

**California Regional PM₁₀ and PM_{2.5} Air Quality Study (CRPAQS)
Data Analysis Task 2.4**

**BACKGROUND AND BOUNDARY CONDITIONS FOR
PARTICULATE MATTER AND PRECURSORS IN THE
SAN JOAQUIN VALLEY IN WINTER**

**TECHNICAL MEMORANDUM
STI-902325-2779-TM**

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July 29, 2005

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ABSTRACT

The spatial and temporal variability of ambient particulate matter (PM), its speciated components (e.g., organic carbon, ammonium nitrate), and gaseous precursors (e.g., oxides of nitrogen [NO_x] and volatile organic compounds [VOCs]) in the San Joaquin Valley (SJV) in California was examined to assess the contributions of background air pollution during winter PM episodes. High concentrations of PM organic carbon (OC) were spatially limited to core urban sites while high concentrations of PM ammonium nitrate were regionally distributed throughout the SJV. Concentrations of PM and its precursors were typically lower at the elevated sites surrounding the SJV than at monitoring sites located on the SJV floor. Transport of material into the SJV was most likely to occur through drainage flow from the Sierra Nevada Mountains or by vertical mixing. In addition, boundary sites were often influenced by flow from the SJV in the afternoon and thus were not always representative of “clean” background air. Significant amounts of PM were transported into the San Francisco Bay Area from the Sacramento and San Joaquin Valleys during the winter episode.

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1. INTRODUCTION

Particulate matter (PM) concentrations in the San Joaquin Valley (SJV) often exceed the National Ambient Air Quality Standards (NAAQS) for size fractions under 10 and 2.5 micrometers (PM₁₀ and PM_{2.5}, respectively). Understanding the physical and chemical mechanisms that control PM formation, removal, and transport is a prerequisite to the development of effective control strategies.

Ambient PM concentrations are a result of emissions and *in situ* formation, wet and dry deposition, and transport. Primary PM (e.g., dust, soot, and pollen) is the result of direct emissions of particles from anthropogenic, geologic, and biogenic sources into the atmosphere. Secondary PM is formed from the chemical and physical transformation of atmospheric gases into aerosols (e.g., ammonium nitrate, ammonium sulfate, and secondary organic aerosol). Removal of atmospheric PM can occur through wet and dry deposition. For regional pollutants, such as PM_{2.5} and ozone, transport can play a large role in causing high local concentrations.

Historically, air pollution transport into the SJV has contributed to poor air quality. Numerous studies have shown that transport of ozone and its precursors into the SJV from the San Francisco Bay Area (Bay Area)(see **Figure 1-1**) contribute to the ozone problem in the Sacramento and San Joaquin Valleys (i.e. the Central Valley) (Smith et al., 1981; Carroll and Baskett, 1979; Roberts and Main, 1989; Roberts et al., 1990; Blumenthal et al., 1997; Hering and Cass, 1999). Transport of PM and its precursors during the spring, summer, and fall can also contribute to high PM concentrations in the SJV (Smith et al., 1981; Chow et al., 1996), even from as far away as Asia (VanCuren and Cahill, 2002). However, spring, summer, and fall PM concentrations are typically lower than concentrations during winter PM episodes, especially for PM_{2.5} (Chow et al., 1993; Ipps, 1987; Watson et al., 1987; Chow et al., 1992; Motallebi et al., 2003). In the planning study for the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS), non-anthropogenic background PM concentrations and sources outside the SJV were shown to be unimportant for PM concentrations in the SJV during winter PM episodes (Collins, 1998). However, this conclusion was based on a limited number of monitoring sites primarily located within the SJV.

The CRPAQS field study was designed to investigate annual and wintertime PM concentrations in the SJV. As a part of this study, ambient air monitoring was conducted in locations representative of boundary and/or background conditions where air flows into or out of the SJV. For these goals, measurements were obtained at two types of sites: (1) nonanthropogenic background sites designed to monitor concentrations absent anthropogenic emissions and (2) regional background sites, not impacted by local emissions, designed to monitor the concentrations upwind of receptor sites. Measurements of PM and its precursors were made from December 1999 to February 2001 to assess the nature of the high PM episodes. Specifically, the boundary and/or background site concentrations were used to address three questions: (1) what are typical boundary and background concentrations for winter PM episodes in the SJV; (2) how much do the background concentrations and emissions sources outside the SJV contribute to high PM concentrations in the SJV during episodes; and (3) what is the flux of PM and precursor material across the transport planes during episodes?

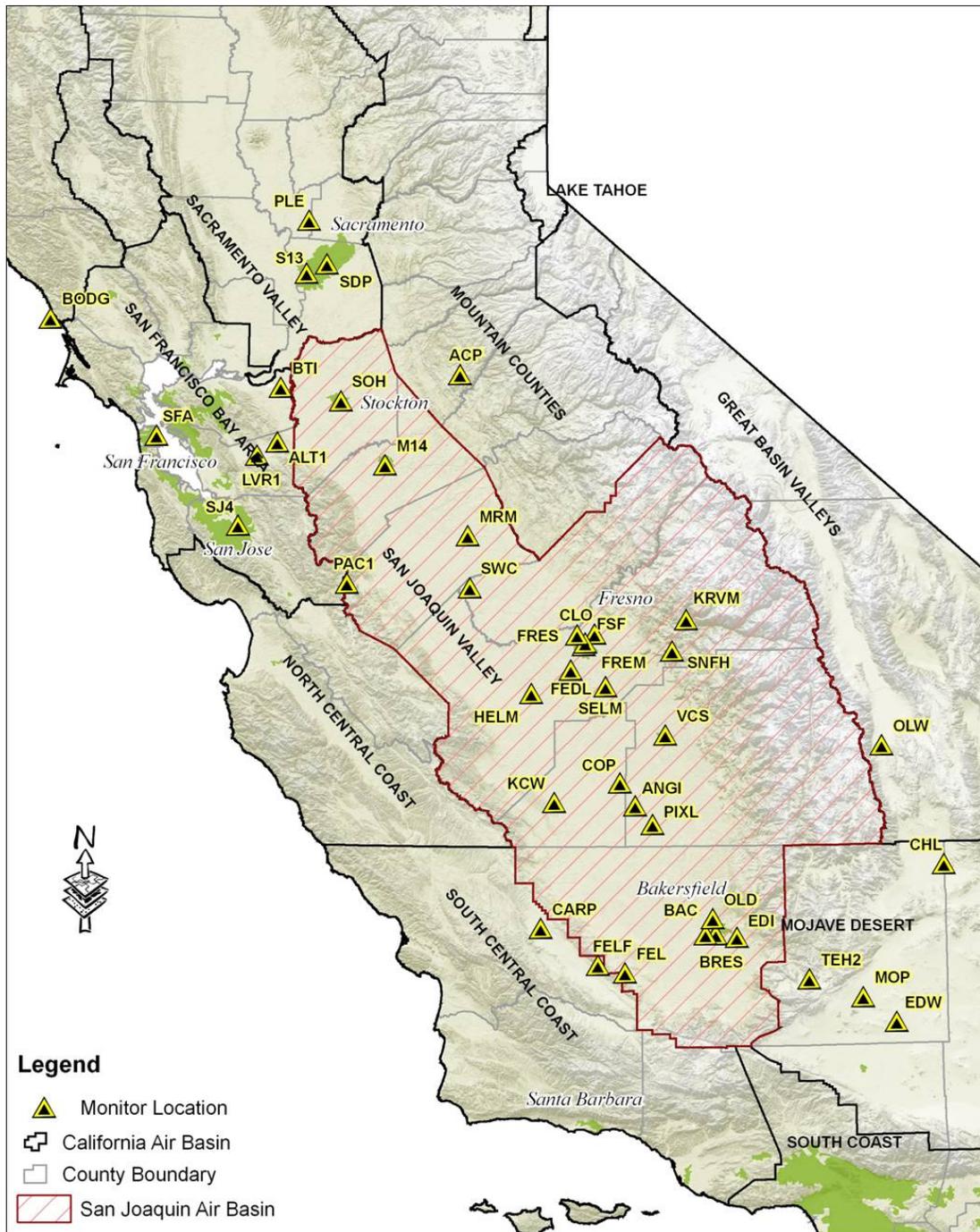


Figure 1-1. Locations of air quality and/or meteorological monitoring sites in the CRPAQS study (site name abbreviations are defined in Table 1-1) and flux planes for assessing transport between the SJV and the San Francisco Bay Area.

Table 1-1. List of likely background, boundary, interbasin, and intrabasin transport sites.

Site Code	Site Name	Site Type	Site Purpose
ACP	Angels Camp	Satellite	Intrabasin gradient; background; vertical
ALT1	Altamont Pass	Satellite	Interbasin transport
BODB	Bodega Bay	Satellite	Background
BTI	Bethel Island	Satellite; Winter anchor	Interbasin transport
CARP	Carrizo Plain	Satellite	Intrabasin gradient; interbasin transport; visibility
CHLV, CHL	China Lake	Satellite	Background; interbasin transport
EDW	Edwards	Satellite; Summer anchor	Visibility; background
FELF	Fellows Foothills	Satellite	Intrabasin gradient; vertical gradient
KRVM, KRV	Trimmer	Satellite	Interbasin transport
LVR1	Livermore	Satellite	Interbasin transport
MOP	Mojave	Satellite	Background; interbasin transport
OLW	Olancha	Satellite	Background
PAC1	Pacheco Pass	Satellite	Interbasin transport
PLEG, PLE	Pleasant Grove	Satellite	Intrabasin transport; possible background
SFA	San Francisco	Satellite	Interbasin transport
SJ4	San Jose 4 th Street	Satellite; Winter anchor	Interbasin transport; community exposure
SNFH	Sierra Nevada Foothills	Satellite; Winter anchor	Vertical gradient; intrabasin gradient; visibility
SOH	Stockton	Satellite	Intrabasin transport
TEH2	Tehachapi Pass	Satellite	Interbasin transport; visibility
TEJ	Tejon Pass	Satellite	Interbasin transport
WAG	Walnut Grove	Satellite	Vertical gradient
YOSE, YOT, YOY	Yosemite	Satellite	Background; vertical gradient

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2. METHODOLOGY

The air quality and meteorological monitoring sites are shown in Figure 1-1. Of particular interest to this study are the sites located outside the SJV. From the west, these sites include elevated sites likely to represent boundary conditions such as Altamont Pass (ALT1), Pacheco Pass (PAC1), Carrizo Plain (CARP), and Foothills above Fellows (FELF). In the Sierra Nevada Mountains, the elevated sites likely to represent boundary conditions were Angels Camp (ACP), Sierra Nevada Foothills (SNFH), and Kings River Valley (KRVM). Tehachapi Pass (TEH2) in the south represented the most likely boundary site in the southern passes. Of note, many of these sites are at elevations greater than a few hundred meters above the Valley floor. Other sites that may capture background concentrations being transported into the Valley from the west include the rural coastal site in Bodega Bay (BODG) and the urban sites in San Francisco (SFA), San Jose Fourth St. (SJ4), and Livermore First St. (LVR1). Sites in the south and east beyond the elevated pass sites include Mojave-Poole (MOP), Edwards Air Force Base (EDW), China Lake (CHL), and Olancho (OLW).

The type, frequency, and duration of measurements vary among air quality monitoring sites. Most boundary and background sites provided 24-hr measurements of PM and its components (i.e., ammonium nitrate, organic carbon, elemental carbon, ammonium sulfate, and crustal elements). Some background sites also provided light scattering measurements from nephelometers (b_{sp}); these measurements can be used as a surrogate for $PM_{2.5}$ mass (Richards et al., 1999; Chow et al., 2002; Richards et al., 1998; Alcorn et al., 2004). These sites represent a combination of well-instrumented anchor sites, which operated on a combined continuous and routine schedule, and lightly instrumented satellite sites, which operated during intensive operations periods (IOPs) forecasted to be high PM events. The site purpose was established in the planning phase and determined the extent of instrumentation and frequency of measurements. Sites listed in s 1-1 were designated to monitor background concentrations, concentrations gradients within or between air basins (i.e., within the SJV or between the SJV and the Bay Area, for example), or to understand how concentrations varied vertically. The Sierra Nevada Foothills and Bethel Island sites were both anchor sites and possible boundary sites. A more detailed description of the measurements and the CRPAQS field campaign has been reported elsewhere (Magliano and McDade, 2001; Magliano et al., 1999a; Watson et al., 1998; McDade, 2002).

The CRPAQS measurements were obtained from late 1999 until early 2001. Multiple wintertime episodes occurred during this period with frequent exceedances of the daily $PM_{2.5}$ and PM_{10} NAAQS. This analysis focuses on a measurement period from December 1, 2000, through February 3, 2001. Daily sampling of PM and its components were obtained at anchor sites and a number of non-anchor sites during the IOPs within this two-month winter period. The largest number of NAAQS exceedances occurred during a three-week PM episode from December 14, 2000, to January 7, 2001.

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3. RESULTS AND DISCUSSION

3.1 WINTER 2000/2001 EPISODE DESCRIPTION

Figure 3-1 shows 24-hr PM_{2.5} concentrations at CRPAQS measurement sites from December 14, 2000, through January 7, 2001. PM₁₀ concentrations at SJV sites in the winter were predominantly composed of PM_{2.5}, and the episode was driven by chemical components primarily residing in the fine PM fraction ($d < 2.5 \mu\text{m}$). The time interval between measurements varied, as most sites provided PM_{2.5} filter measurements from a combination of one-in-six-day sampling and four-days-in-a-row IOP sampling; most sites recorded measurements on December 14, 20, and 25-28, and January 1, and 4-7, 2001.

PM_{2.5} concentrations increased throughout the time period at most sites. The highest concentrations were seen on January 1 in Fresno, Bakersfield, and Sacramento; concentrations at rural southern site peaked on January 5 or 6 and concentrations at sites north of Pacheco Pass peaked on January 6 or 7. This temporal pattern indicates a general buildup of PM concentrations during the episode. The increasing concentrations coincided with light and stagnant winds, low mixing heights, and cold surface temperatures throughout the SJV. Because the SJV is bordered by the coastal range to the west and the Sierra Nevada Mountains to the east, low mixing heights result in stagnant air remaining in the SJV until a meteorological front passes through (Smith et al., 1996; Lilly et al., 2004).

The spatial distribution of PM_{2.5} concentrations illustrates the regional nature of winter PM pollution within the topographic boundaries of the SJV. PM_{2.5} concentrations were highest at urban sites in Fresno and Bakersfield. Outside urban areas, concentrations at the Valley floor increased from the north to the south and were typically higher than those in the Bay Area. Additionally, concentrations were lower at elevated sites on the sides of the Central Valley (e.g., at ACP and SNFH in the Sierra, and at PAC1 in the coastal range) than in the Valley itself. Elevated sites on the eastern, southern, and western borders had PM_{2.5} concentrations significantly lower than those in the Valley; this suggests that the high PM_{2.5} concentrations were limited to the first three to five hundred meters above sea level for most of the episode and that the PM_{2.5} concentrations in air potentially flowing into the Valley were much lower than those within the Valley.

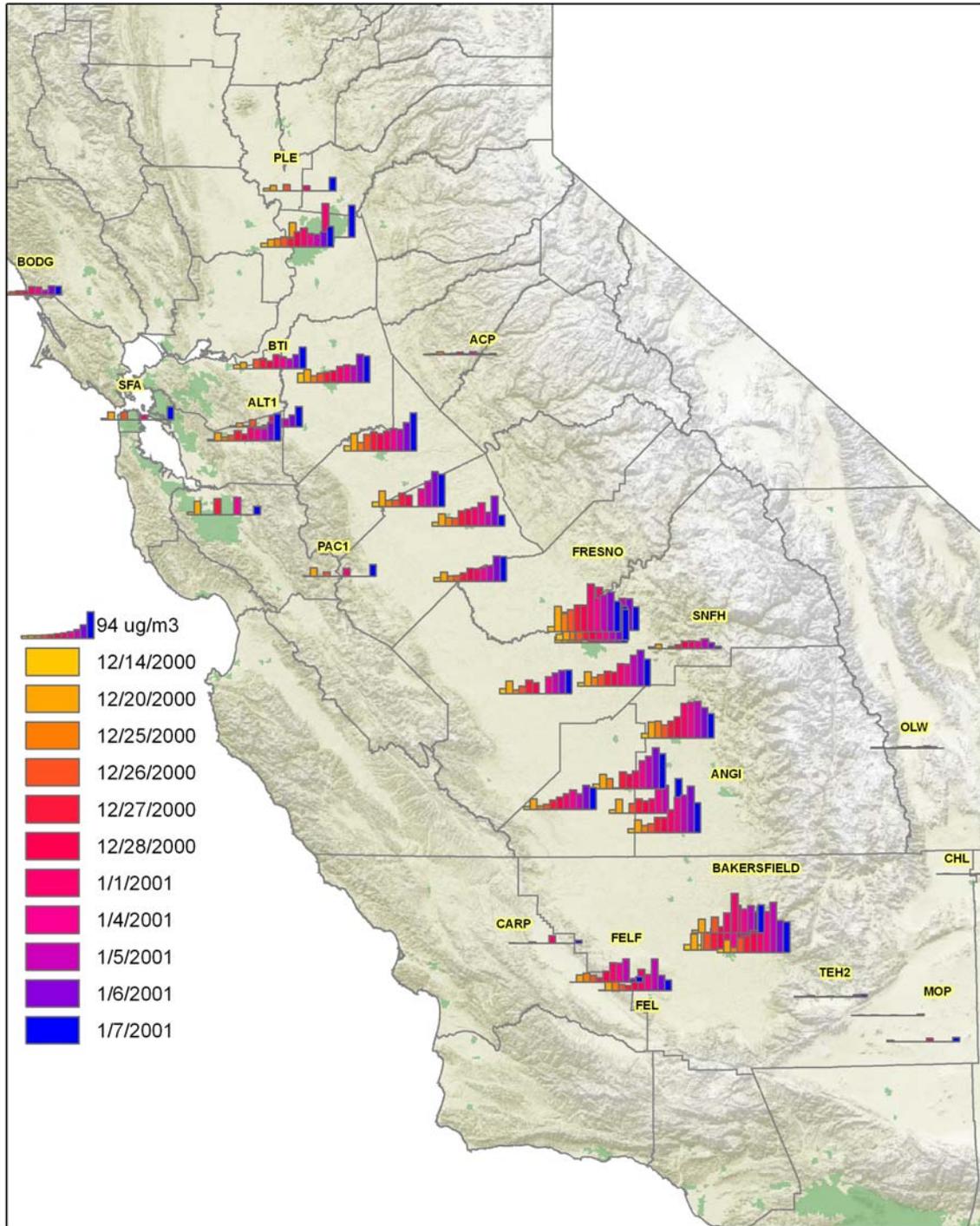


Figure 3-1. PM_{2.5} concentrations ($\mu\text{g}/\text{m}^3$) from December 14, 2000, through January 7, 2001, at CRPAQS monitoring sites. Note that measurements are not available or not shown for multiple days between December 14, 2000, and January 7, 2001.

Wintertime PM_{2.5} in the SJV was composed of a number of chemically distinct components. Ammonium nitrate, ammonium sulfate, organic material (OM=1.4[OC]), elemental carbon (EC), and crustal material (i.e., 1.89[Al] + 2.14[Si] + 1.4[Ca] + 1.43[Fe]) typically accounted for over 95% of the measured PM_{2.5} mass during winter episodes. **Figure 3-2** shows the average 24-hr concentrations of ammonium nitrate, OM, EC, ammonium sulfate, and crustal material spatially averaged over all sites in the SJV during the three-week winter episode. The ammonium nitrate and OM components were over 80% of the total PM_{2.5} mass, while the remaining components contributed about 15% of the remaining mass. Component concentrations generally increased from December 14 until January 6. Ammonium nitrate concentrations increased by over a factor of 10 during the episode, while concentrations of OM and other components increased by only a factor of 3 or so. Ammonium nitrate and OM both accounted for about the same amount of mass at the beginning of the episode but ammonium nitrate was clearly the largest component of PM_{2.5} mass at most sites by the end of the episode.

Figure 3-3 shows the buildup of ammonium nitrate aerosol at all CRPAQS sites during the winter 2000/2001 episode. Ammonium nitrate can be classified as a regional pollutant, as it was relatively homogeneously distributed throughout the Valley compared to other PM components; this homogeneity was evident on a smaller scale during the 1995 Integrated Monitoring Study (IMS95) (Magliano et al., 1999b; Kumar et al., 1998). Ammonium nitrate concentrations in the Fresno and Bakersfield urban areas were quite similar to concentrations at the Angiola (ANGI) and Helm (HELM) rural sites. Ammonium nitrate concentrations at most rural sites were within a factor of two of the urban sites and were temporally correlated with the urban sites. Ammonium nitrate concentrations were typically higher in the southern Central Valley than in the northern Central Valley or in the Bay Area.

Elevated sites like SNFH, ACP, and ALT1 measured significantly lower ammonium nitrate concentrations than urban or rural sites on the Valley floor. Within the Valley, ammonium nitrate concentrations were relatively homogeneous. As shown in Figure 3-2, ammonium nitrate was the largest component of mass on the most polluted days during the SJV episode, accounting for approximately 55% of PM mass on average at all sites. Moreover, 24-hr average ammonium nitrate concentrations correlated ($R^2 = 0.80$) with total PM_{2.5} mass during the winter episode. This observed spatial pattern suggests that PM ammonium nitrate was essentially confined within the Central Valley by topography during this episode.

PM_{2.5} OM was, on average, the second largest component of PM during the episode, although it was the largest component at a few urban sites. **Figure 3-4** shows OM concentrations in the SJV during the 2000/2001 winter episode. In contrast to ammonium nitrate, OM concentrations showed significant spatial variability within the SJV. Particulate OM concentrations were high at the urban core sites and low at most rural sites. At distances more than 50 km from the urban areas, OM concentrations typically declined by a factor of three or more. Emissions of OM at the urban core are either not rapidly transported to the rural sites or are diluted too much to substantially impact rural sites. Concentrations of OM at elevated sites were comparable to concentrations at rural sites on the Valley floor. Possible positive and negative OC measurement artifacts due to semivolatile adsorption and volatilization on the undened quartz filters are not large enough to account for the magnitude of urban/rural differences seen in Figure 3-4 (Mader and Pankow, 2002; Watson and Chow, 2002; Subramanian et al., 2004). Overall, these spatial patterns of OM suggest that the impact of

emissions was largely confined to the local area and OM concentrations were unevenly distributed over the duration of the episode.

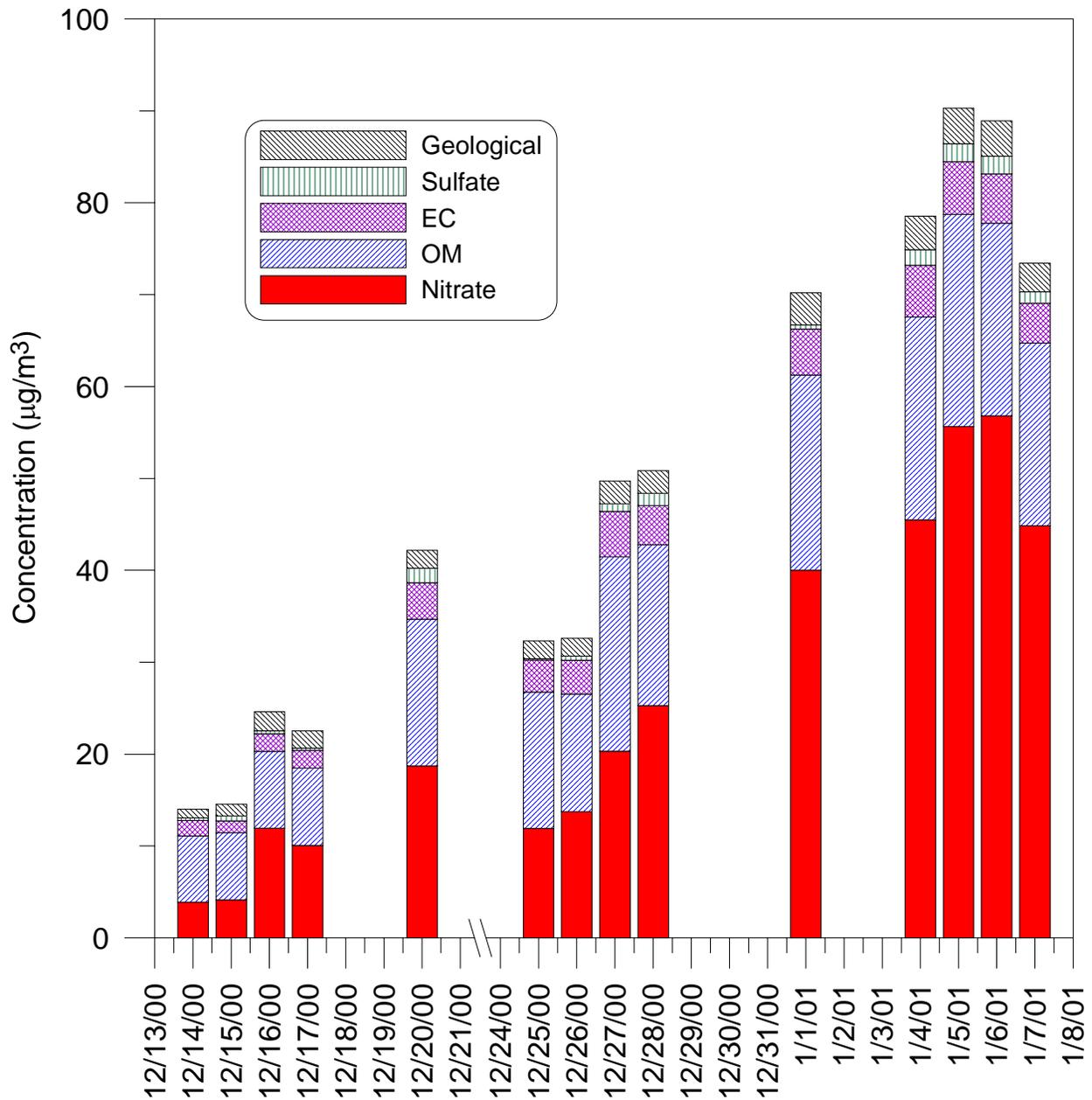


Figure 3-2. Daily concentration ($\mu\text{g}/\text{m}^3$) of $\text{PM}_{2.5}$ chemical components averaged across the SJV sites for 15 representative days between December 14, 2000, and January 7, 2001.

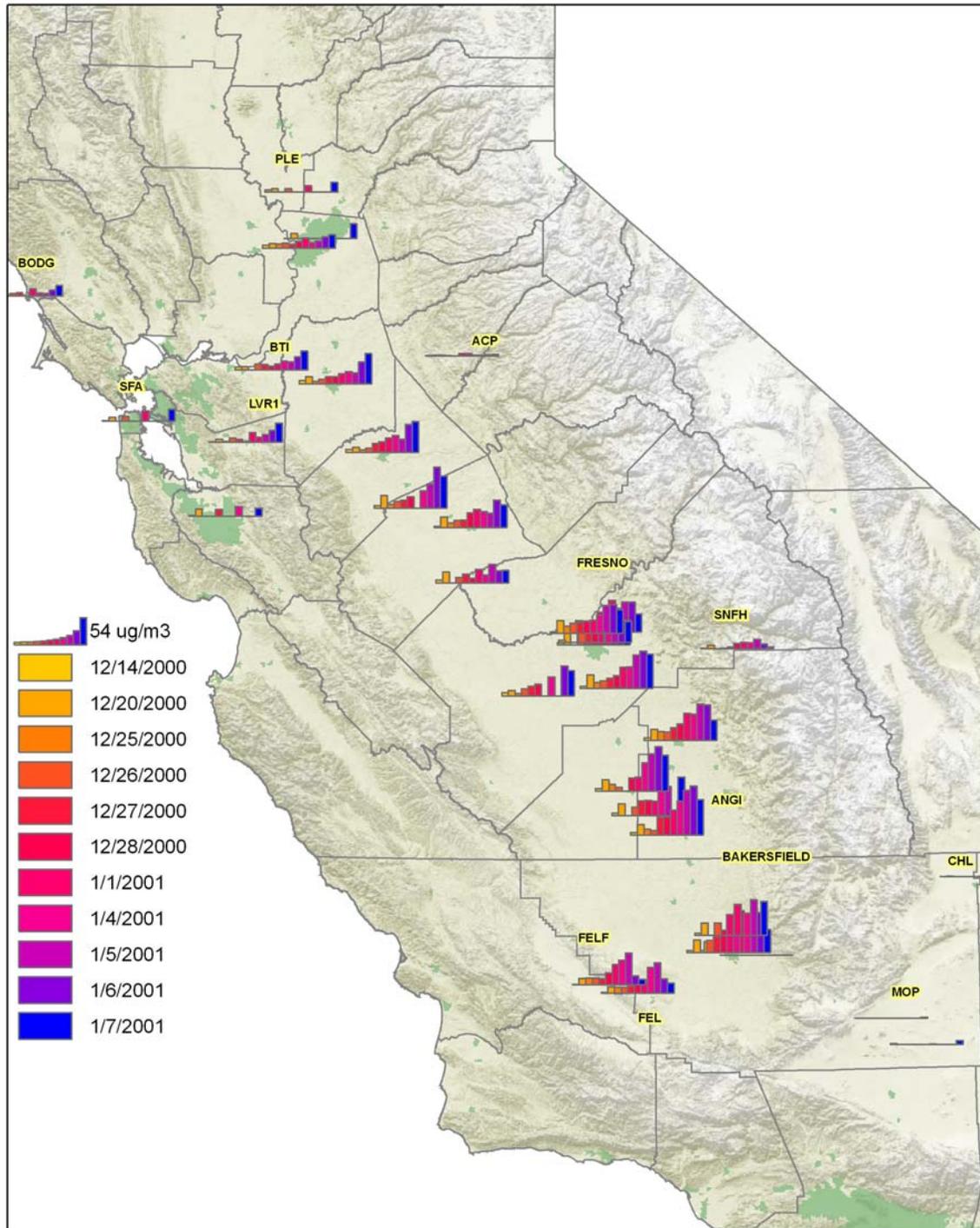


Figure 3-3. Particulate ammonium nitrate concentrations ($\mu\text{g}/\text{m}^3$) from December 14, 2000, through January 7, 2001, at CRPAQS monitoring sites. Note that measurements are not available or not shown for multiple days between December 14, 2000 and January 7, 2001.

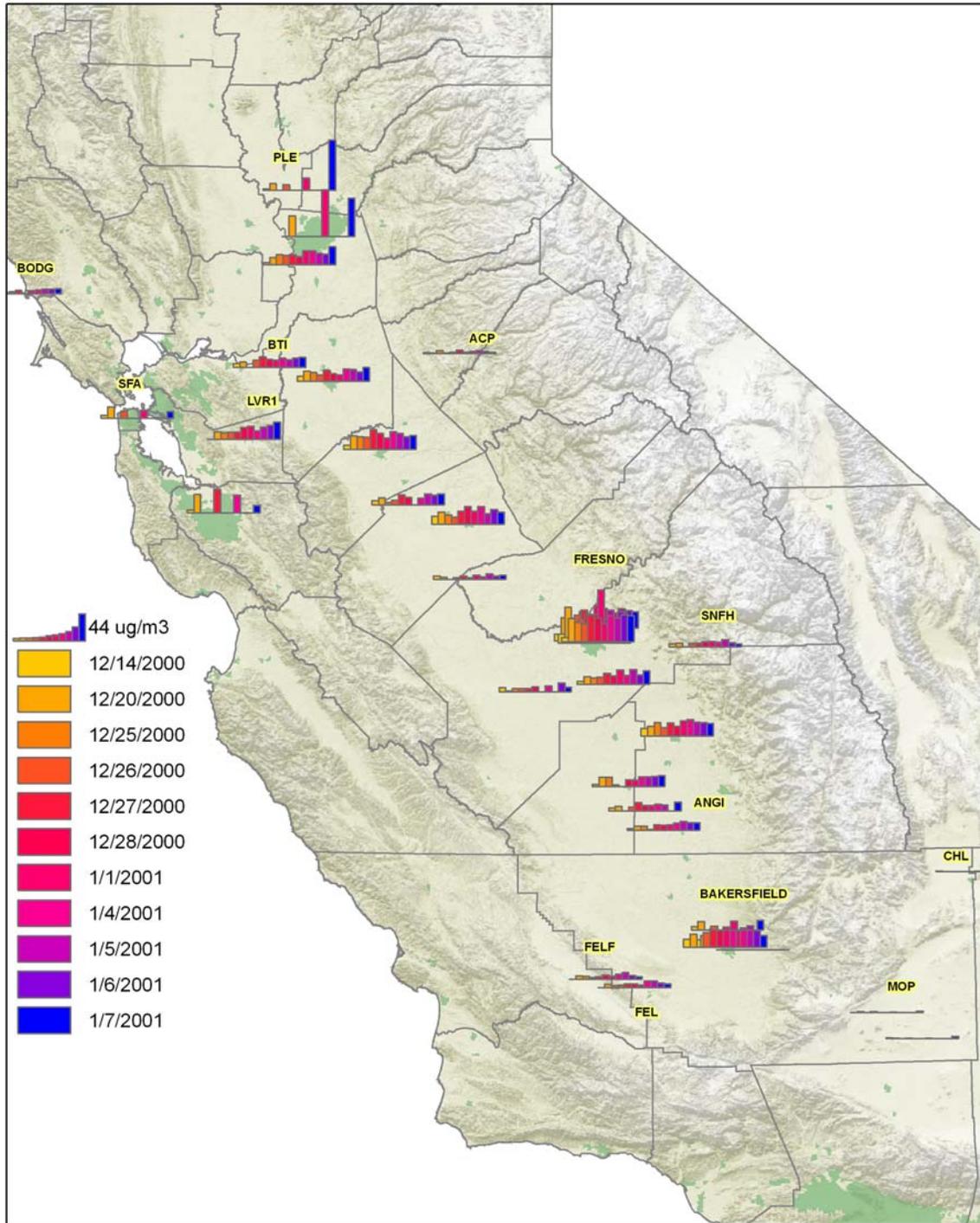


Figure 3-4. Particulate OM concentrations ($\mu\text{g}/\text{m}^3$) from December 14, 2000, through January 7, 2001, at CRPAQS monitoring sites. Note that measurements are not available or not shown for multiple days between December 14, 2000, and January 7, 2001.

The differences in spatial variability of ammonium nitrate and OM can be quantitatively shown with the coefficient of variability (CV) for sites in the SJV. The CV is defined as the ratio of the standard deviation and the mean concentration for all SJV sites on a given day. The daily CV for the spatial variability of ammonium nitrate concentrations at SJV sites was about $0.4 (\pm 0.05 = 95\% \text{ confidence interval})$, despite an increase in ammonium nitrate concentrations by a factor of 10 during the episode. In contrast, the daily CV for OM was almost twice as large ($0.7 \pm 0.1 = 95\% \text{ confidence interval}$) as that for ammonium nitrate even though concentrations of OM increased by about a factor of 2 to 3 during the episode. This shows that the differences in the spatial patterns in Figures 3-3 and 3-4 are significantly different.

The spatial variability of the three other PM components differed. The sulfate component of $\text{PM}_{2.5}$ showed spatial variability similar to the ammonium nitrate component, with a CV of about 0.3. The EC component showed spatial variability very similar to that of OM (CV of 0.75), which was likely due to common emission sources. Finally, the geological component exhibited very large spatial (and temporal) variability, with a CV of about 1.1. This variability may be partially due to the small concentrations of geological material (i.e., less precision in the measurements), or may indicate that geological emissions were a localized phenomenon.

The contrast in spatial variability between the ammonium nitrate and OM components of $\text{PM}_{2.5}$ in the SJV winter episodes provides information on the spatial extent of the production of ammonium nitrate. $\text{PM}_{2.5}$ OM and ammonium nitrate are both subject to the same meteorological transport conditions, yet ammonium nitrate concentrations are relatively homogeneous and OM concentrations are much higher in the urban source areas. In addition, OM and ammonium nitrate components are expected to have the majority of their mass in a similar size fraction ($\text{PM}_{0.1}$ to PM_1) (Lighty et al., 2000; Hughes et al., 1999; Bench et al., 2002) and, therefore, the rates of removal should be approximately the same. In summary, the likely explanation for the difference in spatial variability is the spatial distribution of the emissions or precursors. Primary OM emissions occur predominantly from mobile sources and wood smoke located in urban areas. The formation of ammonium nitrate from NO_x precursors (Lurmann et al., 2004) must occur throughout the SJV to account for its spatial homogeneity.

3.2 NON-ANTHROPOGENIC BACKGROUND

Collins (1998) showed that non-anthropogenic background concentrations were not a significant contributor to SJV $\text{PM}_{2.5}$ concentrations. Ammonium nitrate, ammonium sulfate, OM, and EC originate from anthropogenic sources in the SJV. The crustal component of $\text{PM}_{2.5}$ was usually less than one $\mu\text{g}/\text{m}^3$ during winter episodes. Moreover, geological material in the SJV during winter stagnation episodes was at least partially due to agricultural activity and/or road dust.

Typical annual average $\text{PM}_{2.5}$ concentrations at remote sites in California were on the order of 1.5 to 3.5 $\mu\text{g}/\text{m}^3$ (Motallebi et al., 2003; IMPROVE, 2003). Wintertime $\text{PM}_{2.5}$ concentrations at the cleanest remote sites (i.e., Lassen National Park, Redwood North Coast National Park, and Yosemite National Park) in California were 1.0 to 2.0 $\mu\text{g}/\text{m}^3$. Assuming these concentrations are solely due to nonanthropogenic sources, 1.0 to 2.0 $\mu\text{g}/\text{m}^3$ is likely the best estimate for typical nonanthropogenic background concentrations in the SJV. Regardless,

this concentration range was not significant compared to the typical anthropogenic concentrations experienced in the SJV or compared to the NAAQS.

3.3 WINTER INTERBASIN TRANSPORT

PM and its precursors were not transported into the SJV in significant amounts during wintertime episodes. Wind rose plots for the western boundary site of ALT1 (37.76° N and 121.46° W), shown in **Figure 3-5**, indicate that the net flux of air was most frequently out of the Central Valley during winter episodes. During the afternoon, when mixing heights are highest, wind flow was predominantly from the east; the average wind speed at these sites was ≤ 1 m/s from the east. Pollution roses in Figure 3-5 show nephelometer b_{sp} measurements plotted as a function of wind direction. Nephelometer measurements from the winter correlate very well with $PM_{2.5}$ concentrations in the SJV (Richards et al., 1999; Chow et al., 2002; Alcorn et al., 2004). $PM_{2.5}$ concentrations were highest at the Altamont Pass ALT1 when the wind blew from the east. The nighttime and morning measurements for the Altamont site ALT1 show a higher frequency of winds blowing into the SJV, but the PM concentrations associated with westerly winds are lower than those associated with easterly winds. At the end of the episode, the net flux into the Bay Area transferred significant amounts of $PM_{2.5}$ from the Sacramento and San Joaquin Valleys. Wind and pollution roses for PAC1 (not shown) indicate similar patterns. Pre- and post-episode periods were characterized by strong frontal passages and high winds that reduced PM concentrations.

Wind roses at the eastern boundary site of KRVM (36.876° N and 119.192° W), shown in **Figure 3-6**, indicate that the airflow was either on upslope (west northwest) or downslope (east southeast) flow. Wind data for the Sierra Nevada Foothills site show very similar patterns. The wind direction was directly aligned with the axis of the canyons to the east of the foothill sites. Upslope flow dominated during the afternoon; drainage flow occurred at night and in the mornings. The net flow was weak into the SJV from the foothills (< 1 m/s) during the winter. Pollution roses of nephelometer b_{sp} , shown in Figure 3-6, indicate that PM concentrations were low at KRVM during the winter. Using the b_{sp} measurements as a surrogate for $PM_{2.5}$ concentrations, PM concentrations in the afternoon during upslope flow were estimated to be about the same as nighttime concentrations and typically higher than $10 \mu\text{g}/\text{m}^3$. These measurements indicate that air flowing up the foothills in the afternoon then turned around in the evening and flowed back down to the Valley during the evening drainage flow. Morning concentrations at the eastern boundary sites were more often representative of clean background air (i.e., well below $10 \mu\text{g}/\text{m}^3$). These inflow $PM_{2.5}$ concentrations were well below the concentrations typical of sites on the Valley floor. Therefore, $PM_{2.5}$ concentrations from the available Sierra Nevada Mountain sites transported to the SJV would reduce $PM_{2.5}$ concentrations on the Valley floor.

Meteorological model estimates of winds within Central California during the winter 2000/2001 episode provide a broader view of the interbasin transport of pollutants. **Figure 3-7** shows the surface wind field developed with the diagnostic CALMET model for California at 0600 PST on January 4, 2001. (Additional details on the meteorological modeling can be found in Lilly et al., 2004 (Lilly et al., 2004). Winds inside the SJV were generally stagnant; light winds blew from the SJV to the San Francisco Bay Area, and air entered the SJV through

drainage flow from the Sierra Nevada Mountains and by and vertical mixing; this particular wind field was typical of days in this episode. This model analysis is consistent with the predominant winter wind patterns described by the California Air Resources Board (ARB) (Hayes et al., 1984), as well as the air quality analysis shown here. There was also no evidence for significant transport from the South Coast Air Basin to SJV (i.e., from Los Angeles). These modeled wind fields and pollution roses indicate that air was not transported into the SJV from polluted areas. Transport of PM and precursors into the SJV from the Sierra Nevada Mountains was negligible during the winter study period; in fact, any transport from this area would reduce, not enhance, SJV PM concentrations.

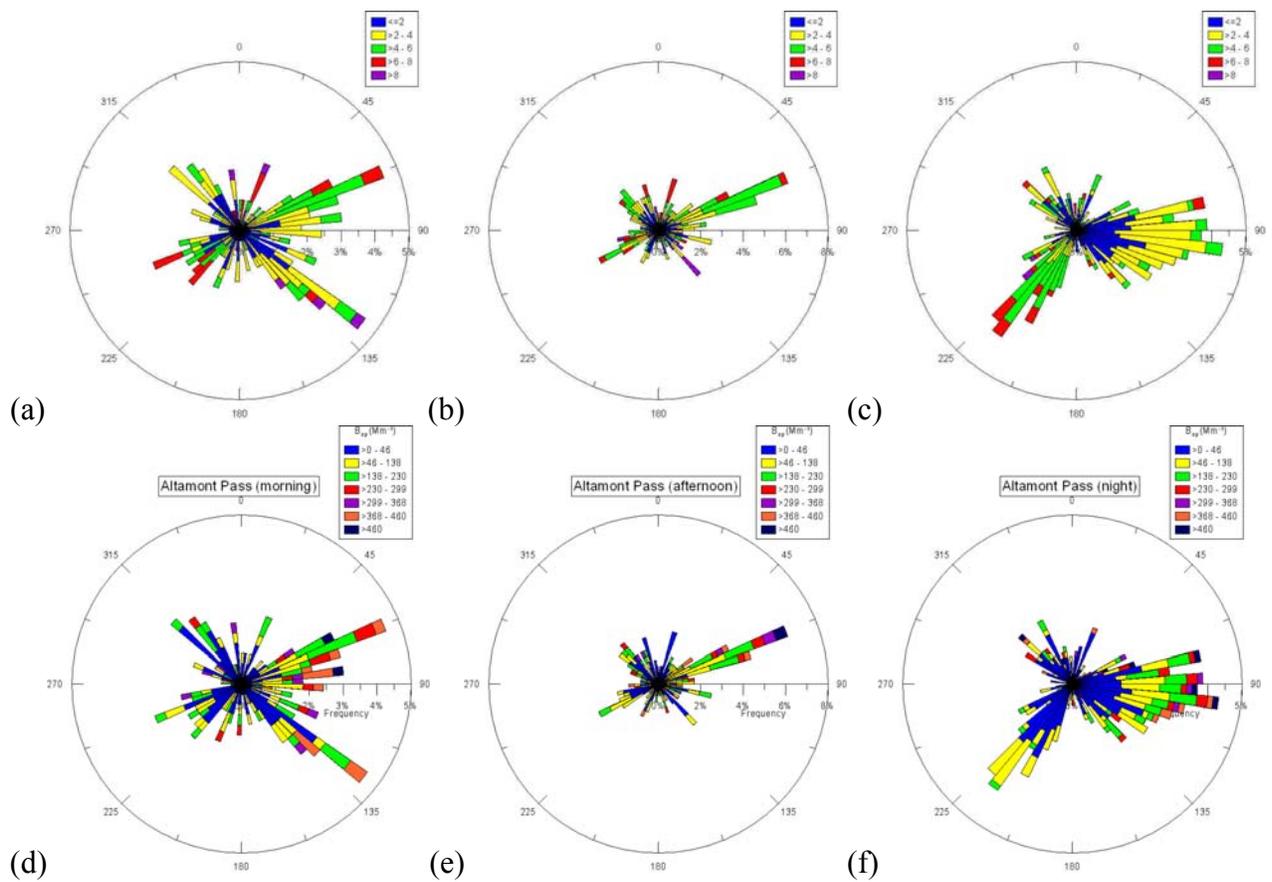


Figure 3-5. Wind (top) and pollution (bottom) roses from ALT1 site during the winter episode from 0600 to 1100 (a, d), 1200 to 1700 (b, e), and 1800 to 0500 (c, f) PST. Pollution roses plot the measured b_{sp} from the nephelometer and the direction from which the wind blew during the measurements; higher values correlate with higher PM concentrations.

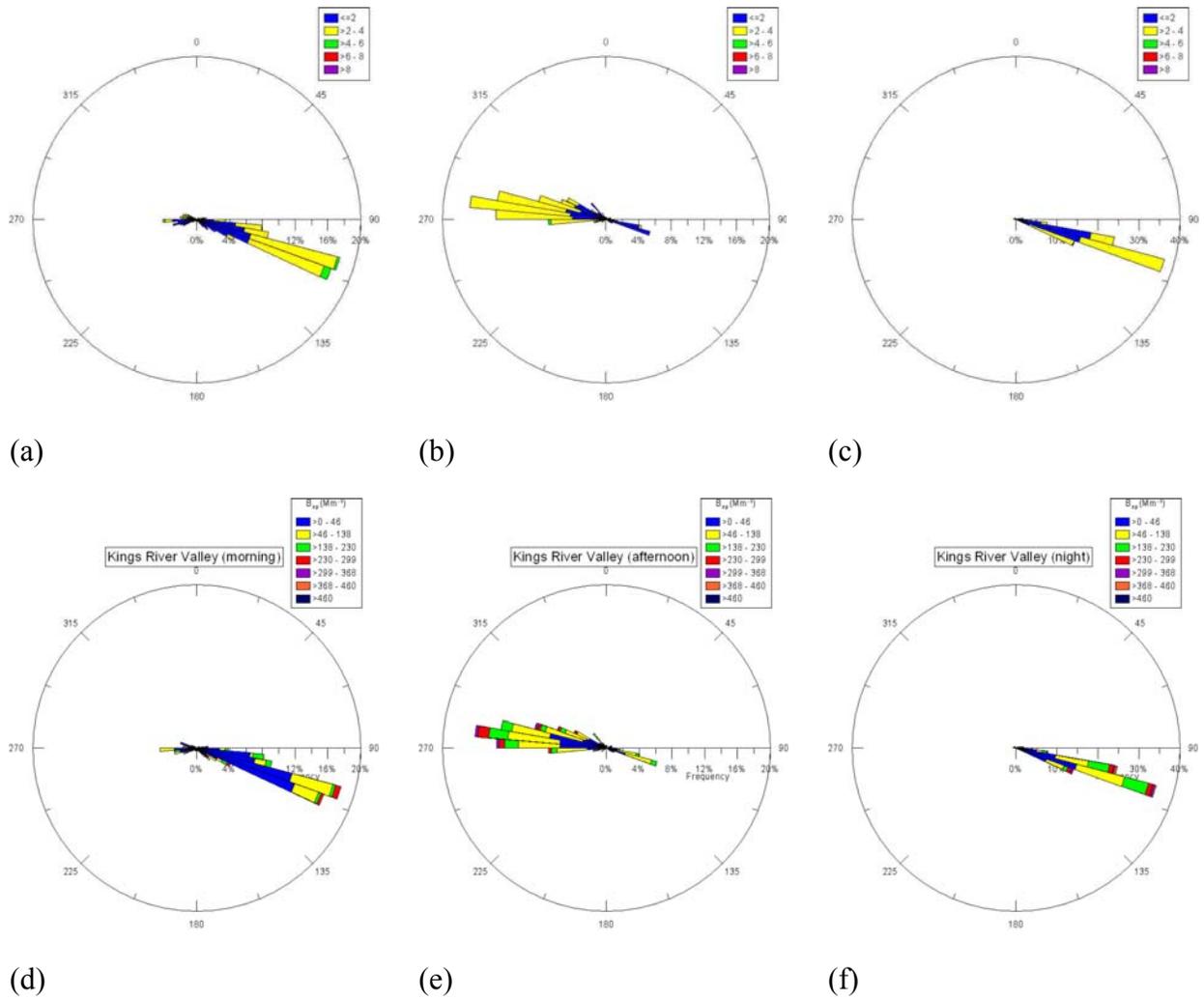


Figure 3-6. Wind (top) and pollution (bottom) roses from the KRVM site during the winter episode from 0600 to 1100 (a, d), 1200 to 1700 (b, e), and 1800 to 0500 (c, f) PST.

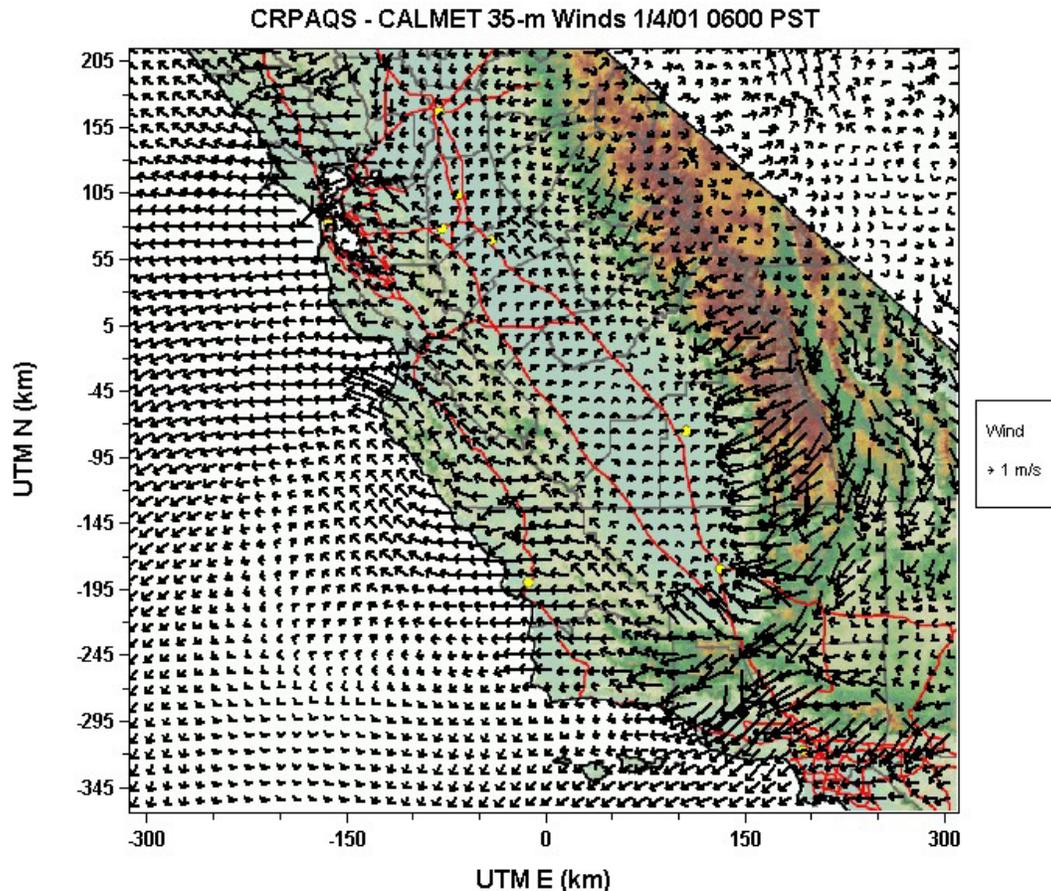


Figure 3-7. Modeled wind fields at 35 m above ground at 0600 PST on January 4, 2001, in California. The length of the arrow indicates the magnitude of the wind speed (Lilly et al., 2004).

3.4 BOUNDARY SITE CONCENTRATIONS

PM_{2.5} concentrations at the elevated boundary sites (sites with elevations more than 200 m above the Valley floor) were usually substantially cleaner than concentrations in the SJV. Typical PM concentrations at the boundary sites were less than half those at the rural sites on the SJV floor. Moreover, boundary sites like ALT1, PAC1, SNFH, and KRVM exhibited higher concentrations when impacted by air originating from the SJV than from elsewhere. Average PM_{2.5} concentrations during the winter episode by site are shown in **Figure 3-8**. The two Fellows sites (FELF at 510 m elevation and FEL at 360 m elevation) located in the southwestern SJV experienced the highest PM_{2.5} 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 nearby CARP site (at elevation 600 m) located west of the first coastal ridge in the coastal range had an average PM_{2.5} concentration that was a factor of three lower than the Fellows sites. In addition, the PM_{2.5} concentrations at MOP and EDW sites located south of the Tehachapi Pass were also very low. We suspect the mixing heights were not sufficiently high to impact either the CARP or MOP sites to the south. Therefore, the

topography of the Central Valley’s border appears to be an effective boundary for high PM_{2.5} concentrations. Air mixing down from the elevated sites will dilute the high PM concentrations in the SJV during winter episodes.

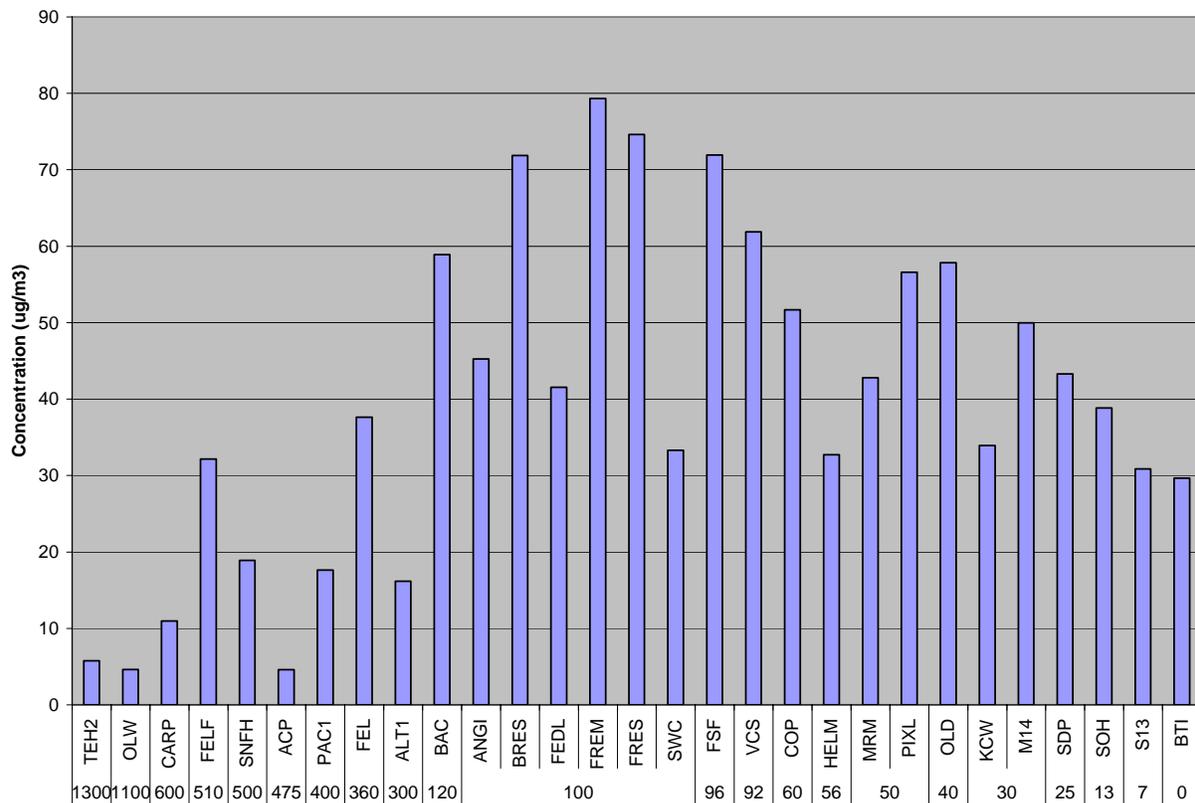


Figure 3-8. Average PM_{2.5} concentrations (µg/m³) from December 2, 2000, through February 3, 2001, at elevated, rural, and urban sites. Site elevations (shown below the site codes) within each category decreases from left to right.

Measurements of precursor concentrations (NO_x, NO_y, VOCs, SO₂, NH₃, etc.) at boundary sites were limited. Characterizing the precursor concentrations entering the Valley from the boundary sites from the Sierra Nevada Mountains was limited to the measurements at the SNFH site. Typical concentrations were determined by averaging the measurements during the IOPs. **Figure 3-9** compares the average concentrations of PM and precursors during IOPs at SNFH with the average concentrations at the rural anchor site, ANGI. The average concentrations of nitrogen species at the SNFH site were 2 to 5 times lower than those measured at ANGI. The concentrations of OC and VOCs measured at both sites were within 20% of each other. However, the average concentrations during the IOPs showed the influence of SJV air during the afternoons and evening periods, as demonstrated by the wind roses in Figure 3-6. These concentrations were not representative of clean Sierra Nevada background air. Concentrations of nitrogen species were even lower in the morning periods (0500-1000) than they were during the rest of the day. Concentrations of carbon species were highest in the evenings at SNFH, which may be attributable to nearby residential wood-burning or bonfires at SNFH.

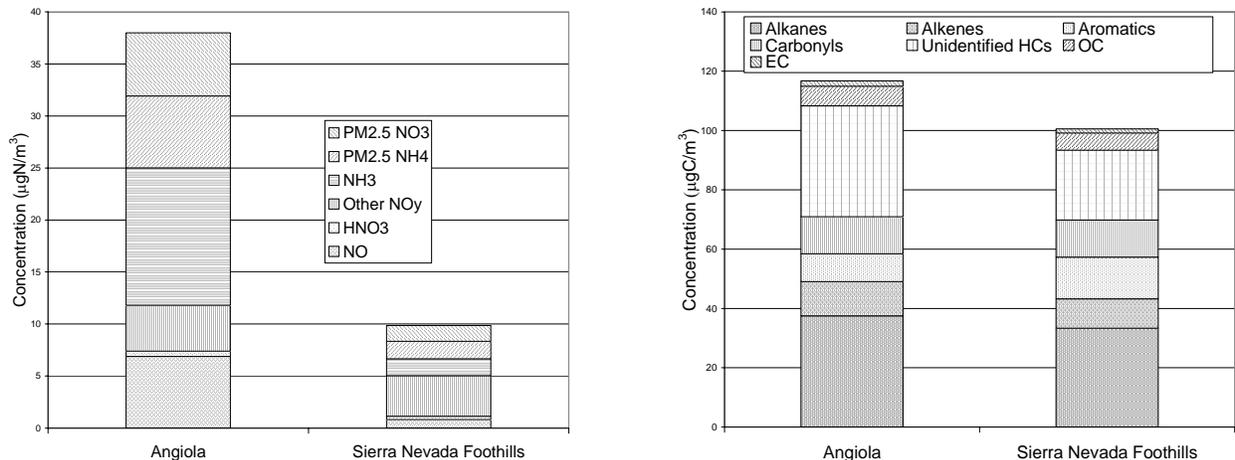


Figure 3-9. Comparison of PM_{2.5} and gaseous precursor concentrations at ANGI and SNFH for carbonaceous species (right) and nitrogenous species (left). PM_{2.5} species are denoted with diagonal patterns.

3.5 SPRING, SUMMER, AND FALL INTERBASIN TRANSPORT

Predominant wind patterns in California in the spring, summer, and fall seasons transports pollutants from the San Francisco Bay Area to the Central Valley (Smith et al., 1981; Carroll and Baskett, 1979; Roberts and Main, 1989; Roberts et al., 1990; Blumenthal et al., 1997). Transport of PM_{2.5} or precursors into the SJV from the Bay Area may significantly impact annual average PM_{2.5} and PM₁₀ concentrations. In turn, these elevated annual average concentrations may make it more difficult to attain annual average PM_{2.5} and/or PM₁₀ NAAQS. **Table 3-1** lists the median concentrations of PM_{2.5} mass and reconstructed PM_{2.5} mass from the speciated components at selected sites from March through October 2000. PM₁₀ mass was ignored because the coarse fraction tends to have a shorter atmospheric residence time (i.e., on the order of hours rather than days). Reconstructed PM_{2.5} mass was calculated by summing the major speciated components (OM, EC, ammonium nitrate, sulfate, and geological). Concentrations of PM_{2.5} at these sites were typically below 20 $\mu\text{g}/\text{m}^3$ on all days and little temporal variability was seen. Median concentrations of PM_{2.5} mass measured using Teflon filters at western boundary sites were between 3 and 5 $\mu\text{g}/\text{m}^3$. Median concentrations of reconstructed PM_{2.5} mass at the same sites were typically 8 $\mu\text{g}/\text{m}^3$.

There were very large differences between total PM_{2.5} mass measured on Teflon filters and reconstructed PM_{2.5} mass measured on quartz, Teflon, and Nylon filters. At many of the boundary sites, the difference in concentrations varied by a factor of two between the methods. Teflon filters lose volatile ammonium nitrate and organic compounds, while quartz filters can adsorb semivolatile organic compounds (Zhang and McMurry, 1992; Hering and Cass, 1999; Turpin et al., 2000; Turpin and Lim, 2001). A complete analysis of the possible systematic biases in each technique is beyond the scope of this study. Therefore, the two methods were used to construct a range of concentrations that may typically be expected to flow into the Central Valley from the Bay Area.

Table 3-1. Median measured PM_{2.5} concentrations (µg/m³) from Teflon filters and median reconstructed PM_{2.5} concentrations from speciated PM_{2.5} components measured on quartz filters at selected CRPAQS sites from March through October 2000.

Site	Median PM _{2.5} Mass (FRM)	Mean PM _{2.5} Mass (FRM) and 95% CI	Median Reconstructed PM _{2.5} Mass	Mean Reconstructed PM _{2.5} Mass and 95% CI
Angel's Camp	3.5	3.5 ± 0.6	8.0	8.0 ± 1.1
Altamont Pass ^a	3.5	4.2 ± 0.7	NA	NA
Angiola	12.0	13.6 ± 2.8	12.2	13.8 ± 2.5
Bethel Island ^a	3.4	4.0 ± 0.8	7.7	8.2 ± 1.1
Bodega Bay	6.3	7.2 ± 1.8	3.2	3.9 ± 0.7
Pacheco Pass ^a	2.7	3.0 ± 0.6	NA	NA
San Francisco ^a	5.0	5.7 ± 1.1	7.7	8.3 ± 1.6
Sierra Nevada Foothills	5.9	6.2 ± 1.0	11.5	11.6 ± 1.8
Tehachapi Pass	7.2	7.5 ± 1.2	NA	NA

^a Sites located on the western boundary of the SJV.

3.6 INTERBASIN FLUX ESTIMATES

The amount of air entering the Bay Area from the Central Valley during the 2000 winter episode was calculated with estimated mixing heights and net wind speeds. The estimated fluxes are listed in **Table 3-2**. Two flux planes' areas were calculated using piecewise integration over topographical boundaries in the Bay Area under the assumption that average 24-hr mixing heights during the winter were 400 m (MacDonald, 2004). The northern flux plane extended from about 10 miles west of Fairfield to about 10 miles east of Richmond (see Figure 1-1). The southern flux plane extended about 10 miles across the Altamont Pass due east of Livermore. Due to uncertainties in mixing heights and topography above the passes, upper and lower bounds on the pollutant fluxes were estimated assuming minimum and maximum flux plane areas. Net wind speeds were calculated using 10-m meteorological measurements from either the Altamont Pass or Travis Air Force Base stations for each flux plane. SJV PM_{2.5} concentrations were taken from average Bethel Island concentrations during the last two weeks of the episode, although concentrations were higher toward the end of the episode. The estimated total flux (i.e., sum of the two flux plane estimates) ranged from 20 to 50 tons of PM_{2.5} transported into the Bay Area per day in the second half of the 2000 and 2001 winter episode. The upper range of the estimated flux of PM_{2.5} was more than half of the locally produced primary emissions of PM_{2.5} (87 tons per day) as listed in the ARB emissions inventory for 2003 (California Air Resources Board, 2003). Even the lower bound of the flux estimates was 20% of the estimated Bay Area air basin emissions. Thus, transport of PM and its precursors from the Central Valley to the Bay Area may increase PM_{2.5} concentration in the Bay Area during Central Valley PM episodes.

Table 3-2. Range of estimated PM_{2.5} flux from the Central Valley into the Bay Area during the winter 2000/2001 episode. The range of assumptions used were also provided.

Site	Area (10 ⁶ m ²)	Wind Speed (m/s)	Concentration (µg/m ³)	Flux (kg/sec)	Flux (tons/day)
Altamont Pass (Max)	1.6	1.6	45	0.11	10
Altamont Pass (Min)	0.67	0.9	35	0.02	2
Carquinez Straits (Max)	10	1	45	0.46	39
Carquinez Straits (Min)	6.4	0.86	35	0.19	17

Similarly, the amount of PM_{2.5} flowing into the SJV from the Bay Area in the spring, summer, and fall seasons was estimated using flux calculations based on previous work by Roberts and Main (Roberts and Main, 1989). PM_{2.5} concentration ranges were taken from Table 3-1. Typical daytime mixing heights of 1500 m were taken from radar wind profiler measurements at Tracy and from those used in Roberts and Main (Roberts and Main, 1989). Vertical profiles of b_{sp} over Bethel Island and Tracy indicated that PM_{2.5} concentrations may decrease by as much as a factor of two from the surface to 1500 meters. Therefore, the aloft flux of pollutants may be lower than that at the surface. **Table 3-3** shows the calculated flux of pollutants into the SJV. The wind speed of 1.7 m/s was considered the net daily value into the SJV, while 5 m/s was used to find the flux during peak wind conditions. Net fluxes under typical daily conditions ranged from 8 to 20 tons of PM_{2.5} transported into the SJV per day, while peak daily values would contribute three times as much mass. The uncertainty in these estimates is at least a factor of two. These concentrations are significant but small compared to the average daily emissions in the SJV of 150 tons per day (California Air Resources Board, 2003).

Table 3-3. Estimated flux of PM_{2.5} into the SJV during spring through fall.

Area (10 ⁶ m ²)	Wind Speed (m/s)	Concentration (µg/m ³)	Flux (kg/sec)	Flux (tons/day)
18	1.7	2.7	0.08	8
18	1.7	7	0.2	20
18	5	2.7	0.2	23
18	5	7	0.6	60

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4. CONCLUSIONS

The spatial and temporal variability of ambient particulate matter, its speciated components and gaseous precursors in the San Joaquin Valley in California was examined to assess the contributions of background air pollution during winter PM episodes. Transport of material into the SJV was most likely to occur through drainage flow from the Sierra Nevada Mountains or vertical mixing during winter PM episodes. 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, since 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. There was evidence that the flux of PM_{2.5} from the Central Valley into the San Francisco Bay Area can be a significant contributor to high PM_{2.5} concentrations in the Bay Area. From spring through fall, this flux is reversed and the Bay Area likely contributes a small but significant amount of PM_{2.5} to the Central Valley.

High concentrations of PM organic carbon were spatially limited to core urban sites while high concentrations of PM ammonium nitrate were regionally distributed throughout the SJV. The regional homogeneity of ammonium nitrate concentrations coupled with the stagnant wind conditions provides evidence that production of ammonium nitrate occurs at similar rates throughout the valley. In contrast, the OC component of PM indicates that production rates were much higher in the urban areas than at rural sites.

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