

Processes Influencing Secondary Aerosol Formation in the San Joaquin Valley during Winter

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ABSTRACT

Air quality data collected in the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) are analyzed to qualitatively assess the processes affecting secondary aerosol formation in the San Joaquin Valley (SJV). This region experiences some of the highest fine particulate matter (PM_{2.5}) mass concentrations in California ($\leq 188 \mu\text{g}/\text{m}^3$ 24-hr average), and secondary aerosol components (as a group) frequently constitute over half of the fine aerosol mass in winter. The analyses are based on 15 days of high-frequency filter and canister measurements and several months of wintertime continuous gas and aerosol measurements. The phase-partitioning of nitrogen oxide (NO_x)-related nitrogen species and carbonaceous species shows that concentrations of gaseous precursor species are far more abundant than measured secondary aerosol nitrate or estimated secondary organic aerosols. Comparisons of ammonia and nitric acid concentrations indicate that ammonium nitrate formation is limited by the availability of nitric acid rather than ammonia. Time-resolved aerosol nitrate data collected at the surface and on a 90-m tower suggest that both the daytime and nighttime nitric acid formation pathways are active, and entrainment of aerosol nitrate formed aloft at night may explain the spatial homogeneity of nitrate in the SJV. NO_x and volatile organic compound (VOC) emissions plus background O₃ levels are expected to determine NO_x oxidation and nitric acid production rates, which currently control the ammonium nitrate levels in the SJV. Secondary organic aerosol formation is significant in winter, especially in the Fresno urban area. Formation of secondary organic aerosol is more likely limited by the rate of VOC oxidation than the availability of VOC precursors in winter.

IMPLICATIONS

A substantial portion of wintertime PM_{2.5} in the SJV is secondary formation. Emission control strategies designed to achieve compliance with the National Ambient Air Quality Standards for PM_{2.5} in this area must address the role of gaseous NO_x and VOC emissions in the episodic PM_{2.5} problem. CRPAQS data analyses suggest that reductions in emissions (NO_x and VOC) that will reduce nitric acid will be more effective in reducing secondary ammonium nitrate aerosol concentrations than reductions in ammonia emissions. Reductions in VOC emissions will reduce secondary organic aerosol concentrations and most likely contribute to reductions in ammonium nitrate concentrations.

INTRODUCTION

Ambient concentrations of particulate matter (PM) in California's San Joaquin Valley (SJV) exceed the National Ambient Air Quality Standards (NAAQS) for fine PM (PM_{2.5}) and coarse PM ([PM₁₀] particles with aerodynamic diameters $< 2.5 \mu\text{m}$ and $10 \mu\text{m}$, respectively). The magnitude and frequency of PM concentrations in excess of health-based standards resulted in designation of the area as a severe nonattainment area for PM₁₀ by the U.S. Environmental Protection Agency (EPA).¹ State and local agencies are implementing known control technologies and are developing comprehensive emission control strategies to ultimately attain compliance with the PM NAAQS; however, many questions remain regarding the most effective methods to achieve PM air quality goals.

The California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) was designed to improve the scientific understanding of excessive PM levels in Central California. Its objectives were to determine where and when populations experience excessive exposures, as defined by the air quality standards, and how to cost-effectively reduce those exposures to acceptable levels. The CRPAQS is an integrated effort that includes air quality and meteorological field measurements, emissions characterization, data analysis, and air quality modeling. The CRPAQS field study consisted of a long-term campaign from December 1, 1999, through February 4, 2001, a winter intensive study within the period of December 1, 2000, through February 3, 2001, and a fall intensive study within the period of October 9, 2000, through November 14, 2000.

One important goal of the CRPAQS is to improve the understanding of the processes that affect secondary PM. Numerous studies²⁻⁷ in the SJV have shown that the two most abundant constituents of PM_{2.5} in winter are secondary ammonium nitrate and carbonaceous aerosols. Up to 14% (on average) of the organic aerosol was estimated to be secondary, even during the winter,⁷ and other secondary species, such as ammonium sulfate, contribute to the total burden of secondary PM_{2.5}. Secondary aerosol species are formed from gaseous emissions of nitrogen oxides (NO_x), sulfur dioxide (SO₂), ammonia (NH₃), and volatile organic compounds (VOCs). The extent of the problem is more severe than in most other nonattainment areas, because the concentrations of the secondary components of PM (as a group) at times exceed the $65 \mu\text{g}/\text{m}^3$ 24-hr PM_{2.5} NAAQS.⁸ The implication of high concentrations of secondary species is that PM_{2.5} emission control strategies must address gaseous secondary PM precursor emissions to achieve attainment of the

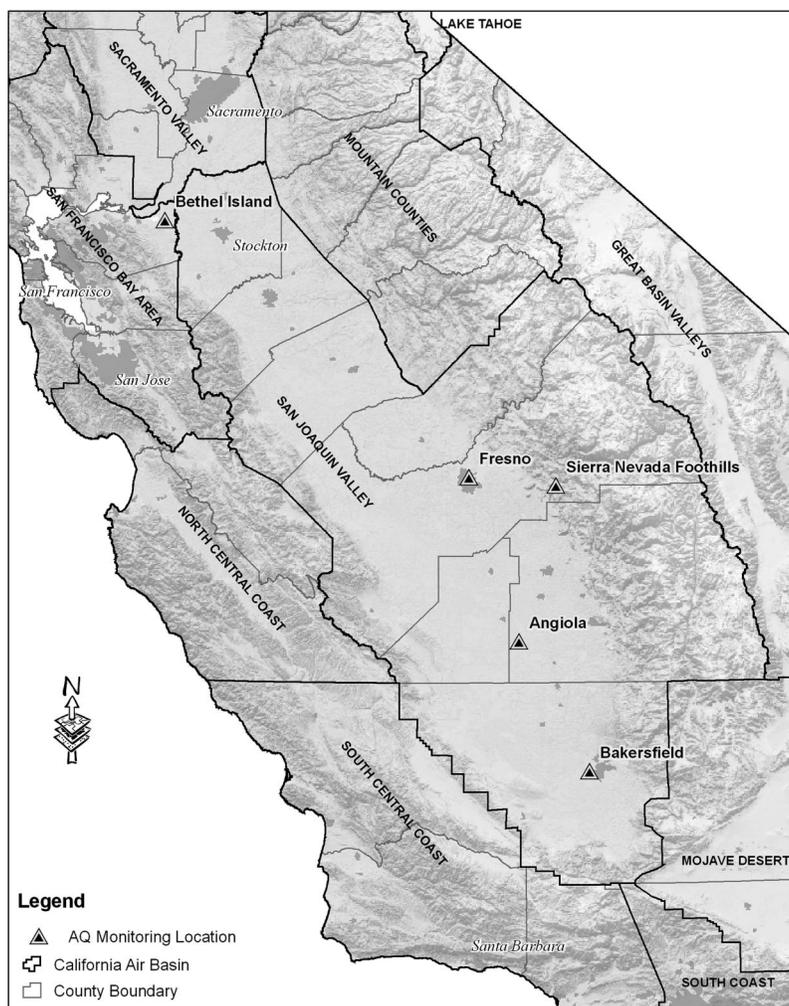


Figure 1. Locations of the five core CRPAQS air monitoring sites.

standards. The understanding of the chemical mechanisms and physical gas-to-aerosol transformation processes is incomplete, especially with respect to the relative rates of daytime and nighttime formation of ammonium nitrate and the formation of secondary organic aerosols.

Measurement data collected in the CRPAQS are analyzed in this paper to characterize the phase distributions of precursor and PM species and to qualitatively assess the processes affecting secondary aerosol formation in the SJV. The specific objectives are to: (1) describe and interpret the gas-aerosol phase distributions; (2) estimate the extent of secondary organic aerosol formation; (3) evaluate when, where, and which precursor species limit the formation of secondary aerosols; and (4) assess evidence for the relative importance of the nighttime and daytime mechanism of nitric acid formation.

EXPERIMENTAL WORK

Data from the five air monitoring locations in or near the SJV with the most extensive chemical characterization of ambient concentrations during the CRPAQS winter intensive study were used for this analysis. The locations of the stations are shown in Figure 1. Fresno and Bakersfield are the two largest urban areas in the SJV and host multiple air monitoring stations. The First Street site in Fresno,

which is an EPA Supersite,⁹ and the California Street site in Bakersfield were selected. Angiola is a rural site in the middle of the southern SJV located halfway between Fresno and Bakersfield. Sierra Nevada Foothills is a rural site located 50 km east of Fresno at an elevation ~400 m above the valley floor in the foothills. Bethel Island is a suburban site located 60 km east of San Francisco and 200 km northwest of Fresno on the boundary between the San Francisco Bay Area and the SJV. Angiola and Sierra Nevada Foothills were special sites established for the CRPAQS, whereas Fresno, Bakersfield, and Bethel Island are long-term routine air monitoring sites. Air quality monitoring at Angiola included data collection at the surface and on a 90-m tower.

Integrated measurements were made for 3- to 8-hr sampling intervals on 15 intensive operations period (IOP) days between December 15, 2000, and February 3, 2001. Multileg sequential samplers collected filters for subsequent analysis of $PM_{2.5}$ mass by electrobalance; $PM_{2.5} NO_3$, SO_4 , and NH_4 by ion chromatography; nitric acid and NH_3 by denuder difference; and $PM_{2.5}$ elemental carbon (EC) and organic carbon (OC) by the IMPROVE thermal-optical reflectance protocol.^{10,11} NH_3 and nitric acid measurements were obtained at the Angiola, Sierra Nevada Foothills, and Fresno sites. Polished stainless steel

canisters were used to collect samples for subsequent analysis of C2-C12 hydrocarbons by cryofocusing gas chromatography (GC) and flame ionization. Dinitrophenyl-hydrazine-coated cartridges were used to collect samples for subsequent analysis of C1-C7 carbonyls by liquid chromatography and ultraviolet detection. Hydrocarbon and carbonyl compound measurements were obtained at four of the five sites. Hourly continuous measurements were obtained for O₃ by ultraviolet absorption, NO/reactive odd nitrogen (NO_y) by chemiluminescence (unfiltered), and PM_{2.5} NO₃ by flame volatilization. Only data from continuous instruments were available from the Angiola tower. In addition, hourly surface temperature, relative humidity, wind speed, and wind direction measurements were available for these five locations. The precision and accuracy of the measurement technologies are described elsewhere,^{9,12-14} as are the meteorological conditions on the 15 sampling days.¹⁵

RESULTS

Phase Distributions

The combination of continuous and integrated measurements of nitrogen species allows us to construct relatively complete phase distributions for species derived from NO_x emissions and from NH₃ emissions. The resolvable NO_x-related species include gaseous NO, HNO₃, and other NO_z, and nitrate ion in PM_{2.5}. The gaseous other NO_z, which includes NO₂, HONO, NO₃, N₂O₅, and organic nitrates, was determined by subtracting NO, HNO₃, and PM_{2.5} NO₃ from the unfiltered NO_y. The uncertainties of the other NO_z concentrations are inherently larger than those for the directly measured species, like NO, because they are determined by difference. The NH₃-related nitrogen species are gaseous NH₃ and ammonium ion in PM_{2.5}. Nitrate and ammonium ions in fog water and coarse particles are ignored in this analysis, because there was little fog during this period, and the measurements of coarse particle nitrate were limited. Previous measurements in the SJV⁵ and in Southern California^{16,17} indicate that coarse particle nitrate concentrations are typically 10–20% of fine particle nitrate concentrations. The particle nitrate fractions reported here should be interpreted as lower limits because of the omission of coarse nitrate. The nitrogen species concentrations are expressed in units of micrograms of nitrogen per cubic meter for comparability.

Table 1 shows the 15-day average concentrations of NO_x-related nitrogen species at the five SJV sites. The 15-day average concentrations of NO_x-related nitrogen species ranged from 8 μgN/m³ in the Sierra Nevada Foothills to 78 μgN/m³ in Bakersfield. The total concentration of NO_x-related species in the Fresno urban area was 6 times higher than at Sierra Nevada Foothills, located just 50 km east of Fresno 400 m above the valley. The average phase-partitioning showed substantially more nitrogen (2–12 times more) in gaseous species than in PM at all of the locations. The phase distributions show that gaseous NO was the most abundant NO_x-related species in Bethel Island, Fresno, and Bakersfield, comprising 57–64% of the nitrogen. Gaseous NO comprised 12% and 39% of the total nitrogen in NO_x-related species at Sierra Nevada Foothills and Angiola, respectively. Nitric acid was a small portion of the nitrogen (1–5%) at the three sites where it

was measured. The other gaseous nitrogen species (other NO_z) comprised 60% of the NO_x-related nitrogen concentrations at Sierra Nevada Foothills and 25–35% at Angiola, Bethel Island, Fresno, and Bakersfield. The aerosol nitrate composed 8–9% of the NO_x-related nitrogen concentrations at urban sites and 23–34% of the NO_x-related nitrogen concentrations at rural sites. Within the SJV, the urban and rural aerosol nitrate concentrations were quite similar on average. The differences in percentage of nitrogen in the aerosol phase reflect lower gaseous nitrogen species concentrations in rural areas than in urban areas.

The 15-day average diurnal variation of the nitrogen species phase distribution is illustrated in Figure 2. The total nitrogen species concentrations were highest in the 5:00–10:00 a.m. period of the morning and lowest in the 1:00–4:00 p.m. period of the afternoon. The dominant species shifted from the precursor species, NO, in the morning to the product species (HNO₃, other NO_z, and PM_{2.5} NO₃) in the afternoon. The percentage of NO_x-related nitrogen in the aerosol phase was highest in the afternoon (1:00 p.m. to 4:00 p.m.) at all five locations. At this time of day, 40–50% of the nitrogen was partitioned to the aerosol phase at the rural sites (Angiola and Sierra Nevada Foothills), whereas only 18–35% of the nitrogen was in the aerosol phase in the afternoon at Bethel Island, Fresno, and Bakersfield. The aerosol nitrogen had less diurnal variation than the gaseous nitrogen species, which is consistent with its chemical stability in cool winter conditions and its long atmospheric lifetime compared with the other nitrogen species. The diurnal variations of NO concentrations were especially large; NO concentrations increased at night when mixing was limited and in the morning when emissions were high and subsequently decreased during the day because of dilution and chemical reactions. Entrainment of O₃ from aloft as the mixing height rises is believed to accelerate the oxidation of NO in the winter months. Dilution is less evident in the product species because their formation from NO oxidation offsets some of the effects of dilution. For aerosols, entrainment of PM_{2.5} NO₃ from aloft (as discussed below) is likely to counteract the effects of dilution and, in some cases, enhance surface PM_{2.5} NO₃ concentrations during the day.

The average phase distributions of nitrogen species related to NH₃ emissions are also shown in Table 1. The 15-day average concentration of gaseous NH₃ plus PM_{2.5} ammonium ranged from 3.3 μgN/m³ at Sierra Nevada Foothills to 20 μgN/m³ at Angiola, indicating that large spatial gradients exist across the SJV. The average level of NH₃-related nitrogen species at Fresno (12 μgN/m³) was midway between the levels at Angiola and Sierra Nevada Foothills. The average gas/aerosol partitioning was 49%/51% at Sierra Nevada Foothills, 60%/40% at Fresno, and 66%/34% at Angiola. Time-resolved data (not shown) indicate only modest diurnal variation in the phase partitioning. For example, the average gas/aerosol partitioning is 75%/25% from 12:00 a.m. to 10:00 a.m. and 55%/45% from 10:00 a.m. to 4:00 p.m. at Angiola where the NH₃-related nitrogen concentrations were high. Angiola and Sierra Nevada Foothills experienced higher ammonium concentrations in the afternoon than in the morning,

Table 1. The 15-day average distribution of NO_x-related, NH₃-related, SO₂-related, and carbonaceous compounds at the five core CRPAQS air monitoring sites in winter.

Chemical Constituent		Location				
		Bethel Island	Fresno	Bakersfield	Angiola	Sierra Nevada
NO	μg-N/m ³	16.2	32.2	50.2	6.9	0.8
	%NO _y	57	63	64	39	12
HNO ₃	μg-N/m ³	NA	0.4	NA	0.5	0.3
	%NO _y	NA	1	NA	3	5
Other NO _z	μg-N/m ³	12.4	18.9	28	10.4	5.4
	%NO _y	35	28	26	25	60
PM _{2.5} NO ₃	μg-N/m ³	2.3	4.3	7.3	6.1	1.5
	%NO _y	8	8	9	34	23
NH ₃	μg-N/m ³	NA	7.2	NA	13.1	1.6
	%TNH ₃	NA	60	NA	66	49
PM _{2.5} NH ₄	μg-N/m ³	2.6	4.8	7.9	6.9	1.7
	%TNH ₃	NA	40	NA	34	51
SO ₂	μg-S/m ³	NA	NA	1.4	NA	NA
	%S	NA	NA	62	NA	NA
PM _{2.5} SO ₄	μg-S/m ³	NA	NA	0.9	NA	NA
	%S	NA	NA	38	NA	NA
Alkanes	μg-C/m ³	65.6	78.1	NA	38.8	31.6
	%C	42	30	NA	32	32
Alkenes	μg-C/m ³	21.1	39.3	NA	12.0	9.4
	%C	13	15	NA	10	10
Aromatics	μg-C/m ³	20.6	42.9	NA	10.3	13.7
	%C	13	17	NA	9	14
Carbonyls	μg-C/m ³	6.7	21.8	NA	12.4	12.3
	%C	4	8	NA	10	13
Nonreactive NMOC	μg-C/m ³	15.2	11.8	NA	13.5	3.7
	%C	10	5	NA	11	4
Unidentified HCs	μg-C/m ³	33.3	51.7	NA	37.5	23.3
	%C	21	20	NA	31	24
PM _{2.5} OC	μg-C/m ³	7.4	19.3	NA	6.7	5.7
	%C	5	8	NA	6	6
PM _{2.5} EC	μg-C/m ³	2.5	5.7	NA	1.8	1.3
	%C	2	2	NA	2	1

Notes: NA = not measured at the location. HNO₃ was not measured at Bethel Island and Bakersfield, and the %NO_y is calculated assuming zero HNO₃ concentration for these locations.

which is presumably a result of daytime ammonium nitrate and ammonium sulfate formation.

SO₂ concentrations have been reduced to low levels in California, and only a few air monitoring stations currently have monitors that measure SO₂ concentrations. Although sulfate aerosol was measured at many locations in the CRPAQS, SO₂ was measured at only one of the five core stations in the SJV. Table 1 lists the 15-day average concentrations of SO₂ and PM_{2.5} SO₄ at Bakersfield during the winter IOPs. The average total sulfur concentration was 2.3 μgS/m³. The average SO₂-related sulfur species were partitioned as 62% SO₂ and 38% PM_{2.5} SO₄ on a sulfur mass basis. The relative partitioning of sulfur species varied little by time of day. The average SO₂ concentrations did not follow the typical diurnal pattern for precursor species because they were highest during midday when ventilation conditions were optimum. Aerosol sulfate concentrations were low and had little or no diurnal variation at this site. The lack of strong time variation suggests that the sulfur species are more regional than local in nature. The absence of fog during this period may have limited the conversion of SO₂ to sulfate.

For evaluation of the phase distribution of carbonaceous species, concentrations of gaseous reactive C2-C12 hydrocarbons, gaseous C1-C7 carbonyl compounds, and PM_{2.5} OC and EC were considered. The concentrations of semi-VOCs as well as organics in fog water were ignored. Table 1 lists the 15-day average concentrations of gaseous alkanes, alkenes, aromatics, carbonyls, and unidentified hydrocarbons and the PM_{2.5} OC and EC at four locations in the SJV. The average total carbon concentrations were 97, 119, 156, and 258 μgC/m³ at Sierra Nevada Foothills, Angiola, Bethel Island, and Fresno, respectively. The urban-rural differences in total carbon are quite similar to those for total NO_x-related nitrogen. The distributions of gaseous compounds at Fresno averaged 33% alkanes, 17% alkenes, 19% aromatics, 9% carbonyls, and 22% unidentified hydrocarbons, which is similar to previous wintertime observations.¹⁸ The rural locations had smaller percentages of alkenes and aromatics and higher percentages of carbonyls than Fresno, indicating that a portion of the more reactive VOCs react during transport to the rural sites. The VOC composition at Bethel Island was higher in alkanes and lower in carbonyls than at Fresno, indicating

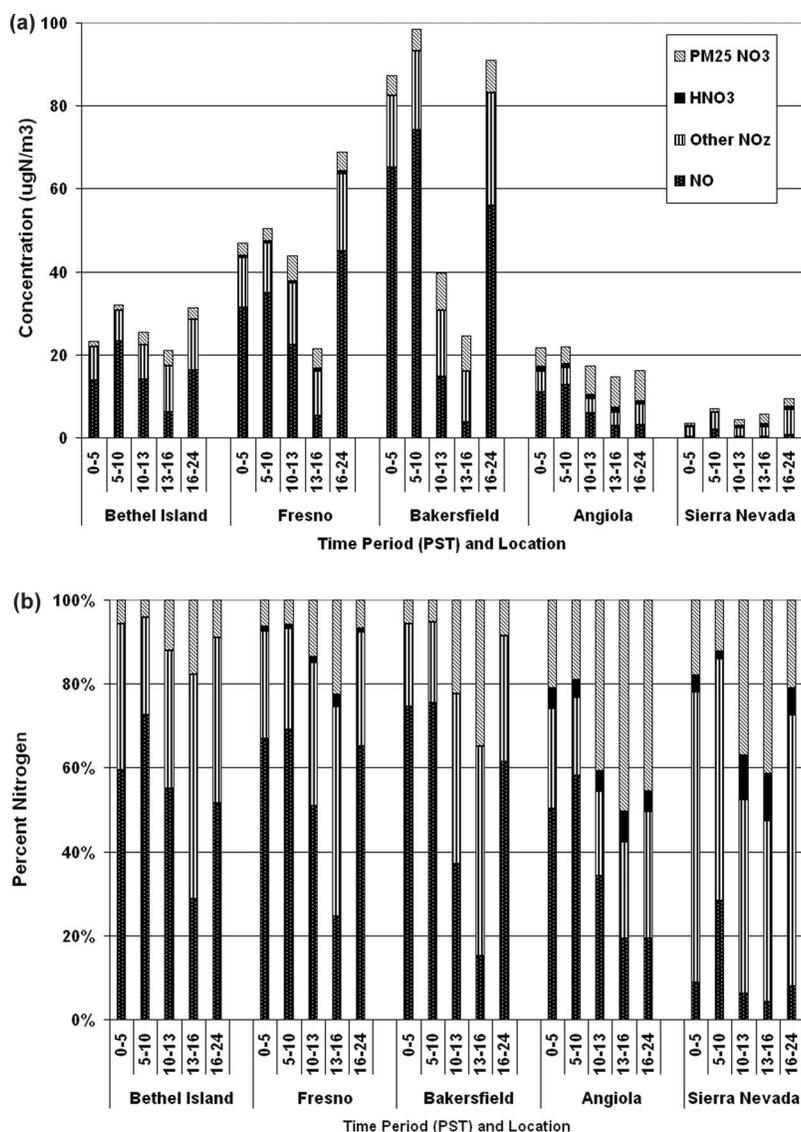


Figure 2. The 15-day average concentrations (a) and relative distributions (b) of NO_x -related compounds by sampling period at the five core CRPAQS air monitoring sites in winter. HNO_3 was not measured at Bethel Island and Bakersfield.

a less reactive and less oxidized mixture. The aromatic hydrocarbons and heavier alkenes are the likely precursors to organic aerosol formation.¹⁹ As Table 1 indicates, the average portion of total carbon in the aerosol phase was 7%, 7%, 6%, and 10% at Sierra Nevada Foothills, Angiola, Bethel Island, and Fresno, respectively. The aerosol carbon was 75–81% OC and 19–25% EC. Comparison of organic aerosol carbon to the approximate pool of organic aerosol precursors (assumed here for illustrative purposes to include the aromatics, half of the alkenes, and half of the unidentified HCs) suggests that there was approximately four times more gaseous precursor carbon than aerosol carbon at Fresno. Although the aerosol yield from these precursor species may only be 10–25% on a carbon basis, the data suggest that a significant reservoir of organic aerosol precursors exists in the winter air.

The diurnal variation in the phase-partitioning of total carbon, shown in Figure 3, indicates that total carbon concentrations were higher in the morning and evening than at midday at three sites. Total carbon at

Angiola peaked midday, presumably because of transport from the source areas. The aerosol fraction of total carbon was small in all of the sampling periods.

The principal implication of the observed phase distributions of nitrogen, sulfur, and carbon is that a large reservoir of gaseous precursors is available for conversion to aerosol-phase species in most parts of the SJV. Although photo-oxidation rates of NO_x and VOCs are slower in winter than in summer, the stagnant meteorological conditions extend pollutant residence times, which results in significant secondary aerosol production in winter.

Secondary Organic Aerosol Formation

As in many parts of the United States, carbonaceous material makes up a substantial portion of the $\text{PM}_{2.5}$ in the SJV. Assuming the mass of organic material (OM) is 1.4 times the carbon, which is probably a lower limit,²⁰ the carbonaceous aerosol (OM+EC) was 20–51% of the $\text{PM}_{2.5}$ mass, on average, during the 15 CRPAQS winter IOP days

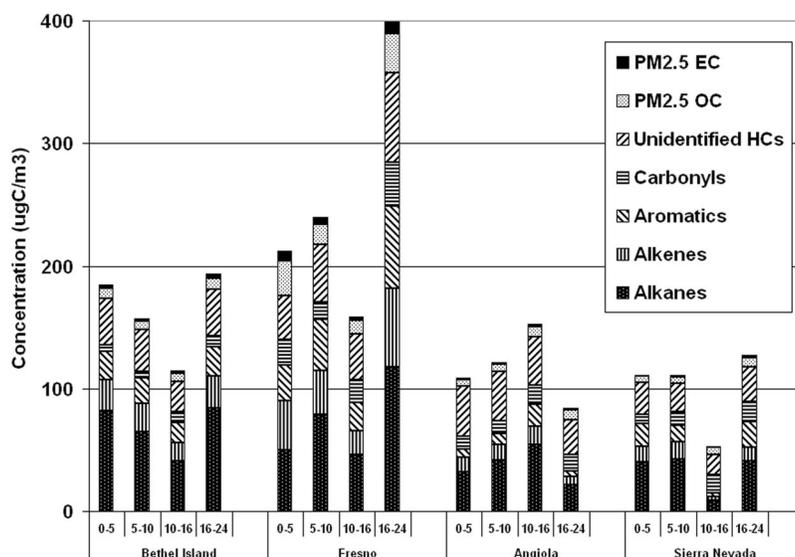


Figure 3. The 15-day average distribution of carbonaceous compounds by sampling period at four core CRPAQS air monitoring sites in winter.

(see Figure 4). The carbonaceous aerosol is either emitted directly in particulate form as primary emissions or is produced as a secondary product from VOC oxidation, primarily from aromatics, isoprene, monoterpenes, and sesquiterpenes.^{19,21,22} Soot measured as EC is believed to be entirely primary. Routine OC measurements do not distinguish the primary and secondary components of OC. Even detailed GC/mass spectrometry laboratory molecular analyses of organic species in PM cannot reliably differentiate all of the primary and secondary organic compounds. Although primary emissions can be measured and estimated in emission inventories, determining the extent of secondary OC (SOC) in PM_{2.5} is much more difficult and relies on estimation techniques. Environmental chamber experiments, molecular chemical analyses, kinetic and mechanistic studies of the chemical reactions, and detailed modeling have been conducted to improve the understanding of the SOC formation and its contribution to PM_{2.5}.^{7,19,23-39} These studies show that SOC can be between 15% and 60% of the total OC,

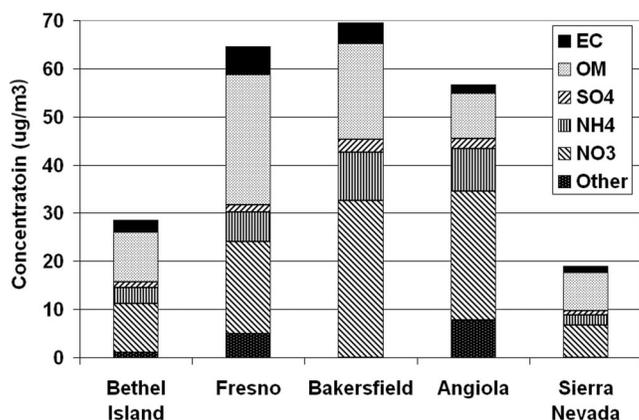


Figure 4. The 15-day average distribution of PM_{2.5} chemical components at the five core CRPAQS air monitoring sites in winter. Other PM is calculated from PM mass minus EC, OM, SO₄, NH₄, and NO₃, rather than measured, and is zero in Sierra Nevada Foothills and -1.6 μg/m³ in Bakersfield (data not shown).

demonstrating the importance of the SOC contribution to total OC and, therefore, PM_{2.5}. The studies suggest that SOC formation processes are complex and that even the most detailed models have substantial uncertainties.

Instead of detailed modeling or molecular chemical analysis, the ratio of OC to EC can be used to estimate the amount of SOC in a given sample,^{7,20,34,36,38,40} because carbonaceous aerosol emissions generally include both OC and EC. If an OC/EC ratio that is both characteristic of primary emissions and relatively constant within the period of interest can be determined, then additional OC that drives the ambient ratio above this base level can be assumed to be secondary. The amount of SOC can, therefore, be estimated as:

$$SOC_i = OC_i - EC_i \left[\frac{OC}{EC} \right]_{\text{Primary}} \quad (1)$$

This simple method can conveniently and inexpensively be applied to large numbers of samples.

To obtain the primary OC/EC ratio, we relied on measured ambient concentration data rather than emission inventory estimates. Ambient concentration ratios from four of the five SJV sites with detailed PM measurements were used to establish a consistent lower bound relationship between OC and EC. OC and EC concentrations are compared in Figure 5 for subdaily samples at Bethel Island, Bakersfield, Fresno, and Angiola when the OC/EC ratio was <3.5. Ratios from the fifth site, Sierra Nevada Foothills, were excluded because the remote downwind location of the site made it less suitable for determining primary OC/EC ratios and, in fact, very few samples collected at the site met the OC/EC <3.5 criterion. The cutoff of 3.5 is likely an upper limit of the ratio for samples dominated by primary emissions and is higher than the primary ratios estimated for older data.^{7,20,36-38,41,42} The high degree of correlation data ($r^2 = 0.93$) between OC and EC in CRPAQS data with OC/EC <3.5 indicates that this threshold is sufficient to obtain a

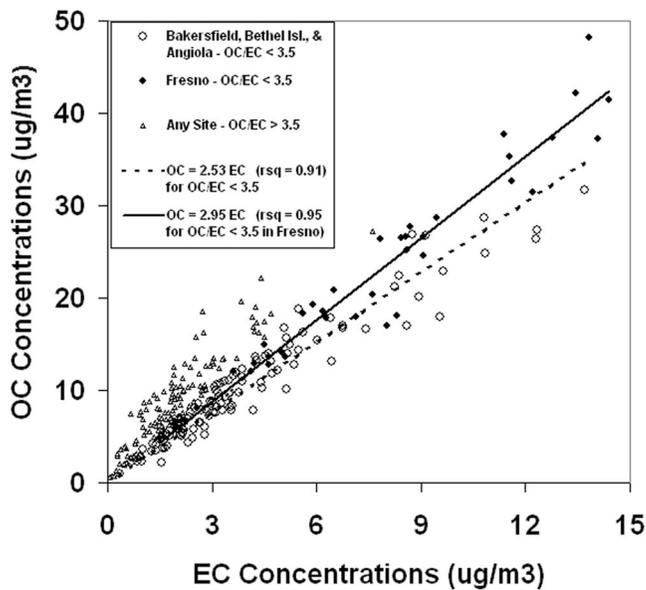


Figure 5. Comparison of PM_{2.5} OC and EC concentrations for a subset of samples where the ratio of OC to EC was <3.5. The measurements include samples collected during various sampling periods at four core CRPAQS air monitoring sites on 15 days in winter.

consistent baseline relationship between OC and EC. The relationships were examined by site and as a group. A linear regression of the grouped data from the four sites indicates a primary OC/EC ratio of 2.74. Regressions for individual site data yield primary OC/EC ratios of 2.47, 2.55, 2.60, and 2.95 for Bethel Island, Bakersfield, Angiola, and Fresno, respectively. The similarity of the apparent primary OC/EC ratios at the first three sites suggested that a combined ratio (OC/EC = 2.53; $r^2 = 0.91$) would be appropriate. Conditions at Fresno clearly show higher OC/EC ratios (2.95; $r^2 = 0.95$) than those at other sites, which can probably be explained by higher amounts of wood smoke emission in Fresno than in other areas.⁴³ If the intercept is not set to zero, the primary ratio is

similar (e.g., 2.92 at Fresno), and the intercept is small (0.2 $\mu\text{gC}/\text{m}^3$). It has been hypothesized that the intercept is indicative of noncombustion and/or background OC and may need to be included in the calculation of SOC in some environments.^{37,42} The small intercept in this analysis is consistent with the conceptual model of SJV PM⁴³ and is not used in this analysis. For the Sierra Nevada Foothills site, which represents a transport receptor area with low primary PM emission rates, the primary OC/EC ratio (2.74) derived from all of the four other sites was assigned. This average primary OC/EC ratio derived from the 2000/2001 CRPAQS data is noticeably higher than the ratio of 2.40 derived with the same method using the 1995 Integrated Monitoring Study (IMS95) data.⁷

The 15-day average estimated distribution between primary and SOC for each period and site is shown in Figure 6. The 24-hr average SOC concentration was 1.1 $\mu\text{gC}/\text{m}^3$ and 13% of total OC at Bethel Island; 2.6 $\mu\text{gC}/\text{m}^3$ and 16% of OC at Bakersfield; 3 $\mu\text{gC}/\text{m}^3$ and 13% of OC at Fresno; 1.9 $\mu\text{gC}/\text{m}^3$ and 32% of OC at Sierra Nevada Foothills; and 2.2 $\mu\text{gC}/\text{m}^3$ and 33% of OC at Angiola. On a percentage basis, the SOC estimates for Bethel Island and the urban sites (Fresno and Bakersfield) were lower than those for the rural sites (Angiola and Sierra Nevada Foothills), presumably because of the influence of fresh primary emissions in the urban areas. The uncertainty in the percentage SOC estimates is large, but the rural-urban differences are large enough to give the authors confidence that the percentage SOC is indeed larger at rural sites on average. The 15-day average SOC percentages of total OC at the CRPAQS urban sites (13–16%) are similar to the 7-day average of 18% estimated in the IMS95 at Fresno and Bakersfield and the 7-day average of 13% estimated for southwest Chowchilla in the IMS95. In contrast, the 15-day average percentage SOC estimated for Angiola is twice the 15%, 7-day average estimated for the nearby Kern Wildlife Refuge site in the IMS95. In addition, the high average percentage of secondary organics estimated for Sierra Nevada Foothills far exceeds IMS95

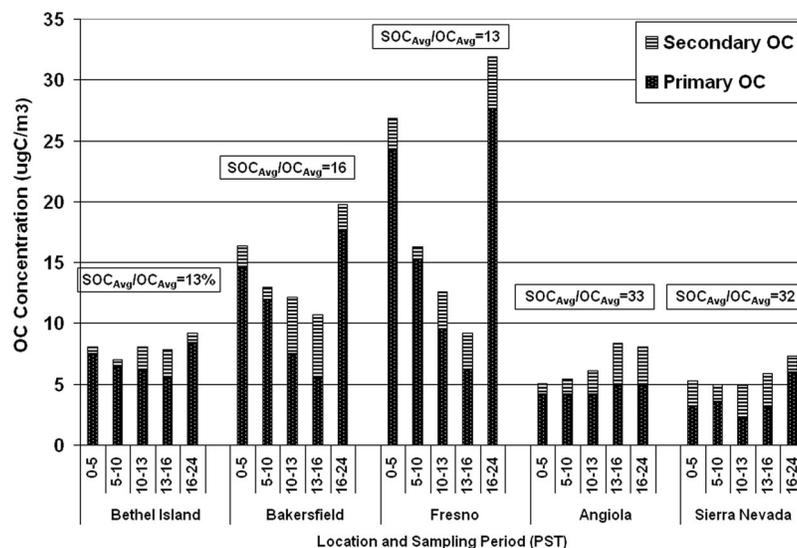


Figure 6. Average measured OC concentrations and estimated distribution of primary and secondary OC by sampling period at the five core CRPAQS air monitoring sites on 15 days in winter.

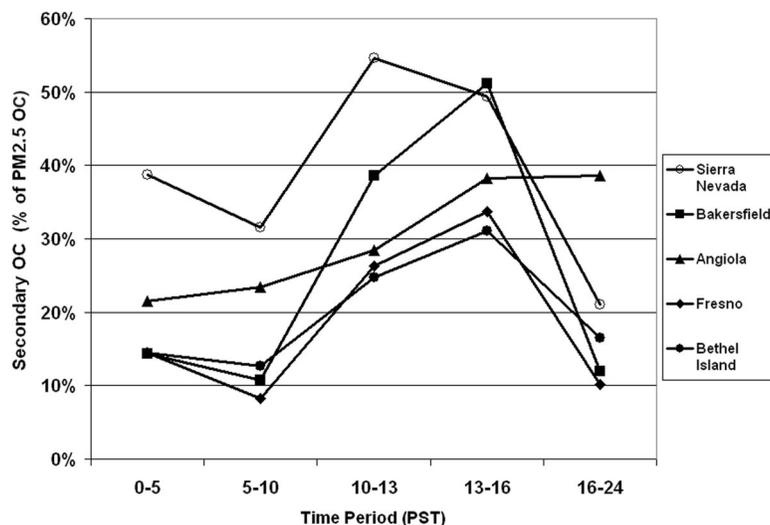


Figure 7. 15-day average estimated secondary percentage of PM_{2.5} OC by sampling period at the five core CRPAQS air monitoring sites in winter.

averages, but there were no comparable elevated foothill sites in the IMS95.

Comparison of SOC estimates to PM_{2.5} mass helps put the contributions in perspective. The 15-day average estimated contribution of secondary organics to PM_{2.5} mass is 5.2%, 5.3%, 5.5%, 5.8%, and 13.8% at Bethel Island, Bakersfield, Fresno, Angiola, and Sierra Nevada Foothills, respectively. The consistency of the contribution of SOC to PM_{2.5} mass in the SJV is notable.

This analysis is fairly insensitive to the cutoff and time of day for the primary OC/EC ratio. Imposing a maximum OC/EC ratio of 4, rather than 3.5, raises the mean primary OC/EC from 2.53 to 2.63 for Bethel Island, Bakersfield, and Angiola and from 2.95 to 3.07 for Fresno and decreases the average SOC percentage of OC by ~2%. Using a lower maximum OC/EC ratio, 3, decreases the mean primary OC/EC from 2.53 to 2.41 for Bethel Island, Bakersfield, and Angiola and from 2.95 to 2.73 for Fresno and increases the average SOC percentage of OC by 3–5%. Likewise, restricting the analysis to samples collected between 5:00 a.m. and 1:00 p.m. with OC/EC ratios <3.5, which minimizes the influence of wood smoke, has no effect on the results for Bethel Island, Bakersfield, and Angiola and decreases the average SOC percentage of OC by ~2% in Fresno.

The day-to-day and period-to-period variability in estimated SOC was relatively high. In Fresno, the estimated daily average SOC ranged from 0 to 9.2 $\mu\text{gC}/\text{m}^3$ and had a coefficient of variation of 0.95. The daily average percentage of SOC in Fresno ranged from 0–32% of total OC and had a coefficient of variation of 0.55. The estimated SOC concentrations in the 3- to 8-hr sampling periods range from 0 at all of the sites to 6.2, 6.7, 11.1, 11.7, and 19.7 $\mu\text{gC}/\text{m}^3$ at Bethel Island, Sierra Nevada Foothills, Bakersfield, Angiola, and Fresno, respectively. These estimates are comparable to the 15–20 $\mu\text{gC}/\text{m}^3$ maximum 3-hr SOC concentrations estimated in the IMS95.⁷ The maximum percentage of SOC in the CRPAQS period data ranged from 69% at Bakersfield to 89% at Sierra Nevada Foothills. The maximum percentage of SOC in the period data was approximately twice as high as that estimated for

similar locations in the IMS95. The very high percentage estimates in some CRPAQS samples may reflect different meteorological conditions, longer episode duration, and possible underestimation of the primary OC/EC ratio (e.g., in samples dominated by wood smoke emissions).

The diurnal patterns in average estimated percentage of SOC are shown in Figure 7. The percentage of SOC reached a maximum in the 10:00 a.m. to 1:00 p.m. period at Sierra Nevada Foothills and in the 1:00 p.m. to 4:00 p.m. period at the four other sites. During peak periods, the estimated 15-day average SOC was 31%, 33%, 38%, 51%, and 54% of total OC at Bethel Island, Fresno, Angiola, Bakersfield, and Sierra Nevada Foothills, respectively. The average diurnal pattern in Fresno, Bakersfield, and Bethel Island showed a slight decline in percentage of SOC from the 12:00–5:00 a.m. period to the 5:00–10:00 a.m. period, followed by higher SOC percentages in the 10:00 a.m. to 1:00 p.m. and 1:00–4:00 p.m. period, and lower SOC percentages in the 4:00 p.m. to 12:00 a.m. period. The percentage of SOC at Sierra Nevada Foothills showed a similar diurnal pattern, except the maximum occurred earlier in the day, in the 10:00 a.m. to 1:00 p.m. period rather than the 1:00–4:00 p.m. period. At Angiola, the percentage of SOC showed a gradual buildup from 12:00–5:00 a.m. to 1:00–4:00 p.m. and then remained high in the late afternoon/evening (4:00 p.m. to 12:00 a.m.). The decrease in the percentage of SOC at four of the five sites at 5:00–10:00 a.m. PST was probably because of higher primary emissions. The rise of SOC during the day is consistent with daytime photochemical production of SOC. Although the percentage of SOC was lower during the nighttime hours, total OC generally rose in the night; and if SOC production was similar to that in the daytime, the percentage of SOC would be expected to decrease. The high percentage of SOC (39%) from 4:00 p.m. to 12:00 a.m. in Angiola and from 12:00–5:00 a.m. at Sierra Nevada Foothills indicated that nighttime production of SOC (via VOC reactions with the NO₃ radical) may have occurred in the rural sites. Another possibility is that this SOC was formed upwind and transported to the sites at nighttime. These diurnal variations are similar to those

observed elsewhere.⁴⁴ Overall, it appears that daytime production of SOC is important in urban areas, and both daytime and nighttime production may be occurring in rural areas. Nighttime condensation of semi-VOCs does not appear to have a large impact during winter episodes in the SJV.

DISCUSSION

Precursor Limitations on Secondary PM Formation

The atmospheric oxidation rates of NO_x , SO_2 , and VOCs are slower in winter than in summer because of limited sunlight and oxidants (O_3 , OH, etc.) in winter. Nonetheless, cool moist winter conditions favor aerosol formation as soon as condensable products are formed from gas-phase reactions.⁴⁵ In addition to sunlight and oxidant limitations, the availability of precursor gases, such as NO_x , SO_2 , NH_3 , and VOCs, or key oxidation products, such as nitric acid, sulfur trioxide, and condensable organic species, may limit secondary PM formation in winter. Knowledge of precursor limitations is critical for the design of effective emission control strategies. The gas-aerosol phase distributions shown in Table 1 indicate that the emitted gaseous precursors, NO_x , SO_2 , and NH_3 , and primarily aromatic hydrocarbons are more abundant than the secondary aerosol species that they form, so the emitted species do not appear to directly limit secondary aerosol formation. The rates of oxidation of emitted species and availability of key oxidation products, such as nitric acid or possibly certain condensable organics, are likely to limit secondary aerosol formation. Ambient measurements are not sufficient to assess the availability of condensable organic species; however, data are available to evaluate whether nitric acid or NH_3 limits ammonium nitrate formation. Ammonium nitrate is the single most abundant compound in most winter $\text{PM}_{2.5}$ samples in the SJV. In designing strategies to reduce ammonium nitrate concentrations, controls that reduce the least abundant precursor involved in its formation are likely to have immediate effectiveness, whereas small or moderate controls on the more abundant precursors may not have any immediate effects. Controls on the more abundant precursors are likely to be effective when the emission reductions are large enough to make it the less abundant precursor.

The thermodynamics of the NH_3 /nitric acid/ammonium nitrate system favor the aerosol phase when temperatures are $<10^\circ\text{C}$.^{46,47} Precursor limitations can be evaluated under conditions where the aerosol phase is favored by comparing the precursor concentrations. Figure 8 shows the ambient concentrations of nitric acid and NH_3 measured in 3- to 8-hr sampling intervals at Angiola, Fresno, and Sierra Nevada Foothills. These concentrations were measured by the denuder difference technique, which has a $\sim 0.2 \mu\text{gN}/\text{m}^3$ limit of detection (LOD) and $\pm 0.5 \mu\text{gN}/\text{m}^3$ uncertainty. A significant number of nitric acid concentrations and a few NH_3 concentrations were below the LOD or negative. At Angiola, where almost half of the nitric acid concentrations were below the LOD, the nitric acid concentrations ranged from -1 to $3 \mu\text{gN}/\text{m}^3$ (excluding one outlier), and the NH_3 concentrations

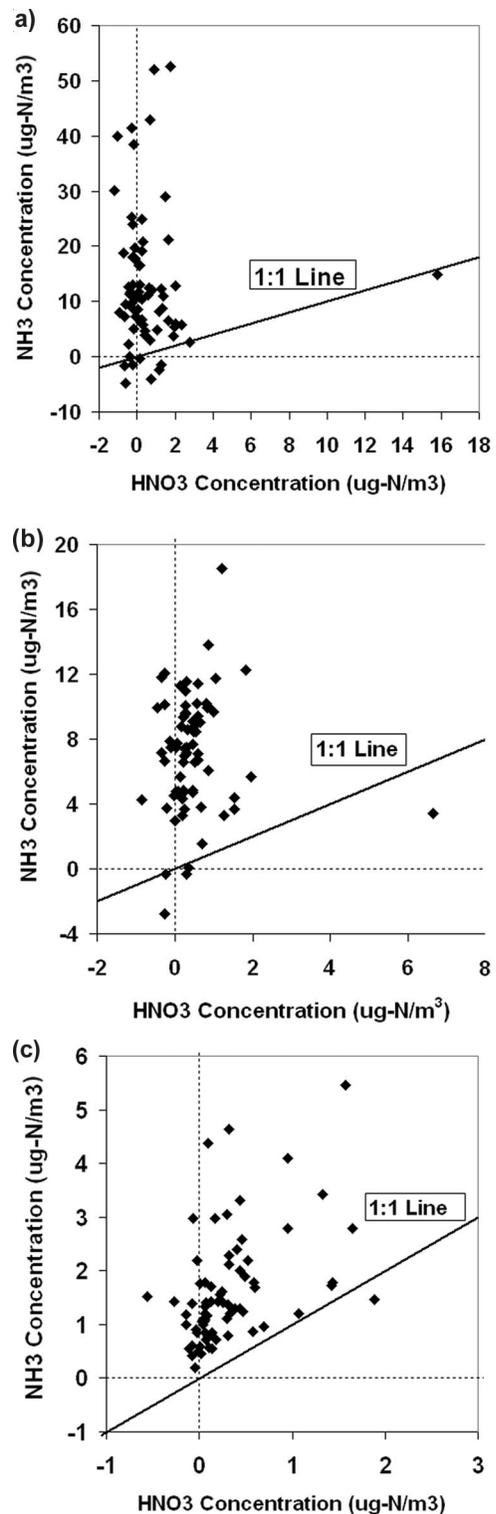


Figure 8. Comparison of NH_3 and nitric acid concentrations from various sampling periods at (a) Angiola, (b) Fresno, and (c) Sierra Nevada Foothills during the CRPAQS winter IOP days. The LOD is $\sim 0.2 \mu\text{gN}/\text{m}^3$ for NH_3 and HNO_3 concentrations.

ranged from -5 to $53 \mu\text{gN}/\text{m}^3$. The high NH_3 concentrations are evidence of strong emissions sources influencing this rural, agricultural site. Although nitric acid levels were low, they slightly exceeded NH_3 in two samples: one with $2.7 \mu\text{gN}/\text{m}^3$ of nitric acid collected at 1:00–4:00 p.m. on February 1, 2001, and another with $16 \mu\text{gN}/\text{m}^3$ of

nitric acid collected at 4:00 p.m. to 12:00 a.m. on January 5, 2001. Conditions at Angiola were rich in NH_3 relative to nitric acid in 35 of 37 samples where both nitric acid and NH_3 concentrations exceeded zero and in 64 of 71 samples where NH_3 concentrations exceeded zero. The preponderance of low nitric acid concentrations irrespective of the NH_3 concentrations indicates that nitric acid is the precursor limiting ammonium nitrate formation in this rural portion of the southern SJV.

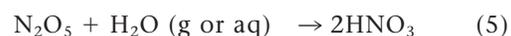
At Fresno, nitric acid concentrations ranged from -1 to $2 \mu\text{gN}/\text{m}^3$, and NH_3 concentrations ranged from -3 to $18 \mu\text{gN}/\text{m}^3$. One sample collected at 1:00–4:00 p.m. PST on February 3, 2001, contained more nitric acid ($6.6 \mu\text{gN}/\text{m}^3$) than NH_3 ($3.4 \mu\text{gN}/\text{m}^3$); however, NH_3 concentrations exceeded nitric acid concentrations in the other 59 of 60 samples where both nitric acid and NH_3 concentrations were positive. NH_3 concentrations at Fresno were approximately half of those at Angiola, yet they were still ~ 1 order of magnitude higher than the nitric acid levels at Fresno; thus, almost all of the data indicate that NH_3 -rich conditions prevail in winter in Fresno.

The concentrations at Sierra Nevada Foothills ranged from -1 to $1.9 \mu\text{gN}/\text{m}^3$ for nitric acid and 0 to $5.4 \mu\text{gN}/\text{m}^3$ for NH_3 . The nitric acid levels were slightly lower than at the other two sites, and the NH_3 levels were much lower than those at Fresno and especially Angiola. Although the data show smaller differences between nitric acid and NH_3 concentrations at Sierra Nevada Foothills than at other sites, the NH_3 concentrations still exceeded the nitric acid concentrations by $>20\%$ in 58 of 60 samples with positive nitric acid concentrations. Conditions are NH_3 rich in all of the samples except ones with 1.1 and $1.9 \mu\text{gN}/\text{m}^3$ collected at 1:00–4:00 p.m. and 4:00 p.m. to 12:00 a.m. on January 31, 2001, where comparable nitric acid and NH_3 levels were observed.

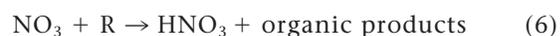
The prevalence of ambient NH_3 concentrations in excess of ambient nitric acid concentrations at these three sites is consistent with findings from the IMS95 (where $>90\%$ of samples were NH_3 rich)^{6,48} and from regional modeling studies.⁴⁹ The CRPAQS data show an eightfold gradient in NH_3 concentration and a twofold gradient in nitric acid concentration between the middle of the SJV, represented by Angiola, and the foothills, represented by Sierra Nevada Foothills. Despite the imprecision of the denuder difference measurement data, the consistent excess of NH_3 over nitric acid levels indisputably shows that secondary ammonium nitrate formation is more limited by nitric acid availability than NH_3 within the SJV and in the foothills. The NO_x -related species distributions described above illustrate the scarcity of nitric acid compared with other gaseous NO_y and $\text{PM}_{2.5}$ nitrate aerosol and the relative abundance of NH_3 compared with $\text{PM}_{2.5}$ ammonium aerosol. These distributions indicate that small or moderate reductions in NH_3 emissions will have little or no effect on ammonium nitrate levels because there is so much excess NH_3 . The results indicate that ammonium nitrate formation is controlled by the formation of nitric acid and, therefore, ultimately controlled by NO_x and VOC emission rates and background O_3 concentrations that control the rate of NO_x oxidation. This analysis is not able to assess the relative benefits of controlling NO_x or VOC emissions for reducing nitric acid levels.

Nitric Acid Formation Pathways

Nitric acid is formed in the daytime primarily from oxidation of NO_2 by the hydroxyl radical (OH) and at night from NO_2 oxidation by O_3 forming the NO_3 radical, which reacts with NO_2 to form N_2O_5 , which, in turn, may react homogeneously or heterogeneously with water to form nitric acid.⁵⁰

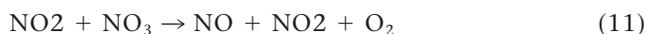
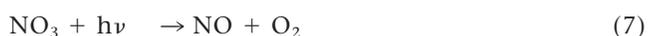


Various organic compounds (R), including aldehydes, alkenes, cresols, phenols, and monoterpenes, react with the NO_3 radical to form nitric acid.



A portion of the organic products formed by NO_3 oxidation of heavier organic compounds (C_6+) are condensable and form secondary organic aerosol.

A number of competing reactions may impede nitric acid formation via the NO_3 pathway, including the photolysis of NO_3 , which destroys NO_3 very quickly in the daylight; the rapid destruction of NO_3 by NO , which inhibits nighttime nitric acid formation in areas with fresh combustion emissions; the thermal decomposition of N_2O_5 forming NO_3 with NO_2 , which may, in turn, react to form NO and NO_2 ; and the reaction of NO_3 with organic compounds to form NO_2 or organic nitrate, rather than nitric acid.



The diurnal pattern of aerosol nitrate concentrations in the SJV suggests that daytime nitric acid formation occurred in the region. The peaks in O_3 concentrations, the key indicator of photochemical activity, typically occurred from 12:00–4:00 p.m. at most SJV sites in winter. The average $\text{PM}_{2.5}$ nitrate levels on CRPAQS IOP days, shown in Figure 9, indicate that ambient nitrate concentrations were highest midday (10:00 a.m. to 1:00 p.m.) at

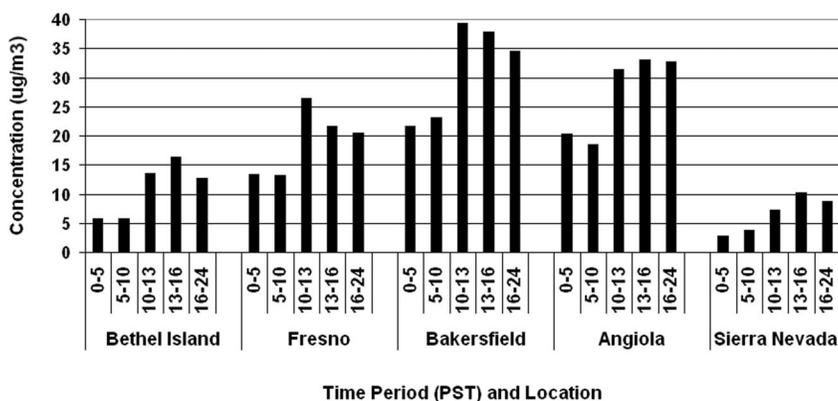


Figure 9. 15-day average PM_{2.5} nitrate concentrations by sampling period at the five core CRPAQS air monitoring sites in winter.

Fresno and Bakersfield and in the afternoon (1:00–4:00 p.m.) at Angiolo, Sierra Nevada Foothills, and Bethel Island. The general coincidence of O₃ and aerosol nitrate peaks suggests a common photochemical process; however, the strength of the daytime nitric acid and aerosol nitrate production mechanism may be limited. If the daytime mechanism was strong and temperatures cool enough to favor the aerosol phase (as they are on most winter days), we might expect continually increasing nitrate aerosol levels for several hours after the O₃ peak. Comparison of the 10:00 a.m. to 1:00 p.m. and 1:00–4:00 p.m. levels suggests that production in the 1:00–4:00 p.m. period was too slow to offset the effects of dilution in urban areas and was barely fast enough to offset dilution in more rural locations. The average diurnal pattern of nitrate at Sierra Nevada Foothills is one that could be expected from photochemical activity, yet the afternoon nitrate peak at this site is more likely because of transport of pollution from the SJV than photochemistry. The average diurnal pattern for the three core sites in the SJV (Fresno, Bakersfield, and Angiolo) suggests that the daytime nitric acid production is relatively slow.

Watson and Chow⁴³ analyzed a January 2000 PM_{2.5} episode in Fresno and found that aerosol nitrate concentrations increased rapidly in the morning. Using data from continuous NO₃, NO, O₃, and black carbon (BC) analyzers, they found that the rapid rise in aerosol NO₃ concentrations coincided with rapid growth of the mixed layer, suggesting that the rapid rise was because of entrainment of aerosol NO₃ from aloft layers, as well as photochemical formation in the surface layer. Continuous aerosol NO₃ concentrations observed in Fresno during the December 28–31, 2000, and February 2–3, 2001, IOPs shown in Figure 10 indicate that aerosol NO₃ concentration increases of 10–20 μg/m³ in 2–3 hr are common between 8:00 a.m. and 12:00 p.m. The rapid increase in aerosol NO₃ coincides with rapid decreases in NO and BC concentrations and increases in O₃ concentrations. The nitrate aloft could be because of carryover of nitrate formed from daytime photochemical reactions on the previous day or nighttime reactions of NO₂ and O₃ isolated from the surface in the aloft layers.

Although direct measurements of the NO₃ radical and N₂O₅ were not made in the CRPAQS, continuous PM_{2.5} NO₃ aerosol measurements were made at a number of locations including the 90-m tower at rural Angiolo.

Continuous NO/NO_y and O₃ measurements were made along with the continuous aerosol NO₃ measurements for 7 weeks in winter on the 90-m tower. Figure 11 shows the NO, O₃, and aerosol NO₃ concentrations for the late December and early February episodes. During the night, O₃ and NO_y (not shown) concentrations ranged from 20 to 50 ppb atop the tower, whereas NO concentrations were usually <1 ppb aloft. The measurements show a pattern in which O₃ decreased at night, whereas aerosol NO₃ increased and NO remained very low. During the night, the aerosol NO₃ concentrations aloft increased by 8–10 μg/m³ during the December 27–31, 2000, episode and by 3–6 μg/m³ in the February 1–3, 2001, episode. Hourly nitrate concentrations aloft reached a maximum of 20 μg/m³ at 6:00 a.m. on December 30, 2000. The aerosol NO₃ concentrations aloft increased on all eight nights from 6:00 p.m. to 12:00 a.m. and then increased or decreased between midnight and sunrise. Fresh emissions impacting the 90-m tower were evident only early on the morning of February 1, 2001, when NO concentrations increased to 25 ppb, and O₃ concentrations decreased to near zero. Aerosol nitrate levels decreased slightly during the nighttime period with elevated NO levels. The prevailing nighttime conditions aloft at Angiolo are conducive to nitric acid formation via the nighttime mechanism. The persistent increases in aerosol NO₃ aloft suggest that the nighttime mechanism forms nitric acid that is quickly converted to ammonium nitrate in the cool NH₃-rich conditions. Conditions for these two episodes were not particularly unusual for winter; the average nighttime NO, NO_y, and O₃ concentrations at 90-m were 1.8, 23, and 28 ppb, respectively, for the entire 7-week monitoring period on the Angiolo tower.

Evidence of nighttime aerosol nitrate formation at the surface in Angiolo was lacking. The continuous aerosol nitrate concentrations at the surface were erratic and did not show the persistent increasing trends that were evident in the data from the 90-m elevation.⁵¹ The apparent lack of nitrate formation at night at the surface is consistent with the near-zero O₃ levels and higher NO levels near the surface than aloft, and a number of studies that indicate NO₃ and N₂O₅ levels decline dramatically near the surface.^{45,52–58}

Meteorological transport of air containing differing amounts of nitrate undoubtedly contributes to the variations in nitrate concentrations; however, winds measured

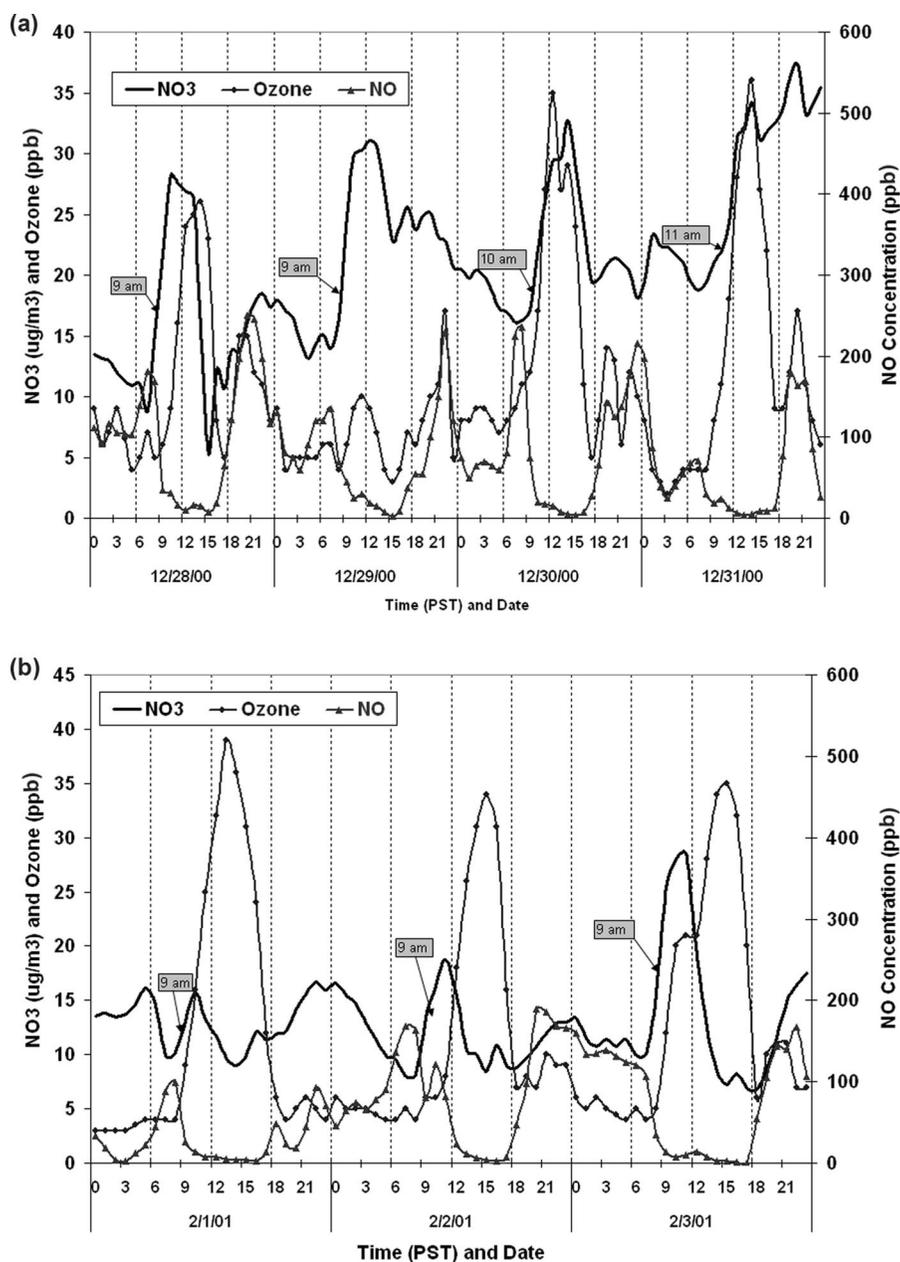


Figure 10. Hourly concentrations of NO, O₃, and PM_{2.5} NO₃ at Fresno on (a) December 28–31, 2000, and (b) February 1–3, 2001.

at 90 m during the December episode were light and variable, mostly <2 m/sec. If meteorological transport was primarily responsible for the nighttime variations in aerosol nitrate aloft, one might expect O₃, NO_y, and aerosol NO₃ concentrations to increase (or decrease) consistently as more (or less) polluted urban air is transported to this rural location. Instead, O₃ consistently decreased, whereas nitrate increased. Transport appears to influence the patterns of concentrations more strongly after midnight than before, because patterns are more erratic after midnight. The rate of nitric acid formation is expected to decrease overnight as the O₃ and NO₂ are depleted, which may partially account for less consistent patterns after midnight. Also, the decreases in O₃ concentration from sunset to sunrise on some nights were larger than can be explained by the amounts of aerosol that NO₃ formed. In a closed inorganic system without fresh NO injections,

~4 ppb of O₃ would be consumed in forming 10 μg/m³ of aerosol NO₃. Nocturnal O₃ decreases >10 ppb are common and suggest that transport and/or additional O₃ destruction reactions are occurring (e.g., O₃ monoterpene reactions).

The significance of nighttime nitric acid production aloft is that it may explain the regional nature of ammonium nitrate in the SJV. As Watson and Chow⁴³ and Pun and Seigneur⁵⁹ have noted, valleywide nighttime production of ammonium nitrate aloft followed by daytime entrainment into the surface layer could explain the spatial homogeneity of wintertime ammonium nitrate levels in the SJV. Conversely, MacDonald et al.¹⁵ have shown that meteorological transport and dispersion are too slow in wintertime SJV PM episodes to explain the observed homogeneity of aerosol NO₃. The CRPAQS data examined here tend to support the valleywide nighttime production

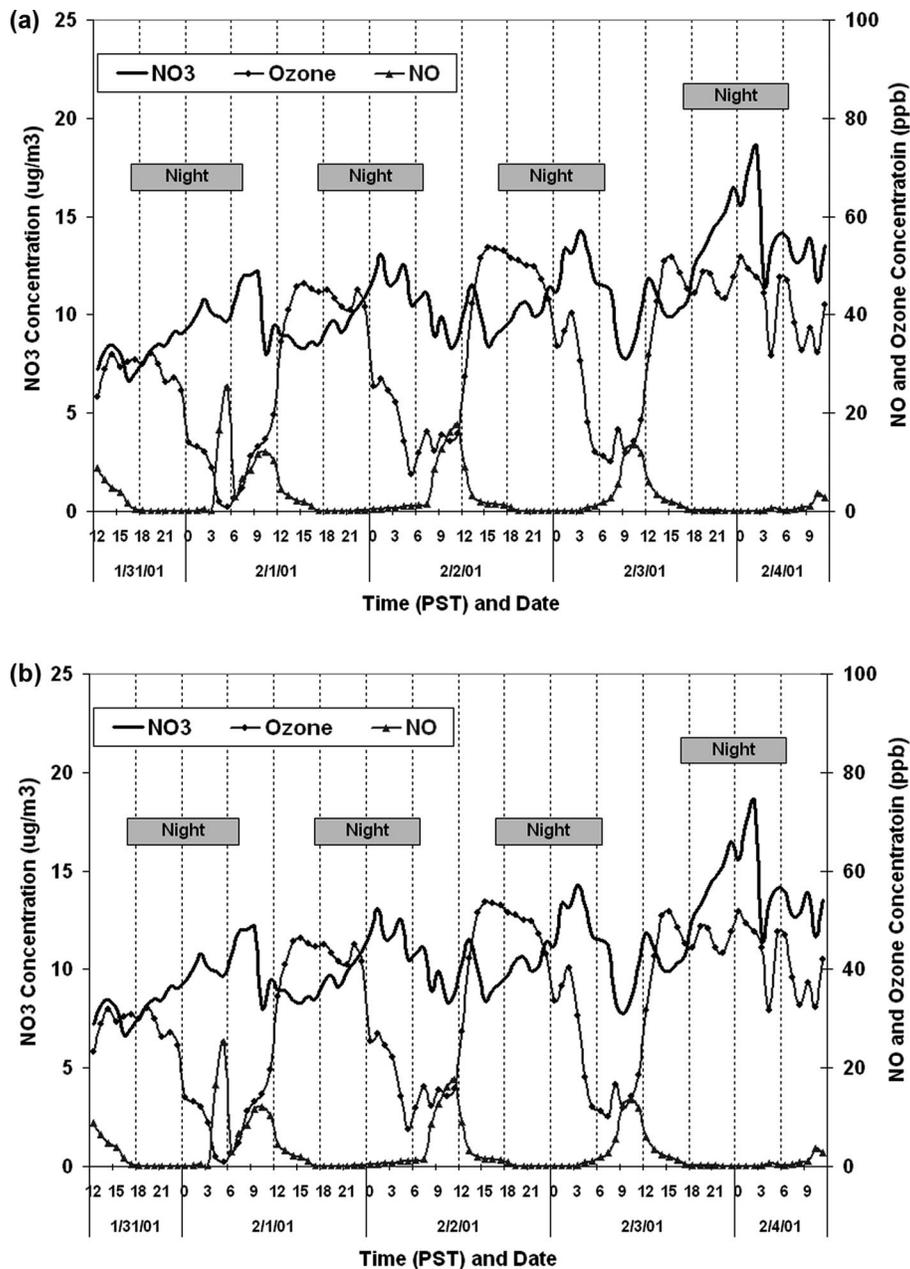


Figure 11. Hourly concentrations of NO, O₃, and PM_{2.5} nitrate at 90-m on the Angiola tower on (a) December 28–31, 2000, and (b) February 1–3, 2001.

aloft hypothesis. The diurnal patterns of concentrations suggest that nighttime nitrate production occurs in addition to daytime production in the winter episodes. Nighttime production aloft occurs in the rural areas like Angiola and, most likely, in urban areas like Fresno. Although NO₂ concentrations are lower in rural areas than in urban areas, nighttime chemical production is likely to be more efficient in the rural areas than in urban areas (because of higher O₃ and lower NO levels), which probably enhances the regional homogeneity of aerosol NO₃.

CONCLUSIONS

Analyses of air quality measurements from the CRPAQS show that there are large amounts of secondary aerosol in

the SJV in winter, especially ammonium nitrate. Comparisons of NH₃ and nitric acid concentrations show that NH₃ is far more abundant than nitric acid, which indicates that ammonium nitrate formation is limited by the availability of nitric acid, rather than NH₃. Examination of the phase-partitioning of NO_x-related nitrogen species and carbonaceous species shows that concentrations of gaseous precursor species are far more abundant than measured aerosol nitrate or estimated secondary organic aerosols. The results indicate that ammonium nitrate formation is ultimately controlled by NO_x and VOC emission rates and background O₃ levels, which control the rate of NO_x oxidation in winter, rather than by NH₃ emissions.

Estimated secondary organic aerosol concentrations are small compared with concentrations of likely VOC precursors; however, the estimated secondary portion of PM_{2.5} OC and PM_{2.5} mass is significant in several locations. For example, the SOC is estimated on average in winter to be 16% and 32% of PM_{2.5} OC mass at Bakersfield and Sierra Nevada Foothills, respectively. As a percentage of PM_{2.5} mass, the estimated secondary organic aerosol is 5.3% and 13.8% at Bakersfield and Sierra Nevada Foothills, respectively. Secondary organic aerosols average 5–6% of PM_{2.5} mass at Fresno, Angiola, and Bethel Island. These estimates show large day-to-day variations and carry substantial uncertainties, because the secondary components were not measured separately from the primary OC components, the SOC estimation technique used here is simplistic, and detailed understanding of the chemical reactions leading to secondary organic aerosols is not well understood. Furthermore, measurements of condensable organic species are not readily available. Despite these limitations, there is evidence of a significant reservoir of organic aerosol precursors in the winter, especially in the urban areas, and there is no evidence in the patterns of OC and estimated SOC that contradicts the expectation that organic aerosol precursor emission rates and rate of atmospheric oxidation are the controlling factors. NO_x emission rates will likely influence the rate of secondary organic aerosol formation, but uncertainties in the chemistry limit quantitative assessment of these effects.

Continuous aerosol nitrate data, in conjunction with NO and O₃ data, suggest that both daytime and nighttime nitric acid formation pathways are active in the SJV. Observations at 90-m above the surface in rural Angiola indicate that ≤10 μg/m³ of aerosol nitrate can be produced aloft in 6–12 hr at night. Increases in aerosol nitrate aloft, especially from sunset to midnight, are fairly common in December and January. Surface measurements at Fresno show rapid increases in aerosol nitrate during the late morning that coincide with rapid decreases in NO and increases in O₃, suggesting that aerosol nitrate is being entrained from aloft as the mixing height increases in the morning. Valleywide nighttime production of ammonium nitrate aloft followed by daytime entrainment into the surface layer is the likely process that explains the unusually high spatial homogeneity of wintertime ammonium nitrate levels in the SJV.

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