

COMPARISON OF PM_{2.5} CHEMICAL COMPOSITION FROM THE FRESNO SUPERSITE DURING WINTERTIME POLLUTION EPISODES IN CENTRAL CALIFORNIA

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ABSTRACT

Five PM_{2.5} samples per day were taken at two urban sites (Fresno and Bakersfield) and one rural (Angiola), one foothill (Sierra Nevada Foothills), and one boundary (Bethel Island) site for 15 days during five episodes in California's San Joaquin Valley from 12/10/2000 to 2/8/2001. These were chemically characterized for mass, elements, ions, and carbon fractions. Urban sites showed large carbon concentrations relative to the non-urban and boundary sites. The elevated foothill location showed lower concentrations than at the other sites, except for cases when the valley-wide layer deepened. Ammonium nitrate concentrations were higher at the rural Angiola site than at the urban Fresno supersite on some occasions. Temporal and spatial variations were explainable in terms of a shallow surface layer forming at night that coupled with the valley-wide layer during the afternoon. Continuous nitrate measurements atop a tall tower at the Angiola site showed substantial nitrate aloft with low NO levels, indicating potential for nighttime formation of nitric acid, which combines with ammonia to create ammonium nitrate. Continuous nitrate measurements at the Fresno supersite showed a sharp increase in nitrate concentrations between 1000 and 1200 PST, when solar-induced vertical mixing commences. Continuous carbon measurements at the Fresno supersite confirmed the morning traffic peak. Carbon also rose throughout the evening at Fresno, consistent with contributions from home heating on cold winter nights.

INTRODUCTION

Elevated PM_{2.5} and PM₁₀ concentrations in California's San Joaquin Valley (SJV) often occur between mid-November and mid-February, when several source contributions are superimposed on each other [1-4]. Episodes showing a peak PM_{2.5} concentration greater than 100 µg/m³ are common in this region. Secondary ammonium nitrate (NH₄NO₃) is the largest component during these episodes. Gaseous nitric acid (HNO₃) concentrations constitute only 10–20% of total nitrate (NO₃⁻) during winter, owing to an abundance of ammonia (NH₃) and low temperatures that favor the particle phase [5]. Organic and elemental carbon (OC, EC) are the next-largest components, but their contributions decrease substantively from urban to rural areas. Ammonium sulfate ((NH₄)₂SO₄) and suspended dust account for the rest of PM_{2.5}, which is typically less than 10% of PM_{2.5} mass.

Previous studies [6, 7] reveal that PM_{2.5} NH₄NO₃ levels are similar at widely separated

monitoring sites throughout the SJV region. The uniformity of NH_4NO_3 concentration over distances of several hundred kilometers, and the separation of large NH_3 emitters in non-urban areas from reactive nitrogen oxide (NO_x) emissions in distant urban areas, are explainable in terms of two hypothesis: 1) secondary NH_4NO_3 is largely formed at the middle or top of a valley atmospheric surface layer (ASL) where precursors are brought in by vertical mixing, and 2) substantial horizontal mixing transport occurs above a shallow surface inversion within the 64,000 km^2 air basin. In contrast, OC and EC are mostly primary aerosol, and their highest concentrations appear near sources, such as motor vehicle and wood combustion emissions that are near the urban centers. ASL vertical mixing would have the opposite effect on the surface NH_4NO_3 and carbonaceous aerosol concentrations; i.e., lowering carbon while increasing NO_3^- levels. This should also lead to a diurnal variation of NH_4NO_3 that differs from OC or EC.

High time-resolved measurements of speciated $\text{PM}_{2.5}$ were carried out at five sites representing urban, rural, and background environments in the SJV. These data are complemented by continuous gas measurements of NO_x and carbon monoxide (CO). A 100 m sampling tower was built at the rural Angiola site for direct upper-layer measurements. Findings from this study are presented in this paper and discussed based on emission, chemistry, and atmospheric dispersion.

EXPERIMENTS

Two urban sites are located at Fresno (FSF) and Bakersfield (BAC), which are the two major cities at the center and south of the SJV, respectively. The Fresno site is part of the United States Environment Protection Agency (EPA) Supersite program [8]. Its immediate environment includes a four-lane artery with moderate traffic levels. The Bakersfield site is on top of a one-story commercial office building within a shopping center in a mixed commercial and residential neighborhood.

The rural site, Angiola (ANG), is between Fresno and Bakersfield and away from any significant mobile or stationary sources. The Bethel Island site (BTI) is at the western boundary of the SJV. This site is also considered rural, but the highly populated San Francisco Bay area is only ~100 km to the west. The Sierra Nevada Foothills site (SNFH) represents the regional background. It is relatively elevated (~600 m mean sea level [MSL]) at the eastern boundary of SJV. Figure 1 illustrates the locations of the five sites.



Figure 1. Five sampling sites in central California during the California Regional Particulate Air Quality Study (CRPAQS).

Maximum 24-hr average PM_{2.5} mass concentrations exceeded 100 µg/m³ during three out of the five winter episodes at the Fresno supersite between 12/10/2000 and 2/8/2001. Four intensive operating periods (IOPs) contained more detailed measurements within longer pollution buildup periods: IOP_1: 12/15/00–12/18/00; IOP_2: 12/26/00–12/28/00; IOP_3: 1/4/01–1/7/01; and IOP_4: 1/31/01–2/3/01. During each IOP, five time-integrated PM_{2.5} samples were collected per day (0-5, 5-10, 10-13, 13-16, 16-24 LST) at each site and analyzed for elements, ions, OC, and EC. Continuous black carbon (BC) measurements were made at FSF using single-wavelength and seven-color aethelometers. BC is light-absorbing carbon, usually comparable to EC, and is a marker for carbon from fossil/bio-fuel combustion. Continuous NO₃⁻ and NO_x measurements were also made at the top of a 100 m tower at Angiola. The contrast between the surface and 100 m Angiola measurements reveals the vertical distribution of pollutants.

RESULTS AND DISCUSSION

The daily averaged NO₃⁻, EC, and OC concentrations during the four IOPs are shown in Figure 2(a)-(c). The highest NO₃⁻ concentration usually occurred at the Bakersfield site. Bakersfield and Angiola are the two most southern sites in this study. The elevated NO₃⁻

levels at the two sites are comparable to those found in the greater Los Angeles area. The NO₃⁻ level decreased towards the northern valley at a steep gradient. Bethel Island measured approximately one-third of the NO₃⁻ concentration of Bakersfield or Angiola. NO₃⁻ at Bethel Island usually peaked 1–2 days after that of Bakersfield; this was especially apparent in IOP_1 and IOP_3, which captured the maximum NO₃⁻ concentration at Bakersfield.

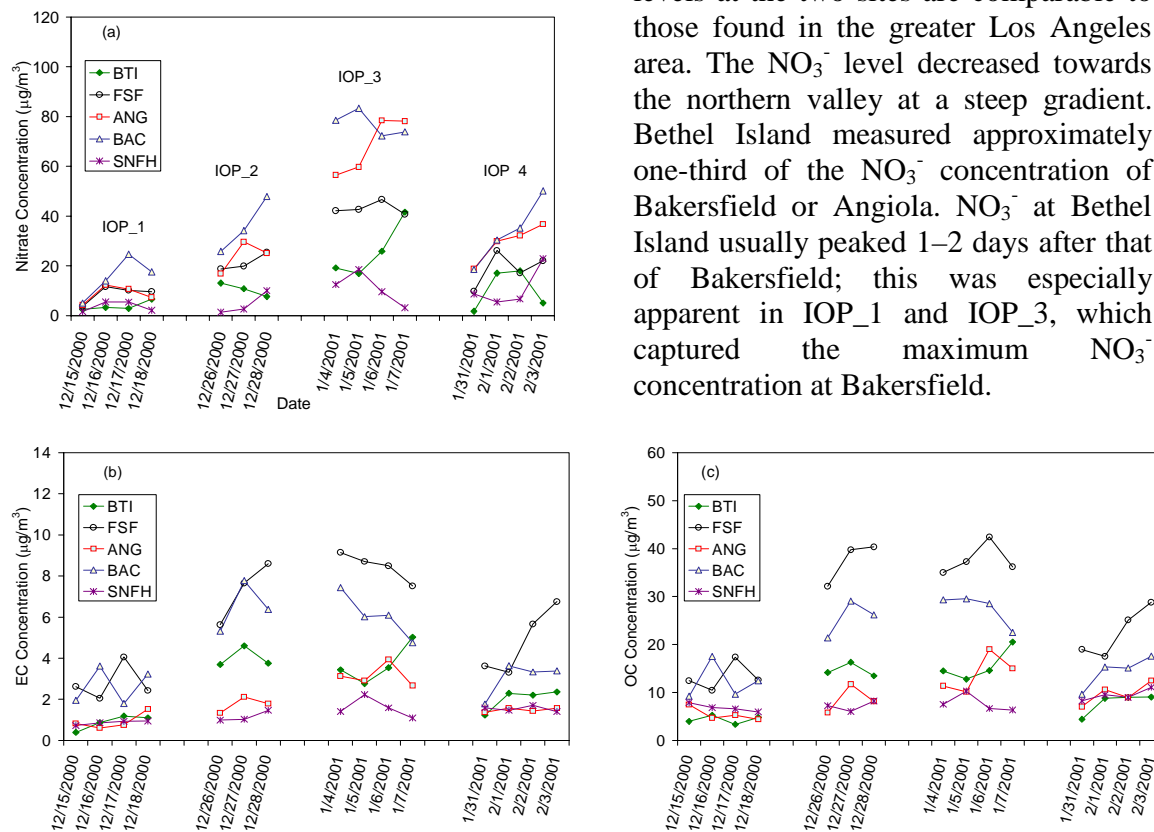


Figure 2. 24-hr PM_{2.5} (a) nitrate (NO₃⁻); (b) elemental carbon (EC); and (c) organic carbon (OC) at Bethel Island (BTI), Fresno (FSF), Angiola (ANG), Bakersfield (BAC), and Sierra Nevada Foothills (SNFH) during four intensive operating periods (IOPs).

The Sierra Nevada Foothills site was occasionally influenced by urban plumes (e.g., the elevated NO_3^- concentration toward the end of IOP_4). Generally, Sierra Nevada Foothills showed lower NO_3^- concentrations than FSF despite being equally distant from BAC.

For EC, the highest concentrations appeared at the two urban centers (FSF and BAC), and the lowest concentrations appeared at the rural/background sites (ANG and SNFH). The major sources of EC are motor vehicle emission and residential wood combustion during the winter. Occasionally, elevated EC levels occurred at the Bethel Island site, likely owing to its population and traffic. The spatial pattern of OC was similar to EC. At Fresno, Bakersfield, and Bethel Island, OC was correlated with EC (r^2 of 0.92–0.95) across the four IOPs, suggesting co-located sources for OC and EC. At the Angiola and Sierra Nevada Foothills sites, this correlation dropped to 0.68 and 0.42, respectively. OC or EC from more distant origins had stronger impacts on these rural sites.

Figure 3 shows the diurnal variation of NO_3^- and OC during IOP_3. During IOP_3, NO_3^- and OC contributed equally to the $\text{PM}_{2.5}$ mass at Fresno. Both NO_3^- and OC showed

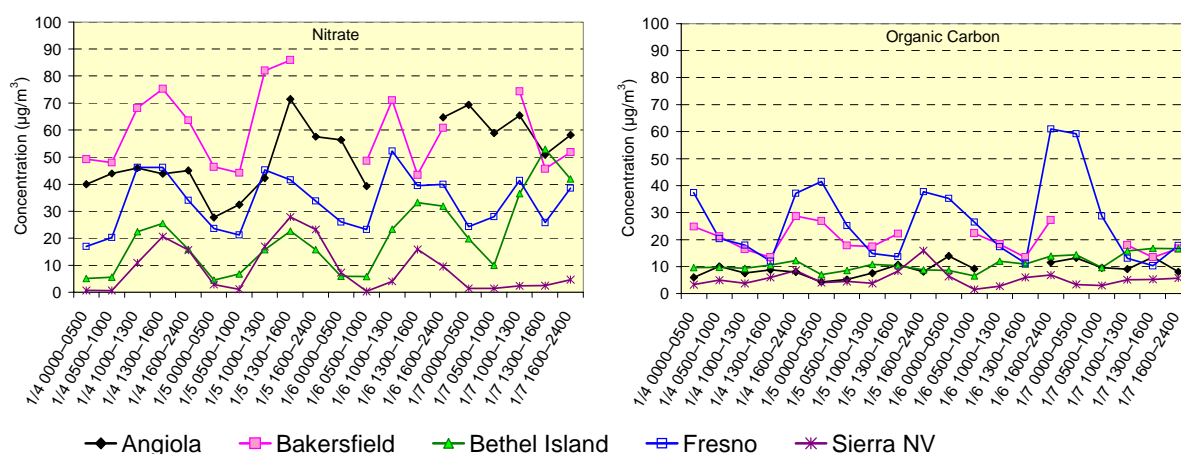


Figure 3. Variation of nitrate (NO_3^-) and organic carbon (OC) during IOP_3.

consistent diurnal patterns, including a nighttime high (1600–0500) for OC and a noon peak (1000–1600) for NO_3^- . The diurnal/nocturnal contrast for NO_3^- is especially apparent at the two boundary rural sites, Bethel Island and Sierra Nevada Foothills. The surface does not begin to heat up until ~9 a.m. during winter. By 1 p.m., the solar-induced turbulence gets strong enough to break the nighttime residual layer and bring the NO_3^- aloft down to the surface. This diurnal variation is consistent with the bulk of NO_3^- staying aloft throughout the valley [7]. At the two boundary sites, this aloft NO_3^- layer becomes thinner, more diluted, and further decoupled from the surface layer. Bakersfield, on the other hand, shows the deepest NO_3^- layer, in which the NO_3^- was often above 50 $\mu\text{g}/\text{m}^3$, even at night.

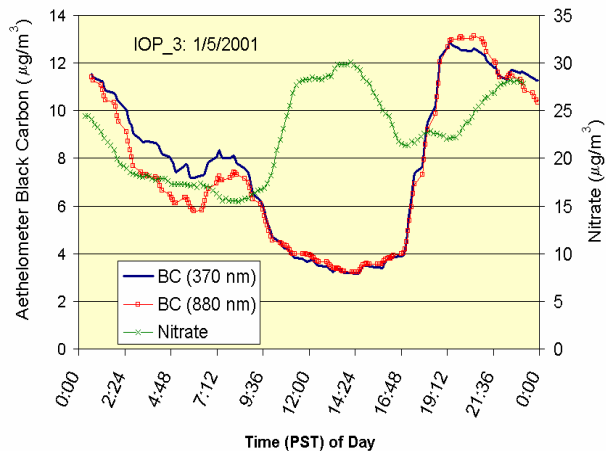


Figure 4. Diurnal variation of black carbon (BC) and nitrate (NO_3^-) at the Fresno supersite on 1/5/2001.

Soluble potassium concentrations also suggest that wood combustion might play a major role in these wintertime $\text{PM}_{2.5}$ episodes. Since OC and NO_3^- are equally important at the Fresno supersite, the dual effects of vertical mixing produce a complicated diurnal pattern for $\text{PM}_{2.5}$.

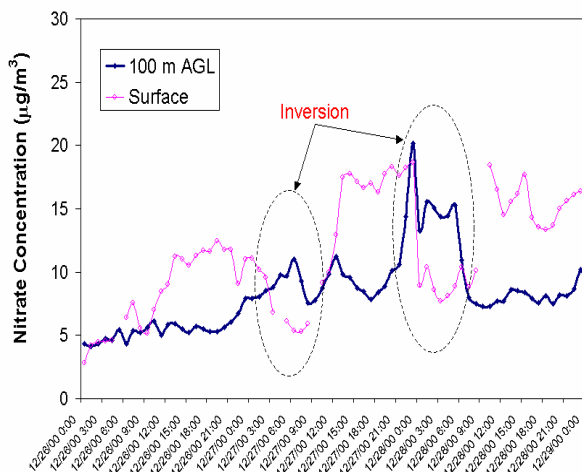


Figure 5. Comparisons of nitrate (NO_3^-) measurements at surface and 100 m above ground level (AGL) at the Angiola site during IOP_2.

boost of surface NO_3^- level after 9 a.m. as turbulent mixing took effect. Higher NO_3^- concentrations at the surface during daytime could also be due to higher NH_3 levels at the

This turbulent mixing has an opposite effect on OC, causing low OC levels in the afternoon, especially for the two urban sites (FSF and BAC). This is evidence of vertical dispersion of OC (and EC) from the surface. The OC and EC concentrations start to build up after 4 p.m. and stay high through the next morning. This nighttime accumulation is more consistent with intensive residential wood combustion for heating at night. The continuous BC measurement at the Fresno supersite indicated a peak around 7 a.m. corresponding to the morning rush hours, but no obvious peak directly corresponding to the evening rush hours (Figure 4).

Concurrent measurements of NO_3^- (through R&P 8400N) at the surface and 100 m above ground level during IOP_2 is shown in Figure 5. $\text{PM}_{2.5}$ NO_3^- at the surface was generally higher than that at 100 m. At night, as the residue layer built up, the NO_3^- level at the surface decreased rapidly compared with that at 100 m, likely due to deposition to the surface. The increase of NO_3^- concentration at 100 m during nighttime partly resulted from the nighttime conversion of NO_x to NO_3^- [9, 10]. An inversion layer of NO_3^- (i.e., NO_3^- concentration increases with altitude) was observed between 3 and 9 a.m. on 12/27/2000 and 12/28/2000 (Figure 5). This inversion layer was responsible for the rapid

surface that create particulate NH_4NO_3 from gaseous HNO_3 .

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REFERENCES

- [1] Chow, J.C.; Watson, J.G.; Lowenthal, D.H.; Solomon, P.A.; Magliano, K.L.; Ziman, S.D.; Richards, L.W. PM_{10} source apportionment in California's San Joaquin Valley; *Atmos. Environ.* **1992**, 26A(18), 3335-3354.
- [2] Chow, J.C.; Watson, J.G.; Lowenthal, D.H.; Solomon, P.A.; Magliano, K.L.; Ziman, S.D.; Richards, L.W. PM_{10} and $\text{PM}_{2.5}$ compositions in California's San Joaquin Valley; *Aerosol Sci. Technol.* **1993**, 18, 105-128.
- [3] Chow, J.C.; Watson, J.G.; Lu, Z.; Lowenthal, D.H.; Frazier, C.A.; Solomon, P.A.; Thuillier, R.H.; Magliano, K.L. Descriptive analysis of $\text{PM}_{2.5}$ and PM_{10} at regionally representative locations during SJVAQS/AUSPEX; *Atmos. Environ.* **1996**, 30(12), 2079-2112.
- [4] Chow, J.C.; Watson, J.G.; Lowenthal, D.H.; Hackney, R.; Magliano, K.L.; Lehrman, D.; Smith, T. Temporal variations of $\text{PM}_{2.5}$, PM_{10} , and gaseous precursors during the 1995 Integrated Monitoring Study in central California; *JAWMA* **1999**, 49(PM), PM 16-PM 24.
- [5] Kumar, N.; Lurmann, F.W.; Chico, T. Modeling the effects of emission changes on $\text{PM}_{2.5}$ using the UAM-AERO model in the South Coast Air Basin, in *Proceedings, $\text{PM}_{2.5}$: A Fine Particle Standard*, Chow, J.C., Koutrakis, P., Eds.; Air & Waste Management Association: Pittsburgh, PA, 1998, pp. 737-747.
- [6] Chow, J.C.; Egami, R.T. *San Joaquin Valley Integrated Monitoring Study: Documentation, evaluation, and descriptive analysis of PM_{10} , $\text{PM}_{2.5}$, and precursor gas measurements—Technical Support Studies No. 4 and No. 8—Final report*; prepared for California Particulate Air Quality Study, California Air Resources Board, Sacramento, CA, by Desert Research Institute: Reno, NV, 1997.

- [7] Watson, J.G.; Chow, J.C. A wintertime PM_{2.5} episode at the Fresno, CA, supersite; *Atmos. Environ.* **2002**, *36*(3), 465-475.
- [8] Watson, J.G.; Chow, J.C.; Bowen, J.L.; Lowenthal, D.H.; Hering, S.; Ouchida, P.; Oslund, W. Air quality measurements from the Fresno Supersite; *JAWMA* **2000**, *50*(8), 1321-1334.
- [9] Atkinson, R.; Winer, A.M.; Pitts, J.N., Jr. Estimation of night-time N₂O₅ concentrations from ambient NO₂ and NO₃ radical concentrations and the role of N₂O₅ in night-time chemistry; *Atmos. Environ.* **1986**, *20*(2), 331-339.
- [10] Smith, N.; Plane, J.M.C.; Nien, C.; Solomon, P.A. Nighttime radical chemistry in the San Joaquin Valley; *Atmos. Environ.* **1995**, *29*(21), 2887-2897.