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

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ABSTRACT

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/PM_{2.5} Air Quality Study (CRPAQS) winter campaign from December 15, 2000 to February 3, 2001. PM_{2.5} 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 PM_{2.5} MOUDI and SFS concentrations revealed high correlations at the Angiola site ($r > 0.93$) but more variability ($r < 0.85$) at the Fresno site for NO₃⁻, sulfate (SO₄²⁻), and ammonium (NH₄⁺). Correlations were higher at Fresno ($r > 0.87$) than at Angiola ($r < 0.7$) 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 PM_{2.5} episode from January 4–7, 2001. There was a direct relationship between GMD and NO₃⁻ and SO₄²⁻ 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, 2006b). 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 PM_{2.5} 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 PM_{2.5} 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

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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. NH₄NO₃ was completely secondary while ammo-

niun sulfate [(NH₄)₂SO₄] 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

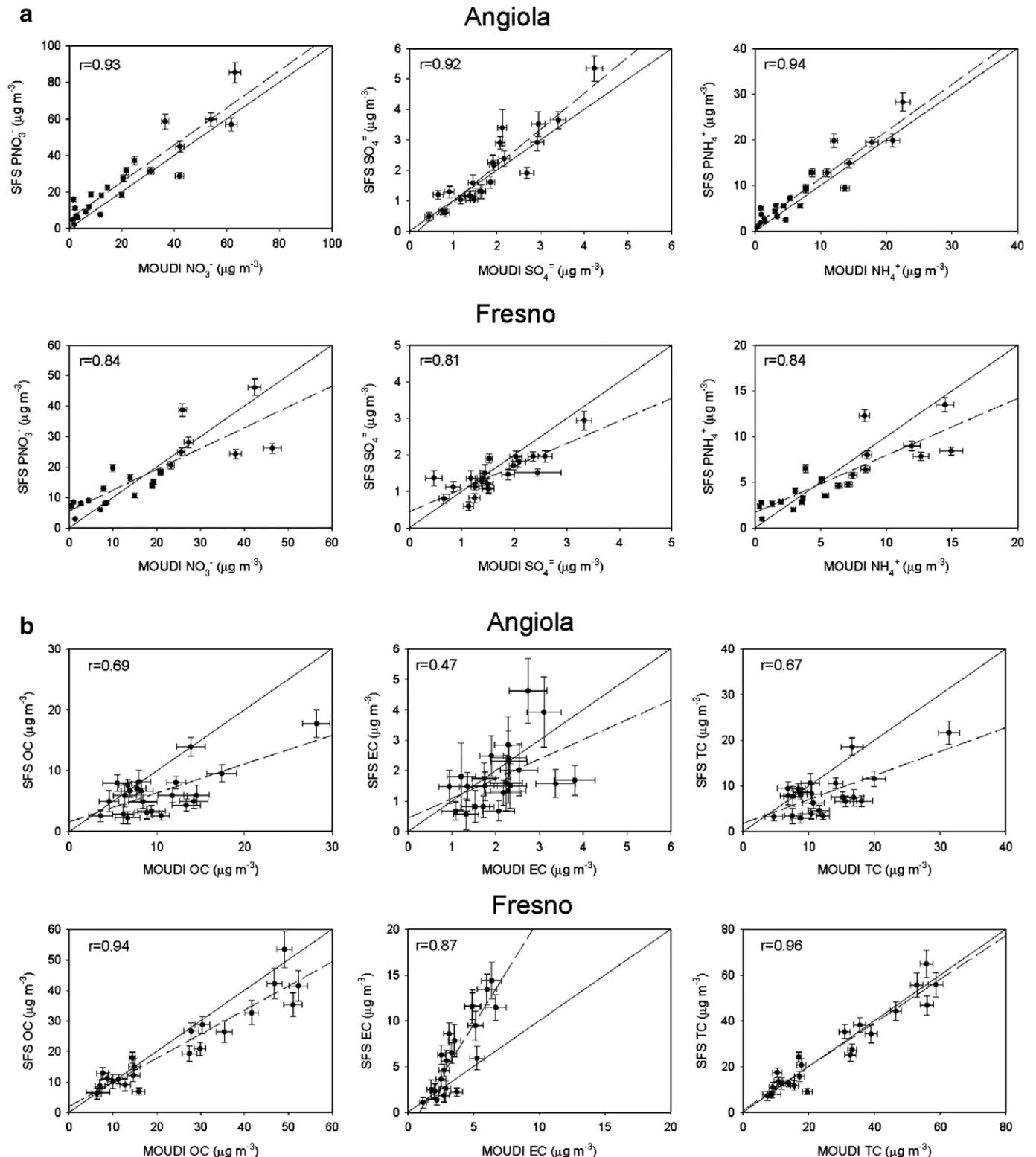


Fig. 1. Relationship between PM_{2.5} Micro Orifice Uniform Deposit Impactor (MOUDI) and sequential filter sampler (SFS) concentrations at the Angiola and Fresno sites for: a) nitrate (NO₃⁻), sulfate (SO₄²⁻), and ammonium (NH₄⁺); and b) organic carbon (OC) and elemental carbon (EC). SFS total particulate NO₃⁻ concentrations (PNO₃⁻) are the sum of NO₃⁻ on the front and backup filters. SFS total particulate NH₄⁺ concentrations (PNH₄⁺) are the sum of the front filter NH₄⁺ and NH₄⁺ (calculated equivalent to NO₃⁻) on the backup filter; r is the correlation coefficient.

SJV to estimate the contributions of aerosol chemical components to particle light extinction. [Hermer 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 (CRPAQS) 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 Supersite, 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 FEP Fluorocarbon Film; DuPont, Circleville, OH) and Teflon-membrane after-filters (R2PJ047; 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. Prefired (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-mem-

brane 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 (TOR; [Chow et al., 1993c, 2001, 2004, 2005b, 2007c](#)) following the IMPROVE protocol. In TOR, four OC fractions evolve 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 ($dC \text{ dlog}D^{-1}$, 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 .

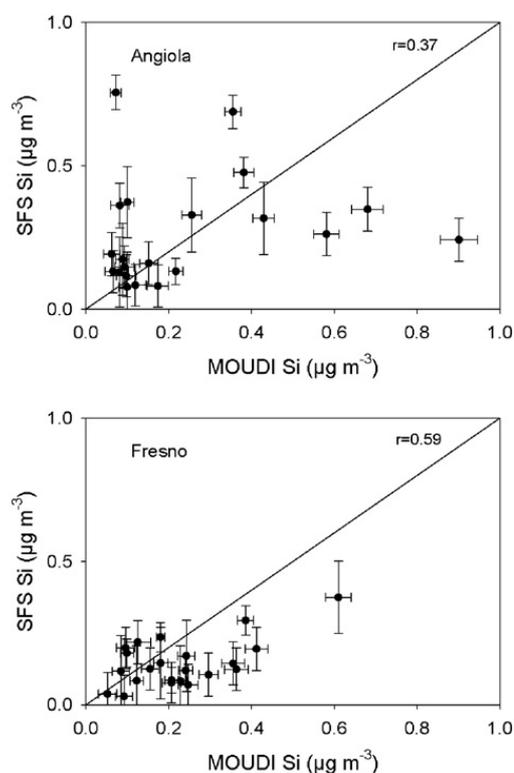


Fig. 2. Relationship between $PM_{2.5}$ MOUDI and SFS silicon (Si) concentrations at the Angiola and Fresno sites.

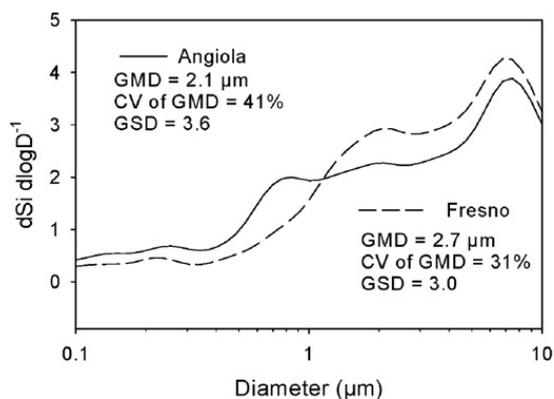


Fig. 3. Average silicon (Si) size distributions at the Angiola and Fresno sites between December 15, 2000 and February 3, 2001.

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 ± 21 and $48 \pm 32\%$ at Angiola and 26 ± 14 and $51 \pm 25\%$ at Fresno of their sums on impactor stages ($< 2.5 \mu\text{m}$), 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 $\text{PM}_{2.5}$ sums.

$\text{PM}_{2.5}$ 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

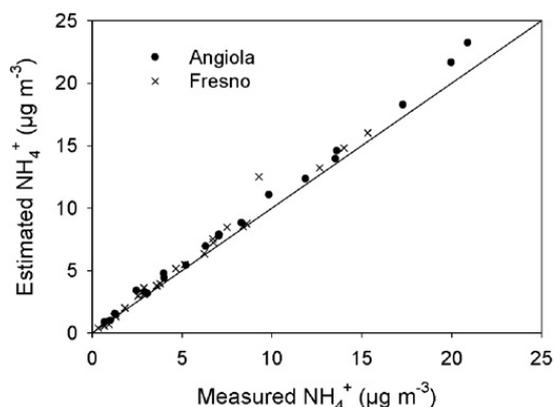


Fig. 4. Relationship between measured and estimated MOUDI ammonium (NH_4^+) concentrations assuming sulfate (SO_4^{2-}) is completely neutralized as ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ at the Angiola and Fresno sites. (Estimated $\text{NH}_4^+ = 0.29 \text{NO}_3^- + 0.375 \text{SO}_4^{2-}$).

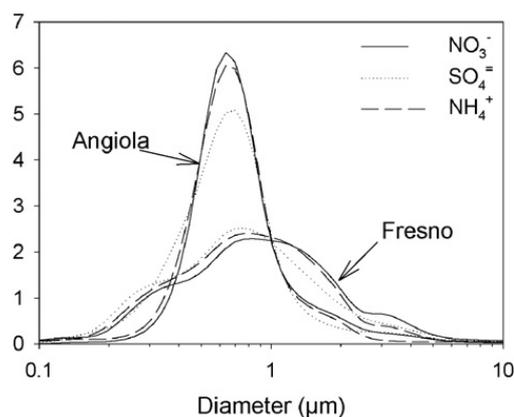


Fig. 5. Average size distributions for nitrate (NO_3^-), sulfate (SO_4^{2-}), and ammonium (NH_4^+) at the Angiola and Fresno sites. Distributions are normalized to total MOUDI stage concentration.

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 $21 \mu\text{g m}^{-3}$ for OC and 1.8 and $6.4 \mu\text{g m}^{-3}$ for EC, respectively.

Fig. 2 shows that inter-sampler correlations for $\text{PM}_{2.5}$ 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 $2.7 \mu\text{m}$ compared to $2.1 \mu\text{m}$ at Angiola. Re-suspension of road dust by urban vehicle traffic is more prevalent in Fresno and may be responsible for the larger

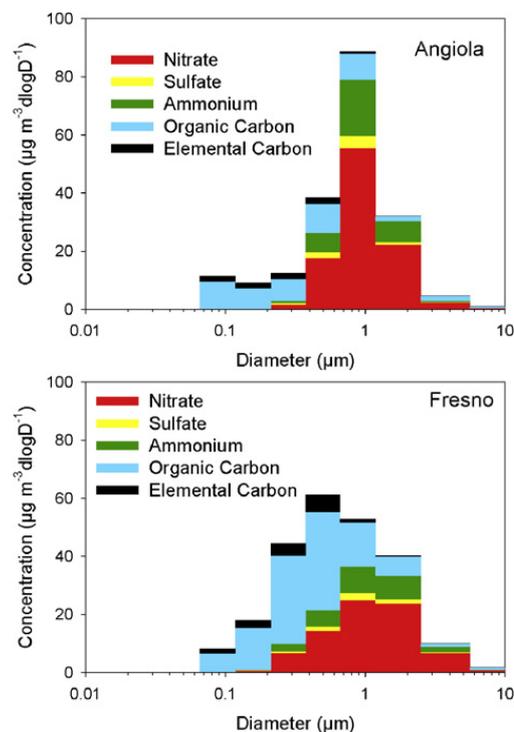


Fig. 6. Average nitrate, sulfate, ammonium, organic carbon, and elemental carbon concentrations, normalized to $d\log D$, on each MOUDI stage at the Angiola and Fresno sites.

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 $\text{PM}_{2.5}$ size cuts, the discrepancy between $\text{PM}_{2.5}$ 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_4NO_3 is the dominant $\text{PM}_{2.5}$ 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_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$, then NH_4^+ can be estimated stoichiometrically (i.e., $0.29 \text{NO}_3^- + 0.375 \text{SO}_4^{2-}$). Total (summed over eight MOUDI stages) measured and estimated NH_4^+ concentrations are compared in Fig. 4. All cases

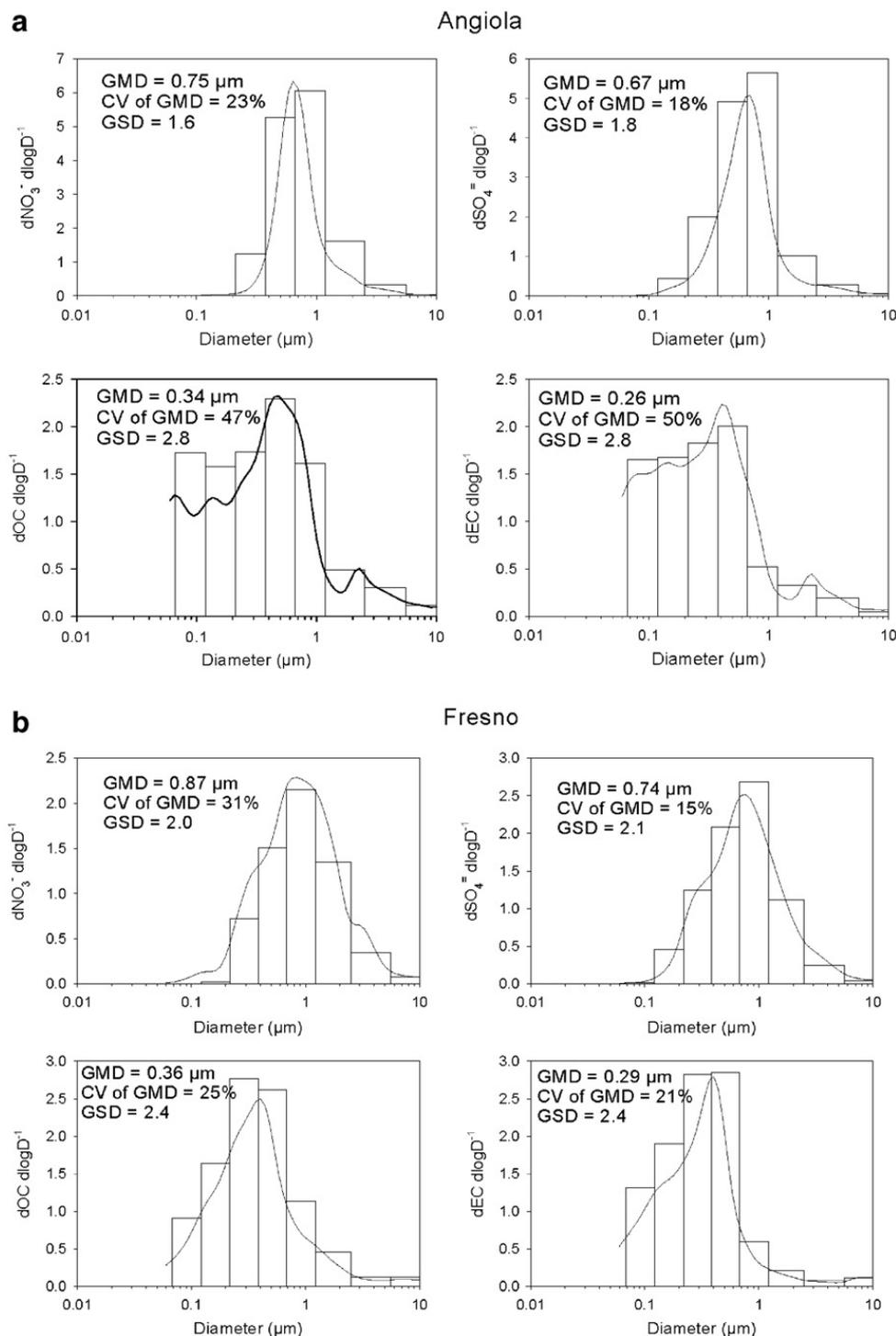


Fig. 7. Average size distributions for nitrate (NO_3^-), sulfate (SO_4^{2-}), organic carbon (OC), and elemental carbon (EC) at the: a) Angiola, and b) Fresno sites. Distributions are normalized to total MOUDI stage concentration. GMD is the geometric mean diameter, CV is 100 times the standard deviation of the GMD divided by the average GMD, and GSD is geometric standard deviation of the distribution.

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 $3 \mu\text{m}$ 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 $\text{dlog}D$, 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 $0.2 \mu\text{m}$ were composed solely of OC and EC, similar to those found in other studies (Chow and Watson, 2007). For sizes larger than $0.2 \mu\text{m}$, 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 $0.67 \mu\text{m}$, respectively. The GMD of $0.67 \mu\text{m}$ for SO_4^{2-} was considerably larger than GMDs of 0.15 – $0.27 \mu\text{m}$ reported near the Grand Canyon at Meadview, 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 $0.26 \mu\text{m}$, respectively, were <50% of than those of 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 $0.056 \mu\text{m}$ stage. The peak diameters for NO_3^- , SO_4^{2-} , OC, and EC were similar (0.5 – $0.7 \mu\text{m}$). 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 deliquescence RH of NH_4NO_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 $0.74 \mu\text{m}$, respectively) 0.07 – $0.12 \mu\text{m}$ 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_4NO_3 in the SJV forms by condensation of ammonia (NH_3) and HNO_3 on $(\text{NH}_4)_2\text{SO}_4$ cores. GMDs for OC and EC (0.36 and $0.29 \mu\text{m}$, 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 $3.6 \mu\text{g m}^{-3}$, respectively) were almost twice those at Angiola (11.1 and $2.2 \mu\text{g m}^{-3}$). 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 $0.056 \mu\text{m}$ 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

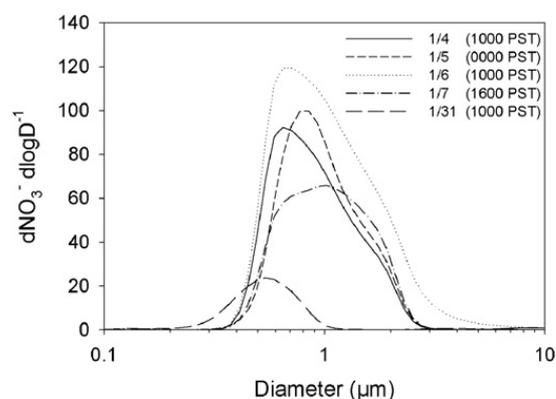


Fig. 8. Evolution of the nitrate (NO_3^-) size distribution during the CRPAQS winter intensive operating period from January 4–7, 2001. Also shown is a size distribution for January 31, 2001, 1000 PST, for comparison.

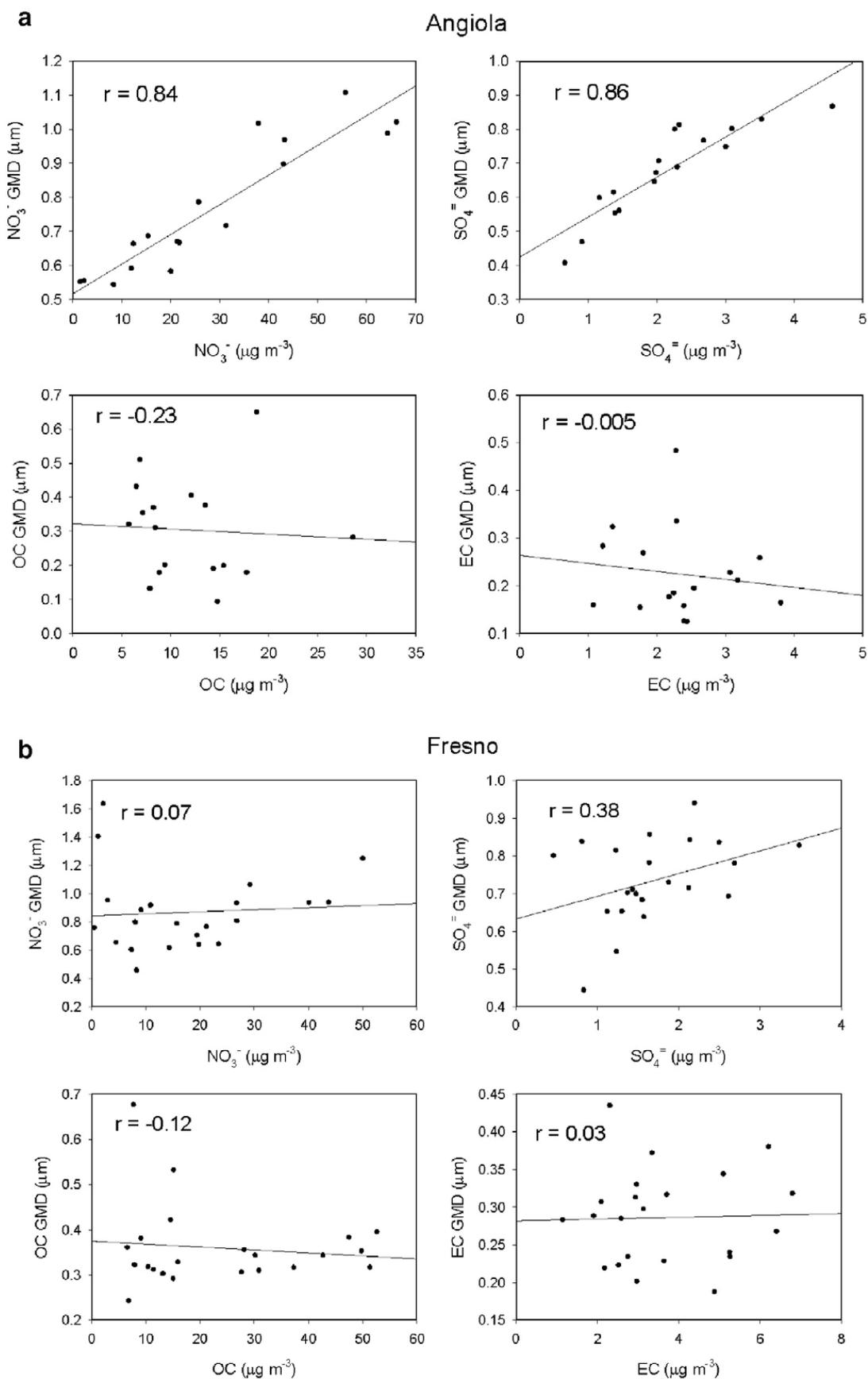


Fig. 9. Relationships between nitrate (NO₃⁻), sulfate (SO₄⁼), organic carbon (OC), and elemental carbon (EC) concentrations and geometric mean diameter (GMD) at the: a) Angiola, and b) Fresno sites.

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.

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 $\mu\text{g m}^{-3}$, 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 $\mu\text{g m}^{-3}$ 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^{2-} , 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

$\text{PM}_{2.5}$ NH_4NO_3 was the dominant aerosol species during the CRPAQS winter intensive operating periods at the rural Angiola and urban Fresno sites. $\text{PM}_{2.5}$ MOUDI NO_3^- concentrations reached 66 $\mu\text{g m}^{-3}$ 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 $\mu\text{g m}^{-3}$, respectively. SO_4^{2-} was present mainly as $(\text{NH}_4)_2\text{SO}_4$.

Correlations between MOUDI and SFS $\text{PM}_{2.5}$ NO_3^- , SO_4^{2-} , and NH_4^+ at Angiola were 0.93, 0.92, and 0.94, respectively. Comparisons for ionic species were more variable at Fresno ($r < 0.85$). Correlations between MOUDI and SFS $\text{PM}_{2.5}$ 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 internally 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 on 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. $\text{PM}_{2.5}$ NO_3^- concentrations at Angiola increased from 43 to 66 $\mu\text{g m}^{-3}$ 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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References

- Bachmann, J.D., 2007. 2007 critical review – will the circle be unbroken: a history of the U.S. national ambient air quality standards. *J. Air Waste Manage. Assoc.* 57, 652–697.
- Barrie, L.A., Staebler, R., Toom, D., Georgi, B., den Hartog, G., Landsberger, S., Wu, D., 1994. Arctic aerosol size-segregated chemical observations in relation to ozone depletion during polar sunrise. *J. Geophys. Res.* 99, 25439–25451.
- Borys, R.D., Lowenthal, D.H., Wetzel, M.A., Herrera, F., Gonzalez, A., 1998. Chemical and microphysical properties of marine stratiform cloud in the North Atlantic. *J. Geophys. Res.* 103, 22073–22085.
- Chow, J.C., Watson, J.G., 1999. Ion chromatography in elemental analysis of airborne particles. In: Landsberger, S., Creatchman, M. (Eds.), *Elemental Analysis of Airborne Particles*, vol. 1. Gordon and Breach Science, Amsterdam, pp. 97–137.
- Chow, J.C., Watson, J.G., 2007. Survey of measurement and composition of ultrafine particles. *AAQR* 7, 121–173. <http://www.aaqr.org/> (accessed April, 2008).
- Chow, J.C., Watson, J.G., Lowenthal, D.H., Solomon, P.A., Magliano, K.L., Ziman, S.D., Richards, L.W., 1993a. PM_{10} and $PM_{2.5}$ compositions in California's San Joaquin Valley. *Aerosol Sci. Technol.* 18, 105–128.
- Chow, J.C., Watson, J.G., Bowen, J.L., Frazier, C.A., Gertler, A.W., Fung, K.K., Landis, D., Ashbaugh, L.L., 1993b. A sampling system for reactive species in the Western United States. In: Winegar, E.D., Keith, L.H. (Eds.), *Sampling and Analysis of Airborne Pollutants*. Lewis Publishers, Ann Arbor, MI, pp. 209–228.
- Chow, J.C., Watson, J.G., Pritchett, L.C., Pierson, W.R., Frazier, C.A., Purcell, R.G., 1993c. The DRI thermal/optical reflectance carbon analysis system: description, evaluation and applications in U.S. air quality studies. *Atmos. Environ.* 27A, 1185–1201.
- Chow, J.C., Watson, J.G., Lu, Z., Lowenthal, D.H., Frazier, C.A., Solomon, P.A., Thuillier, R.H., Magliano, K.L., 1996. Descriptive analysis of $PM_{2.5}$ and PM_{10} at regionally representative locations during SJVAQS/AUSPEX. *Atmos. Environ.* 30, 2079–2112.
- Chow, J.C., Watson, J.G., Lowenthal, D.H., Hackney, R., Magliano, K.L., Lehrman, D., Smith, T.B., 1999. Temporal variations of $PM_{2.5}$, PM_{10} , and gaseous precursors during the 1995 integrated monitoring study in Central California. *J. Air Waste Manage. Assoc.* 49, PM16–PM24.
- Chow, J.C., Watson, J.G., Crow, D., Lowenthal, D.H., Merrifield, T.M., 2001. Comparison of IMPROVE and NIOSH carbon measurements. *Aerosol Sci. Technol.* 34, 23–34.
- Chow, J.C., Bachmann, J.D., Wierman, S.S.G., Mathai, C.V., Malm, W.C., White, W.H., Mueller, P.K., Kumar, N.K., Watson, J.G., 2002. 2002 critical review discussion – visibility: science and regulation. *J. Air Waste Manage. Assoc.* 52, 973–999.
- Chow, J.C., Watson, J.G., Chen, L.-W.A., Arnott, W.P., Moosmüller, H., Fung, K.K., 2004. Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols. *Environ. Sci. Technol.* 38, 4414–4422.
- Chow, J.C., Watson, J.G., Lowenthal, D.H., Magliano, K.L., 2005a. Loss of $PM_{2.5}$ nitrate from filter samples in Central California. *J. Air Waste Manage. Assoc.* 55, 1158–1168.
- Chow, J.C., Watson, J.G., Chen, L.-W.A., Paredes-Miranda, G., Chang, M.-C.O., Trimble, D., Fung, K.K., Zhang, H., Yu, J.Z., 2005b. Refining temperature measures in thermal/optical carbon analysis. *Atmos. Chem. Phys.* 5, 2961–2972. [doi:10.1029/2005-5-2961](https://doi.org/10.1029/2005-5-2961).
- Chow, J.C., Chen, L.-W.A., Watson, J.G., Lowenthal, D.H., Magliano, K.L., Turkiewicz, K., Lehrman, D., 2006. $PM_{2.5}$ chemical composition and spatiotemporal variability during the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS). *J. Geophys. Res.* 111, 1–17. [doi:10.1029/2005JD006457](https://doi.org/10.1029/2005JD006457).
- Chow, J.C., Watson, J.G., Lowenthal, D.H., Chen, L.-W.A., Zielinska, B., Mazzoleni, L.R., Magliano, K.L., 2007a. Evaluation of organic markers for chemical mass balance source apportionment at the Fresno supersite. *Atmos. Chem. Phys.* 7, 1741–1754.
- Chow, J.C., Watson, J.G., Feldman, H.J., Nolan, J., Wallerstein, B.R., Bachmann, J. D., 2007b. 2007 critical review discussion – will the circle be unbroken: a history of the U.S. national ambient air quality standards. *J. Air Waste Manage. Assoc.* 57, 1151–1163.
- Chow, J.C., Watson, J.G., Chen, L.W.A., Chang, M.C.O., Robinson, N.F., Trimble, D., Kohl, S., 2007c. The IMPROVE_A temperature protocol for thermal/optical carbon analysis: maintaining consistency with a long-term database. *J. Air Waste Manage. Assoc.* 57, 1014–1023.
- Chow, J.C., Watson, J.G., Chen, L.-W.A., Ho, S.S.H., Sodeman, D.A., Doraiswamy, P., 2008. Advances in integrated and continuous measurements for particle mass and chemical composition. *J. Air Waste Manage. Assoc.* 58, 141–163.
- Eatough, D.J., Aghdaie, N., Cottam, M., Gammon, T., Hansen, L.D., Lewis, E.A., Farber, R.J., 1990. Loss of semi-volatile organic compounds from particles during sampling on filters. In: Mathai, C.V. (Ed.), *Transactions, Visibility and Fine Particles*. Air & Waste Management Association, Pittsburgh, PA, pp. 146–156.
- Hand, J.L., Kreidenweis, S.M., Kreisberg, N., Hering, S., Stolzenburg, M., Dick, W., McMurry, P.H., 2002. Comparisons of aerosol properties measured by impactors and light scattering from individual particles: refractive index, number and volume concentrations, and size distributions. *Atmos. Environ.* 36, 1853–1861.
- Herner, J.D., Aw, J., Gao, O., Chang, D.P., Kleeman, M.J., 2005. Size and composition distribution of airborne particulate matter in Northern California 1. Particulate mass, carbon, and water-soluble ions. *J. Air Waste Manage. Assoc.* 55, 30–51.
- Herner, J.D., Ying, Q., Aw, J., Gao, O., Chang, D.P.Y., Kleeman, M.J., 2006. Dominant mechanisms that shape the airborne particle size and composition distribution in Central California. *Aerosol Sci. Technol.* 40, 827–844.
- Huang, X.F., Yu, J.Z., He, L.Y., Hu, M., 2006. Size distribution characteristics of elemental carbon emitted from Chinese vehicles: results of a tunnel study and atmospheric implications. *Environ. Sci. Technol.* 40, 5355–5360.
- Huebert, B.J., Zhuang, L., Howell, S., Noone, K., Noone, C., 1996. Sulfate, nitrate, methanesulfonate, chloride, ammonium, and sodium measurements from ship, island, and aircraft during the Atlantic stratocumulus transition experiment/marine aerosol gas exchange. *J. Geophys. Res.* 101, 4413–4423.
- Jung, J.G., Adams, P.J., Pandis, S.N., 2006. Simulating the size distribution and chemical composition of ultrafine particles during nucleation events. *Atmos. Environ.* 40, 2248–2259.
- Li, S.M., Winchester, J.W., 1990. Particle size distribution and chemistry of late winter aerosols. *J. Geophys. Res.* 95, 13897–13908.
- Lowenthal, D.H., Kumar, N., 2004. Variation of mass scattering efficiencies in IMPROVE. *J. Air Waste Manage. Assoc.* 54, 926–934.
- Lowenthal, D.H., Rogers, C.F., Saxena, P., Watson, J.G., Chow, J.C., 1995. Sensitivity of estimated light extinction coefficients to model assumptions and measurement errors. *Atmos. Environ.* 29, 751–766.
- Lurmann, F.W., Brown, S.G., McCarthy, M.C., Roberts, P.T., 2006. Processes influencing secondary aerosol formation in the San Joaquin Valley during winter. *J. Air Waste Manage. Assoc.* 56, 1679–1693.
- Magliano, K.L., Hughes, V.M., Chinkin, L.R., Coe, D.L., Haste, T.L., Kumar, N., Lurmann, F.W., 1999. Spatial and temporal variations in PM_{10} and $PM_{2.5}$ source contributions and comparison to emissions during the 1995 integrated monitoring study. *Atmos. Environ.* 33, 4757–4773.
- Malm, W.C., Pitchford, M.L., 1997. Comparison of calculated sulfate scattering efficiencies as estimated from size-resolved particle measurements at three national locations. *Atmos. Environ.* 31, 1315–1325.
- McDow, S.R., Huntzicker, J.J., 1990. Vapor adsorption artifact in the sampling of organic aerosol: face velocity effects. *Atmos. Environ.* 24A, 2563–2571.
- Mueller, P.K., Hidy, G.M., Baskett, R.L., Fung, K.K., Henry, R.C., Lavery, T.F., Nordi, N.J., Lloyd, A.C., Thrasher, J.W., Warren, K.K., Watson, J.G., 1983. Sulfate Regional Experiment (SURE): Report of Findings. Report Number EA-1901. Electric Power Research Institute.
- Pitchford, M., Malm, W., Schichtel, B., Kumar, N., Lowenthal, D., Hand, J., 2007. Revised algorithm for estimating light extinction from IMPROVE particle speciation data. *J. Air Waste Manage. Assoc.* 57, 1326–1336.
- Richards, L.W., Alcorn, S.H., McDade, C., Couture, T., Lowenthal, D.H., Chow, J.C., Watson, J.G., 1999. Optical properties of the San Joaquin Valley aerosol collected during the 1995 integrated monitoring study. *Atmos. Environ.* 33, 4787–4795.
- Tang, I.N., Munkelwitz, H.R., 1993. Composition and temperature dependence of the deliquescence properties of hygroscopic aerosols. *Atmos. Environ.* 27A, 467–473.
- Turpin, B.J., Huntzicker, J.J., Hering, S.V., 1994. Investigation of organic aerosol sampling artifacts in the Los Angeles Basin. *Atmos. Environ.* 28, 3061–3071. Research & Development available at.
- Turpin, B.J., Saxena, P., Allen, G.A., Koutrakis, P., McMurry, P.H., Hildemann, L.M., 1997. Characterization of the southwestern desert aerosol, Meadview, AZ. *J. Air Waste Manage. Assoc.* 47, 344–356.
- Twomey, S., 1975. Comparison of constrained linear inversion and an alternative nonlinear algorithm applied to the indirect estimation of particle size distributions. *J. Comput. Phys.* 18, 188–200.
- U.S. EPA, 1989. Ambient air monitoring reference and equivalent methods; reference method designation. *Fed. Regist.* 54, 12273.

- Vasilou, J.G., Sorensen, D., McMurry, P.H., 1999. Sampling at controlled relative humidity with a cascade impactor. *Atmos. Environ.* 33, 1049–1056.
- Watson, J.G., 2002. Visibility: science and regulation. *J. Air Waste Manage. Assoc.* 52, 628–713.
- Watson, J.G., Chow, J.C., 1993. Ambient air sampling. In: Willeke, K., Baron, P.A. (Eds.), *Aerosol Measurement: Principles, Techniques and Applications*. Van Nostrand, Reinhold, New York, NY, pp. 622–639.
- Watson, J.G., Chow, J.C., 2001. Ambient air sampling. In: Baron, P., Willeke, K. (Eds.), *Aerosol Measurement: Principles, Techniques, and Applications*, Second Edition. John Wiley & Sons, New York, NY, pp. 821–844.
- Watson, J.G., Chow, J.C., 2002. A wintertime $PM_{2.5}$ episode at the Fresno, CA, supersite. *Atmos. Environ.* 36, 465–475.
- Watson, J.G., Chow, J.C., Lurmann, F.W., Musarra, S., 1994. Ammonium nitrate, nitric acid, and ammonia equilibrium in wintertime Phoenix, Arizona. *J. Air Waste Manage. Assoc.* 44, 405–412.
- Watson, J.G., DuBois, D.W., DeMandel, R., Kaduwela, A.P., Magliano, K.L., McDade, C., Mueller, P.K., Ranzieri, A.J., Roth, P.M., Tanrikulu, S., 1998. Field Program Plan for the California Regional $PM_{2.5}/PM_{10}$ Air Quality Study (CRPAQS). Prepared for the California Air Resources Board, Sacramento, CA. <http://www.arb.ca.gov/airways/crpaqs/publications.htm>.
- Watson, J.G., Chow, J.C., Frazier, C.A., 1999. X-ray fluorescence analysis of ambient air samples. In: Landsberger, S., Creatchman, M. (Eds.), *Elemental Analysis of Airborne Particles*, vol. 1. Gordon and Breach Science, Amsterdam, pp. 67–96.
- Watson, J.G., Chow, J.C., Bowen, J.L., Lowenthal, D.H., Hering, S., Ouchida, P., Oslund, W., 2000. Air quality measurements from the Fresno supersite. *J. Air Waste Manage. Assoc.* 50, 1321–1334.
- Watson, J.G., Chow, J.C., Lowenthal, D.H., Stolzenburg, M.R., Kreisberg, N.M., Hering, S.V., 2002. Particle size relationships at the Fresno supersite. *J. Air Waste Manage. Assoc.* 52, 822–827.
- Watson, J.G., Chow, J.C., Lowenthal, D.H., Kreisberg, N., Hering, S.V., Stolzenburg, M.R., 2006a. Variations of nanoparticle concentrations at the Fresno supersite. *Sci. Total Environ.* 358, 178–187.
- Watson, J.G., Chow, J.C., Park, K., Lowenthal, D.H., 2006b. Nanoparticle and ultrafine particle events at the Fresno supersite. *J. Air Waste Manage. Assoc.* 56, 417–430.
- Watson, J.G., Chen, L.-W.A., Chow, J.C., Lowenthal, D.H., Doraiswamy, P., 2008. Source apportionment: findings from the U.S. supersite program. *J. Air Waste Manage. Assoc.* 58, 265–288.
- Winklmayr, W., Wang, H.C., John, W., 1990. Adaptation of the Twomey algorithm to the inversion of cascade impactor data. *Aerosol Sci. Technol.* 13, 322–331.
- Woo, K.S., Chen, D.R., Pui, D.Y.H., McMurry, P.H., 2001. Measurement of Atlanta aerosol size distributions: observations of ultrafine particle events. *Aerosol Sci. Technol.* 34, 75–87.
- Zhang, X.Q., Turpin, B.J., McMurry, P.H., Hering, S.V., Stolzenburg, M.R., 1994. Mie theory evaluation of species contributions to 1990 wintertime visibility reduction in the Grand Canyon. *J. Air Waste Manage. Assoc.* 44, 153–162.