Size-resolved aerosol chemical concentrations at rural and urban sites in Central California, USA

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Aerosol size distributions were measured with Micro Orifice Uniform Deposit Impactor (MOUDI) cascade impactors at the rural Angiola and urban Fresno Supersites in California’s San Joaquin Valley during the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) winter campaign from December 15, 2000 to February 3, 2001. PM2.5 filter samples were collected concurrently at both sites with Sequential Filter Samplers (SFS). MOUDI nitrate (NO3−) concentrations reached 66 μg/m3 on January 6, 2001 during the 1000–1600 PST (GMT-8) period. Pair-wise comparisons between PM2.5 MOUDI and SFS concentrations revealed high correlations at the Angiola site (rN0.93) but more variability (rN0.85) at the Fresno site for NO3−, sulfate (SO42−), and ammonium (NH4+). Correlations were higher at Fresno (rN0.87) than at Angiola (rN0.7) for organic carbon (OC), elemental carbon (EC), and total carbon (TC). NO3− and SO42− size distributions in Fresno were multi-modal and wider than the uni-modal distributions observed at Angiola. Geometric mean diameters (GMD) were smaller for OC and EC than for NO3− and SO42− at both sites. OC and EC were more concentrated on the lowest MOUDI stage (0.056 μm) at Angiola than at Fresno. The NO3− GMD increased from 0.97 to 1.02 μm as the NO3− concentration at Angiola increased from 43 to 66 μg m−3 during a PM2.5 episode from January 4–7, 2001. There was a direct relationship between GMD and NO3− concentrations at Angiola but no such relationships for OC or EC. This demonstrates that secondary aerosol formation increases both concentration and particle size for the rural California environment.

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1. Introduction

Size-resolved measurements of aerosol chemistry have been used to study chemical processes, transport, and sources of aerosols (Li and Winchester, 1990; Barrie et al., 1994; Huebert et al., 1996) and to estimate aerosol light extinction (Zhang et al., 1994; Lowenthal et al., 1995; Malm and Pitchford, 1997; Chow et al., 2002; Hand et al., 2002; Watson, 2002). Measurements of particle number concentration at the Fresno Supersite (Watson et al., 2000, 2008; Chow et al., 2008) throughout the day in California’s San Joaquin Valley (SJV) show dynamic size distributions that can be associated with primary emissions from engine exhaust and home heating, and with secondary aerosol formation from nucleation and related photochemical processes (Watson et al., 2002, 2006a). Although similar patterns have been found in eastern U.S. cities (e.g., Woo et al., 2001; Jung et al., 2006), these have been dominated by sulfate (SO42−) concentrations. In contrast, the PM2.5 fraction in central California contains little SO42− and is dominated by ammonium nitrate (NH4NO3) and organic carbon (OC; Chow et al., 1993a, 1996, 1999, 2004, 2005a, 2006; Magliano et al., 1999). Wintertime valley-wide PM2.5 and NH4NO3 episodes arise from atmospheric conversion of urban emissions as they are transported and mixed within a 300–500 m deep valley-wide layer that tops a shallow (~20 m) surface layer where primary pollutants accumulate during non-daylight hours (Watson and Chow, 2002; Lurmann et al., 2006). Nitric acid (HNO3), the gaseous precursor of particulate NH4NO3, is formed during both day and night. Source
contributions to PM$_{2.5}$ in Fresno during CRPAQS were estimated by Chow et al. (2007a), with primary PM$_{2.5}$, composed mainly of OC and elemental carbon (EC), from residential wood combustion (RWC) and motor vehicle exhaust. NH$_4$NO$_3$ was completely secondary while ammonium sulfate [(NH$_4$)$_2$SO$_4$] was roughly two-thirds secondary and one-third primary (derived from vehicle exhaust).

Richards et al. (1999) used MOUDI (Micro Orifice Uniform Deposit Impactor; MSP Corporation, Shoreview, MN) cascade impactor concentrations from Bakersfield, CA, in the southern

Fig. 1. Relationship between PM$_{2.5}$ Micro Orifice Uniform Deposit Impactor (MOUDI) and sequential filter sampler (SFS) concentrations at the Angiola and Fresno sites for: a) nitrate (NO$_3^-$), sulfate (SO$_4^{2-}$), and ammonium (NH$_4^+$); and b) organic carbon (OC) and elemental carbon (EC). SFS total particulate NO$_3^-$ concentrations (PNO$_3^-$) are the sum of NO$_3^-$ on the front and backup filters. SFS total particulate NH$_4^+$ concentrations (PNH$_4^+$) are the sum of the front filter NH$_4^+$ and NH$_3$ (calculated equivalent to NO$_3^-$) on the backup filter; $r$ is the correlation coefficient.
SJV to estimate the contributions of aerosol chemical components to particle light extinction. Herner et al. (2005, 2006) used MOUDI concentrations from Bodega Bay, Sacramento, Modesto, Sequoia, and Bakersfield, CA to examine the factors responsible for the evolution of the aerosol size distribution. This paper elaborates on these previous limited size/composition measurements to better understand the chemical nature, formation mechanisms, and transport phenomena that resulted in elevated PM$_{2.5}$ levels measured in central California.

2. Methods

Size-resolved chemical measurements were taken as part of the California Regional PM$_{10}$/PM$_{2.5}$ Air Quality Study (CRA PQS) conducted from December 2, 1999 through February 3, 2001 to understand exceedances of U.S. National Ambient Air Quality Standards (NAAQS) for PM$_{2.5}$ and PM$_{10}$ (Bachmann, 2007; Chow et al., 2007b) in the SJV (Watson et al., 1998). These measurements were made with three MOUDIs each at the Fresno Super Site, in the largest SJV urban area, and at Angiola, a rural site located ~100 km south of Fresno and ~90 km north of Bakersfield, a southern SJV city (Watson et al., 2000). Samples were collected within four time periods per day to separate different source activities and meteorological conditions (0000–0005, 0005–1000, 1000–1600, and 1600–2400 Pacific Standard Time [PST]). These periods were within four Intensive Operating Periods (IOPs) when high levels of PM$_{2.5}$ and nitrate (NO$_3^-$) had been forecast: 1) December 15–18, 2000; 2) December 26–28, 2000; 3) January 4–7, 2001; and 4) January 31–February 3, 2001. MOUDIs were initially equipped with nominal $d_{50}$ (aerodynamic diameter at which 50% of particles of that size are retained by each of the eight stages) of 5.6, 2.5, 1.8, 1.0, 0.56, 0.32, 0.18, and 0.10 µm, followed by an after-filter. After the first IOP, the 1.8 µm stage was removed and a 0.056 µm stage was added. Particles were collected on Teflon films (DuPont FE Fluorocarbon Film; DuPont, Circleville, OH) and Teflon-membrane after-filters (R2P9047; Pall Sciences, Ann Arbor, MI) for measurement of particle mass and elements on MOUDI Unit 1 and water-soluble ion concentrations on MOUDI Unit 2. Pre-fired (600 °C) aluminum foil (0100-96-0573A-X; MSP Corporation, Shoreview, MN) and quartz-fiber after-filters (QAT2500-UP; Pall Sciences, Ann Arbor, MI) on MOUDI Unit 3 collected particles for OC and EC quantification.

The three MOUDIs at each site were collocated with a dual-channel PM$_{2.5}$ Sequential Filter Sampler (SFS; Mueller et al., 1983; U.S. EPA, 1989; Chow et al., 2005b) using Teflon-membrane and quartz-fiber filters. SFS filters were preceded by a PM$_{2.5}$ size-selective inlet (Sensidyne Bendix 240 cyclones) and aluminum oxide tubular HNO$_3$ denuders (Watson and Chow, 1993, 2001; Chow et al., 1993b). NO$_3^-$ volatilized from the quartz-fiber filters was collected on sodium chloride impregnated cellulose-fiber backup filters (31ET; Whatman, Hillsboro, OR). PM$_{2.5}$ samples were collected on the same schedule as the MOUDI except that the 1000–1600 PST period was divided (i.e., 1000–1300 and 1300–1600 PST). Concentrations from the SFS samplers during these two sampling periods were averaged to coincide with the MOUDI 1000–1600 PST sampling period.

Forty-six valid sampling periods were selected for chemical analysis. MOUDI Teflon substrates and SFS Teflon-membrane filters were analyzed for particle mass by gravimetry and elements by X-ray fluorescence (Watson et al., 1999). Water extracts of MOUDI Teflon substrates and SFS quartz-fiber filters were analyzed for chloride (Cl$^-$), NO$_3^-$ and SO$_4^{2-}$ by ion chromatography (IC; Chow and Watson, 1999; Chow et al., 2008), ammonium (NH$_4^+$) by automated colorimetry (AC), and water-soluble sodium (Na$^+$) and potassium (K$^+$) by atomic absorption spectroscopy (AAS). OC and EC were analyzed on MOUDI aluminum foil substrates and on SFS quartz-fiber filters by thermal/optical reflectance converting OC into OC+EC and EC into EC+OP (TO R; Chow et al., 1993c, 2001, 2004, 2005b, 2007c) following the IMPROVE protocol. In TOR, OC and EC were measured at 120, 250, 450, and 550 °C in a helium (He) atmosphere. OC is the sum of the four OC fractions plus pyrolyzed OC (OP) estimated from the reflected laser signal. Three EC fractions evolve at 550, 700, and 800 °C, respectively, in a 98% He/2% oxygen (O$_2$) atmosphere. EC is the sum of the three EC fractions minus OP. It is not possible to quantify OP for MOUDI carbon measurements because the aluminum foil substrates are too reflective. Therefore, the laser split point from the collocated PM$_{2.5}$ SFS is used to separate OC from EC. MOUDI stage concentrations were converted to continuous size distributions (dC dlogD$^{-1}$, where C is mass concentration and D is aerodynamic diameter), using Winklmayr et al.’s (1990) adaptation of Twomey’s (1975) nonlinear iterative algorithm (the “Twomey Inversion”).

3. Results and discussion

3.1. Comparisons between MOUDI and SFS samplers

PM$_{2.5}$ MOUDI chemical concentrations were estimated as the sum of the concentrations on the stages below 2.5 µm.

Fig. 2. Relationship between PM$_{2.5}$ MOUDI and SFS silicon (Si) concentrations at the Angiola and Fresno sites.
Average NO$_3^-$ and SO$_4^{2-}$ concentrations on the after-filter were less than 5% of their sum on the stages, but average OC and EC concentrations on the quartz-fiber after-filters were $40\pm 21$ and $48\pm 32\%$ at Angiola and $26\pm 14$ and $51\pm 25\%$ at Fresno of their sums on impactor stages ($<2.5\ \mu m$), respectively. Relatively large amounts of OC and EC on the after-filter could be explained by: 1) adsorption of volatile organic compounds (VOC) by the quartz-fiber after-filter (Eatough et al., 1990; McDow and Huntzicker, 1990; Turpin et al., 1994); 2) particle bounce of dry particles containing OC or EC (Vasiliou et al., 1999); and 3) OC and EC associated with very small particles. For consistency, the after-filter was excluded from the PM$_{2.5}$ sums.

PM$_{2.5}$ ion and carbon concentrations from MOUDI and SFS samplers at the Angiola and Fresno sites are compared in Fig. 1a and b, respectively. There were high correlations ($r>0.92$) between MOUDI and SFS NO$_3^-$, SO$_4^{2-}$, and NH$_4^+$ at Angiola. At Fresno, inter-sampler correlations for these ions were less than 0.85. It is not clear why comparisons were more variable at Fresno than at Angiola. Correlations between MOUDI and SFS OC, EC, and total carbon (TC; sum of OC plus EC) at Angiola were all less than 0.7. Fig. 1b shows that about a third of the OC and TC pairs fell along the 1:1 line while the remainder fell below it. At Fresno, correlations between MOUDI and SFS OC, EC, and TC were 0.94, 0.87, and 0.96. As seen in Fig. 1b, SFS EC was higher than MOUDI EC. MOUDI and SFS carbon may have been more comparable at Fresno because of higher concentrations in the urban area. Average SFS carbon concentrations at Angiola and Fresno were 6.2 and 21 $\mu g\ m^{-3}$ for OC and 1.8 and 6.4 $\mu g\ m^{-3}$ for EC, respectively.

Fig. 2 shows that inter-sampler correlations for PM$_{2.5}$ silicon (Si) were lower than for ions and carbon fractions: 0.37 and 0.59 at Angiola and Fresno, respectively. MOUDI Si concentrations were higher at both sites for about half of the samples. Fig. 3 shows that average Si size distributions were similar at both sites, although Si mass shifted to larger-particle sizes at Fresno, where the geometric mean diameter (GMD) was 2.7 $\mu m$ compared to 2.1 $\mu m$ at Angiola. Resuspension of road dust by urban vehicle traffic is more prevalent in Fresno and may be responsible for the larger
particles there. Most of the Si mass was associated with particles larger than 2.5 µm at both sites. The ratios of Si concentrations above and below 2.5 µm were 3.2 and 4.7 at Angiola and Fresno, respectively. In addition to the difference in PM$_{2.5}$ size cuts, the discrepancy between PM$_{2.5}$ MOUDI and SFS Si may be related to sample flow rates (30 liters per minute [L min$^{-1}$] in the MOUDI and 20 L min$^{-1}$ in the SFS) and particle bounce in the MOUDI.

3.2. Nitrate and sulfate speciation

NH$_4$NO$_3$ is the dominant PM$_{2.5}$ component in the SJV during winter (OC; Chow et al., 1993a, 1996, 1999, 2005a). Assuming that all of the NH$_4^+$ was present as NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$, then NH$_4^+$ can be estimated stoichiometrically (i.e., 0.29 NO$_3^-$+0.375 SO$_4^{2-}$). Total (summed over eight MOUDI stages) measured and estimated NH$_4^+$ concentrations are compared in Fig. 4. All cases
at both sites fall close to the 1:1 line. Some points above the line suggest either that NO$_3^-$ was associated with a species other than NH$_4^+$ e.g., dust, or that some of the SO$_4^{2-}$ during those periods may have been slightly acidic (i.e., ammonium bisulfate). Fig. 5 shows that average size distributions for NO$_3^-$ and NH$_4^+$ were nearly identical at both sites. A small peak in the NO$_3^-$ distribution above 3 µm at Fresno may represent an association of NO$_3^-$ with coarse-particle dust (Watson et al., 1994).

3.3. Average size distributions

Average concentrations of NO$_3^-$, SO$_4^{2-}$, NH$_4^+$, OC, and EC on each MOUDI stage, normalized to dlogD, at the Angiola and Fresno sites are shown in Fig. 6, which represents average concentrations, not average size distributions. NO$_3^-$, SO$_4^{2-}$, and NH$_4^+$ concentrations were associated with larger particles than were OC and EC at both sites. Particles smaller than about 0.2 µm were composed solely of OC and EC, similar to those found in other studies (Chow and Watson, 2007). For sizes larger than 0.2 µm, OC and EC could have been externally mixed from the ionic species or internally mixed with them to different extents as a function of size. Herner et al. (2006) observed similar MOUDI size distributions at the urban Sacramento, Modesto, and Bakersfield sites within the SJV and attributed the separation of the carbon and inorganic ion size modes to hygroscopicity of the ionic species with the implication that carbon and inorganic ions were externally mixed. However, internal mixtures of EC and hygroscopic SO$_4^{2-}$ have been observed in fresh motor vehicle emissions and at remote sites (Borys et al., 1998; Huang et al., 2006).

The average size distributions, normalized to the sum of the stage concentrations, for the individual species (NO$_3^-$, SO$_4^{2-}$, OC, and EC) are shown as histograms and continuous distributions in Fig. 7. Also shown are the average GMD, coefficient of variation (CV) of the GMDs, and the average of the geometric standard deviations (GSD). The CV of the GMDs indicates the degree to which the peaks of the distributions varied from sample to sample. GSDs represent the dispersion of the individual distributions.

MOUDI samples were collected at ambient relative humidity (RH) and the distributions reflect the effect of hygroscopic growth on particle size. Chow et al. (2005a) found similar inverse relationships between RH and temperature ($T$) at Fresno and Bakersfield. During the winter IOPs, the inter-site correlation between 5- to 8-hour average $T$ was 0.92 and RH was 0.81 at Fresno and Bakersfield. It may be inferred that the variation of RH at Angiola, Fresno, and Bakersfield was affected by the diurnal evolution of the boundary layer and that this evolution was similar at the three sites.

Fig. 7a shows that average NO$_3^-$ and SO$_4^{2-}$ size distributions at Angiola were narrow, with average GSDs of 1.6 and 1.8 and GMDs of 0.75 and 0.67 µm, respectively. The GMD of 0.67 µm for SO$_4^{2-}$ was considerably larger than GMDs of 0.15–0.27 µm reported near the Grand Canyon at Meadowview, AZ during summer, 1992, when the RH was much lower (Turpin et al., 1997). The CVs of the GMDs were relatively small: 23 and 18% for NO$_3^-$ and SO$_4^{2-}$, respectively. Conversely, GMDs for OC and EC at Angiola were more variable and wider, with CVs of 47 and 50%, respectively, and GSDs of 2.8. The GMDs for OC and EC, 0.34 and 0.26 µm, respectively, were <50% of those than NO$_3^-$ and SO$_4^{2-}$, respectively. Unlike NO$_3^-$ and SO$_4^{2-}$, relatively large amounts of OC and EC appeared on the lowest MOUDI stages, including the 0.056 µm stage. The peak diameters for NO$_3^-$, SO$_4^{2-}$, OC, and EC were similar (0.5–0.7 µm). Where the distributions overlapped, OC and EC could have been internally or externally mixed with NO$_3^-$ and SO$_4^{2-}$. However, the presence of OC and EC and the absence of NO$_3^-$ and SO$_4^{2-}$ on the lower MOUDI stages are consistent with OC and EC being externally mixed, at least on the smallest particles for the rural Angiola environment.

The average RH at Fresno exceeded 70% during 75% of the winter IOPs. This value is higher than the deliguescence RH of NH$_4$NO$_3$ at 25 °C (62%; Tang and Munkelwitz, 1993). However, there was no relationship between RH and GMDs for NO$_3^-$, SO$_4^{2-}$, OC, or EC in Fresno. Factors other than hygroscopic growth, such as chemical processing and particle growth may also influence particle sizes at Fresno. Fig. 7b shows that NO$_3^-$ and SO$_4^{2-}$ distributions in Fresno were broader than those at Angiola, with average GSDs of 2.0 and 2.1, respectively. The average distributions appear multi-modal, with GMDs (0.87 and 0.74 µm, respectively) 0.07–0.12 µm larger than those at Angiola. This may reflect a mixture of local emissions and material transported from distant sources. As seen at Angiola, the shapes of the NO$_3^-$ and SO$_4^{2-}$ distributions in Fresno were similar, suggesting that these species were internally mixed. Herner et al. (2006) conjectured that NH$_4$NO$_3$ in the SJV forms by condensation of ammonia (NH$_3$) and HNO$_3$ on (NH$_4$)$_2$SO$_4$ cores. GMDs for OC and EC (0.36 and 0.29 µm, respectively) and average GSDs (2.4) at Fresno were similar to those at Angiola. However, GMDs for OC and EC at Fresno were less variable, with CVs of 25 and 21%, respectively, about half those found at Angiola. Average MOUDI OC and EC concentrations in Fresno (24 and 3.6 µg m$^{-3}$, respectively) were almost twice those at Angiola (11.1 and 2.2 µg m$^{-3}$). This is most likely due to the influence of RWC and vehicular emissions which are prevalent in Fresno and may also explain the relative stability of the OC and EC distributions in Fresno.

OC and EC were also found on the lower MOUDI stages at Fresno, including the 0.056 µm stage, but to a lesser extent than at Angiola. The ratios of OC on the smallest MOUDI stage to total OC at Fresno and Angiola were 0.092 and 0.17, respectively. For EC, the corresponding ratios were 0.13 and 0.16, respectively. The presence of OC and EC and the absence of NO$_3^-$ and SO$_4^{2-}$ on the lower MOUDI stages are consistent with OC and EC being externally mixed, at least on the smallest particles for the rural Angiola environment.

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Fig. 9. Relationships between nitrate (NO$_3^-$), sulfate (SO$_4^{=}$), organic carbon (OC), and elemental carbon (EC) concentrations and geometric mean diameter (GMD) at the: a) Angiola, and b) Fresno sites.
of emissions from Bakers concentrations are consistent with gas-to-particle conversion (Watson et al., 2002; Chow et al., 2006). The evolution of the NO$_3^-$ distribution on subsequent days (Watson and Chow, 2002; Chow et al., 2006) above the boundary layer followed by mixing to the surface extended from Bakersfield in the south to Bethel Island, east of San Francisco, in the north (Chow et al., 2006). These high concentrations are consistent with gas-to-particle conversion of emissions from Bakersfield in south-to-north transport above the boundary layer followed by mixing to the surface on subsequent days (Watson and Chow, 2002; Chow et al., 2006; Lurmann et al., 2006). The evolution of the NO$_3^-$ size distribution at Angiola during this episode is examined in Fig. 8. MOUDI NO$_3^-$ concentrations were 43, 43, 66, and 38 µg m$^{-3}$, respectively, and NO$_3^-$ GMDs were 0.90, 0.97, 1.02, and 1.02 µm, respectively, on January 4 (1000–1600 PST), January 5 (0000–0500 PST), January 6 (1000–1600 PST), and January 7 (1600–2400 PST). Fig. 8 shows that the peak size increased from January 4 to 5 and that the distribution broadened considerably to larger sizes on January 6. The distribution on January 7 was similar to that on January 6 but the concentration was lower. For comparison, the NO$_3^-$ size distribution on the first day of the final winter IOP, January 31, 1000–1600 PST, is also shown in Fig. 8. During this period, the MOUDI NO$_3^-$ concentration was 8.4 µg m$^{-3}$ and the distribution had shifted back to smaller sizes with a GMD of 0.54 µm.

### 3.4. Nitrate episode at Angiola

The highest MOUDI NO$_3^-$ concentration occurred on January 6, 2001 during the 1000–1600 PST sample period at Angiola. This was at the peak of a valley-wide episode that extended from Bakersfield in the south to Bethel Island, east of San Francisco, in the north (Chow et al., 2006). These high concentrations are consistent with gas-to-particle conversion of emissions from Bakersfield in south-to-north transport above the boundary layer followed by mixing to the surface on subsequent days (Watson and Chow, 2002; Chow et al., 2006; Lurmann et al., 2006). The evolution of the NO$_3^-$ size distribution at Angiola during this episode is examined in Fig. 8. MOUDI NO$_3^-$ concentrations were 43, 43, 66, and 38 µg m$^{-3}$, respectively, and NO$_3^-$ GMDs were 0.90, 0.97, 1.02, and 1.02 µm, respectively, on January 4 (1000–1600 PST), January 5 (0000–0500 PST), January 6 (1000–1600 PST), and January 7 (1600–2400 PST). Fig. 8 shows that the peak size increased from January 4 to 5 and that the distribution broadened considerably to larger sizes on January 6. The distribution on January 7 was similar to that on January 6 but the concentration was lower. For comparison, the NO$_3^-$ size distribution on the first day of the final winter IOP, January 31, 1000–1600 PST, is also shown in Fig. 8. During this period, the MOUDI NO$_3^-$ concentration was 8.4 µg m$^{-3}$ and the distribution had shifted back to smaller sizes with a GMD of 0.54 µm.

### 3.5. Relationship between concentration and particle size

Fig. 9a shows good correlations (r) of 0.84 and 0.86 at Angiola between the GMDs and NO$_3^-$ and SO$_4^{2-}$ concentrations, respectively. No such relationships were evident for OC and EC at Angiola or for any of the four species in Fresno (Fig. 9b). The correlation for SO$_4^{2-}$ (0.38) in Fresno was not statistically significant. The results at Angiola are consistent with transport and transformation mechanisms that give rise to elevated NO$_3^-$ concentrations in the SJV (Watson and Chow, 2002; Lurmann et al., 2006). Both particle size and NO$_3^-$ and SO$_4^{2-}$ concentrations increase as urban precursors (nitrogen oxides [NO$_x$] and sulfur dioxide [SO$_2$]) from Bakersfield undergo gas-to-particle conversion during northward transport to Angiola. Pitchford et al. (2007) concluded that gas-to-particle conversion during long-range transport should increase SO$_4^-$, NO$_3^-$, and OC concentrations, particle sizes, and light extinction efficiency at remote U.S. national parks. The evolution of the MOUDI size distributions and chemical concentrations at Angiola demonstrate the importance of chemical transformation at much smaller scales: Angiola is only ~90 km downwind from Bakersfield, the nearest large urban source area.

### 4. Conclusions

PM$_{2.5}$ NH$_4$NO$_3$ was the dominant aerosol species during the CRPAQS winter intensive operating periods at the rural Angiola and urban Fresno sites. PM$_{2.5}$ MOUDI NO$_3^-$ concentrations reached 66 µg m$^{-3}$ on January 6, 2001 during the 1000–1600 PST sampling period. The highest MOUDI SO$_4^{2-}$ concentrations at Angiola and Fresno were 4.6 and 3.5 µg m$^{-3}$, respectively. SO$_2^-$ was present mainly as (NH$_4$)$_2$SO$_4$.

Correlations between MOUDI and SFS PM$_{2.5}$ NO$_3^-$, SO$_4^{2-}$, and NH$_4^+$ at Angiola were 0.93, 0.92, and 0.94, respectively. Comparisons for ionogenic species were more variable at Fresno (r=0.85). Correlations between MOUDI and SFS PM$_{2.5}$ OC, EC, and TC at Fresno were 0.94, 0.87, and 0.96, respectively. Conversely, comparisons for carbon were more variable at Angiola (r=0.7). SO$_4^{2-}$ and NO$_3^-$ size distributions at Fresno were wider (GSD of 2.0–2.1) and multi-modal as compared to those at Angiola (GSD of 1.6–1.8 with a single mode). The broader distributions at Fresno reflect the influence of local and distant sources while only distant sources impacted the rural Angiola site. Average GMDs for NO$_3^-$ and SO$_4^{2-}$ were 0.75 and 0.67 µm, respectively, at Angiola and 0.87 and 0.74 µm, respectively, at Fresno. The similarity of the NO$_3^-$ and SO$_4^{2-}$ distributions at the Angiola and Fresno sites suggests that these species were, in part, externally mixed. OC and EC size distributions were multi-modal, with a wider distribution at Angiola (GSD of 2.8) than Fresno (GSD of 2.4). GMDs for OC and EC were 0.34 and 0.26 µm at Angiola, and 0.36 and 0.29 µm at Fresno, <50% of the GMDs for NO$_3^-$ and SO$_4^{2-}$. The shift of OC and EC distributions to smaller sizes at both sites suggests that these species were, in part, externally mixed. Relatively more OC and EC appeared at the smallest MOUDI stage at Angiola, consistent with RWC contributions associated with larger particles in Fresno.

An intense NO$_3^-$ episode occurred during early January 2001. PM$_{2.5}$ NO$_3^-$ concentrations at Angiola increased from 43 to 66 µg m$^{-3}$ from January 4–6, the NO$_3^-$ GMD increased from 0.97 to 1.02 µm. This is consistent with the hypothesis of Watson and Chow (2002) which explained wintertime NO$_3^-$ episodes in the SJV. In this case, NO$_x$ emissions from Bakersfield were converted to particulate NO$_3^-$ during northward transport to Angiola and particle sizes increased as gas-to-particle conversion occurred in these polluted air masses. There was also a clear direct relationship between NO$_3^-$ and SO$_4^{2-}$ concentrations and their GMDs at Angiola. This was not the case at Fresno, nor were there relationships between carbon (OC or EC) concentrations and their GMDs at either site. The results at Angiola confirm the conjecture of Lowenthal and Kumar (2004) that particle sizes at remote sites vary directly with mass concentration of secondary species such as NO$_3^-$ and SO$_4^{2-}$.

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0.20, respectively. Noting that these represent normalized size distributions, the deficit of small-particle OC and EC in Fresno compared with Angiola may reflect a relative abundance of larger-particle OC and EC at Fresno. This is probably due to RWC contributions in Fresno; Watson et al. (2002) describe the increase in black carbon concentration (the concentration of particles with diameters greater than 0.3 µm) and the particle mean diameter during wintertime evenings in Fresno.
Study (CRPAQS) under the management of the California Air Resources Board and by the U.S. Environmental Protection Agency under Contract #R-82805701. Any mention of commercially available products and supplies does not constitute an endorsement of those products and supplies.

References


