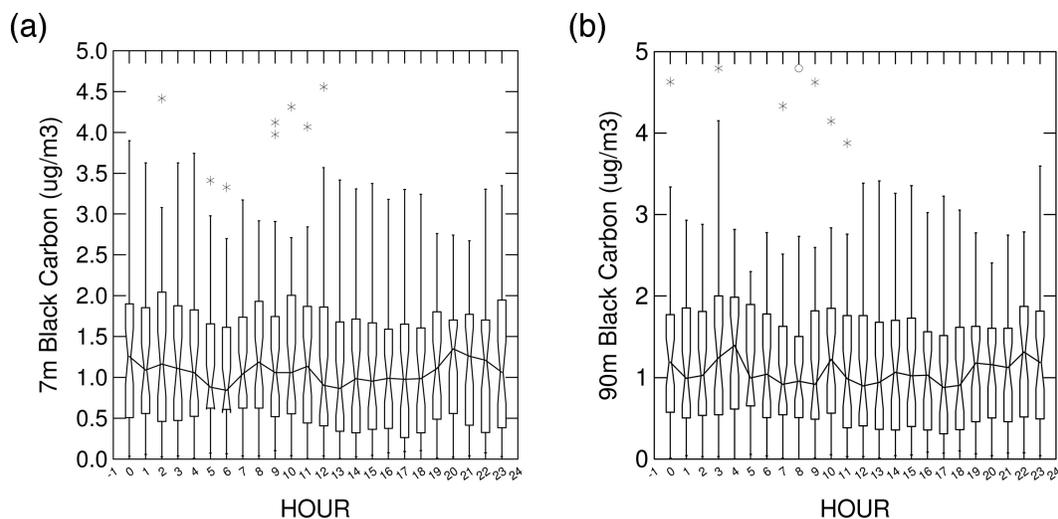
**Figure 9.** Box whisker plots of the ratios of particle counts at 90 m to those at 7 m for (a) 0.32–0.41 μm diameter particles and (b) coarse particles by hour (PST, begin hour).

of hourly 0.32–1.07 μm particle diameter data for the surface and aloft, as well as aerosol nitrate concentrations and relative humidity (RH) aloft, from 12:00 p.m. PST, December 26, 2000, through 12:00 p.m. PST, January 2, 2001. Surface aerosol nitrate data were not of sufficient quality and are not used. During this episode, a nighttime increase in the number of concentrations frequently occurs aloft but rarely at the surface. The aloft increase in the 0.32- to 1.07-μm particle number, denoted by arrows

in Figure 10, often coincides with increases in aloft aerosol nitrate concentrations but not necessarily with increases in aloft RH. Particle growth by water vapor condensation alone does not appear to explain this phenomenon. A likely explanation is that nighttime formation of nitric acid and subsequent condensation of ammonium nitrate on accumulation mode particles, grows the particle size distribution and increases the number of particles in the 0.32–1.07-μm size range. No consistent trend



**Figure 10.** Time series of accumulation mode (0.32–1.07 μm) particle number concentrations (per cm<sup>3</sup>) aloft and at the surface, aloft nitrate concentrations (μg/m<sup>3</sup>), and aloft RH (RH, %) during the December 26, 2000, through January 2, 2001, PM<sub>2.5</sub> episode at Angiola. Arrows indicate periods when aloft nitrate and accumulation mode concentrations increased during the nighttime (5:00 p.m. to 7:00 a.m. PST is shaded in gray), whereas the surface concentrations decreased or remained constant.



**Figure 11.** Box whisker plots of hourly (PST, begin hour) BC concentrations ( $\mu\text{g}/\text{m}^3$ ) at (a) 7 and (b) 90 m.

in the growth of the particle size distribution was observed; additional measurements of particles with diameters  $<0.32 \mu\text{m}$  may be needed to better understand this distribution. The nighttime atmospheric chemistry leading to nitric acid and ammonium nitrate formation can also produce secondary organic aerosol, via volatile organic compound oxidation by the  $\text{NO}_3$  radical, that could also grow the particle size distribution.

#### Angiola Aethalometer BC

As shown in Figure 11, median BC concentrations did not show a large hour-to-hour variability at the surface or aloft at Angiola. Concentrations were typically between  $0.5$  and  $2 \mu\text{g}/\text{m}^3$  with a median at both levels near  $1 \mu\text{g}/\text{m}^3$ . These concentrations are relatively high for a rural environment, and whereas they are lower than the average wintertime concentration at Fresno,<sup>32</sup> Los Angeles,<sup>33,34</sup> or Atlanta,<sup>35,36</sup> they are higher than in other rural areas.<sup>37–39</sup> These high concentrations are consistent with the overall high emissions in the SJV urban areas and the distribution of these emissions throughout the SJV.<sup>4,28,40,41</sup>

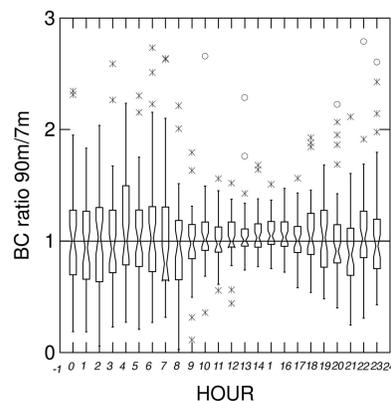
The small hour-to-hour variations in BC concentrations in rural Angiola are, on average, a stark contrast to patterns in Fresno and Bakersfield where local emissions induce significant temporal variability.<sup>4</sup> The pattern in Angiola is characteristic of background concentration measurements. The only likely local source of BC near Angiola is the freeway, which does not appear to influence the observed concentrations. This lack of variability is different from observations of NO concentrations at Angiola, because the fresh NO from freeway traffic is much higher than the background concentration. The difference between NO and BC is expected, because the lifetime of NO is shorter than that of BC because of atmospheric chemistry and deposition. BC exhibits more regional characteristics than NO; thus, the influence from the freeway is less pronounced in comparison with the background concentrations.

The distribution of the ratio of the aloft-to-surface BC concentrations (Figure 12) shows that the median was

close to 1 throughout the day, although there was increased day-to-day variability (i.e., illustrated by the larger boxes in the plots) in the ratio during the nighttime. This lack of a vertical gradient for BC contrasts with that observed with NO and ozone. However, the NO precursor concentrations were subject to rapid chemical formation and depletion, as well as influence from local sources, whereas BC is subject to slower physical removal mechanisms, such as deposition, and is heterogeneously distributed in the region. Therefore, the vertically well-distributed nature of BC is consistent with its long lifetime and nonlocal source origin. A similar diurnal trend in the accumulation mode ratio was also observed and suggests that BC is predominantly in the smaller size fraction or has sources and removal mechanisms similar to those of accumulation mode particles.

#### CONCLUSIONS

Twenty-four-hour integrated  $\text{PM}_{2.5}$  measurements were made at sites around the boundary of the SJV. Analysis of the data during episodes found that  $\text{PM}_{2.5}$  is typically confined to a layer of a few hundred meters above the floor of the SJV. Additionally, vertically resolved measurements of NO, ozone, BC, and aerosol size distribution



**Figure 12.** Box whisker plot of the ratio of BC concentrations at 90 m to those at 7 m by hour (PST, begin hour).

were made at the rural Angiola site in the SJV. Significant stratification between surface measurements and measurements at 90 m was evident, demonstrating the importance and utility of continuously measured tower data to understand the various formation and transport mechanisms that occur at the surface and aloft.

Complementary trends in ozone and NO concentrations between surface and aloft were observed. NO was higher during the night at the surface, because of fresh emissions from a nearby freeway, whereas ozone at the surface was lower than aloft. Higher concentrations of ozone aloft than at the surface led to titration of NO and the potential for significant nighttime nitrate formation aloft.

BC was uniformly distributed in the vertical layer throughout the day and night, demonstrating that it is regionally dispersed. Similar to BC, accumulation mode particles showed, on average, little difference between aloft and surface number concentration. An exception occurred during a PM<sub>2.5</sub> episode, when increases in accumulation mode particles aloft corresponded with increases in nitrate concentrations aloft, suggesting that aloft nitrate formation may be important to PM<sub>2.5</sub> concentrations during episodes. Concentrations of coarse mode particles were higher aloft than at the surface throughout the nighttime and early morning, suggesting that this size range may be impacted by aloft transport and surface deposition effects. Overall, the elevated boundary site and rural tower measurements afforded the opportunity to gain valuable insight into PM transport and chemistry mechanisms impacting the SJV.

## ACKNOWLEDGMENTS

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