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Wintertime particulate pollution episodes in an urban valley of the Western US: a case study

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Abstract

This study investigates the causes of elevated $PM_{2.5}$ concentrations and potential exceedences of the US National Ambient Air Quality Standards (NAAQS) in Truckee Meadows, Nevada, an urban valley of the Western US, during winter 2009/2010. Continuous $PM_{2.5}$ mass and time-integrated chemical speciation data were acquired from a central valley monitoring site with meteorological measurements from nearby sites. All nine days with $PM_{2.5} > 35\,\mu g\,m^{-3}$ experienced 24-h average temperature inversion of 1.5–4.5 °C and snow cover of 8–18 cm. A stagnant atmospheric condition inhibited wind ventilation while highly reflective snow cover reduced daytime surface heating leading to persistent inversion. Elevated ammonium nitrate (NH_4NO_3) and water associated with it are most important to the $PM_{2.5}$ exceedances during this unusually cold and snowy winter. An effective-variance chemical mass balance (EV-CMB) receptor model using locally-derived geological profiles and inorganic/organic markers identified secondary NH_4NO_3 (27–37 %), residential wood combustion (RWC; 11–51 %), and diesel engine exhausts (7–22 %) as the major contributors to $PM_{2.5}$. Paved road dust and de-icing materials were minor, but detectable contributors. RWC is a more important source than diesel for organic carbon (OC), but vice versa for elemental carbon (EC). A majority of secondary NH_4NO_3 is also associated with reactive nitrogen oxides (NO_x) from RWC and diesel engines (including snow removal equipments). Findings from this study may apply to similar situations experienced by other urban valleys.

1 Introduction

Particulate matter (PM), including $PM_{2.5}$ and PM_{10} (PM with aerodynamic diameter equal or less than 2.5 and 10 µm, respectively), are criteria air pollutants regulated by the US Environmental Protection Agency (EPA) for their adverse effects on public health, visibility, vegetation, and ecosystems (USEPA, 2004). There is increasing evidence of association between $PM_{2.5}$ and acute respiratory health problems in elderly,

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children, and sensitive groups (Chow et al., 2006b; Liu et al., 2003; O'Connor et al., 2008; Pope III and Dockery, 2006; Schwartz and Neas, 2000). Temporal and spatial variability of $PM_{2.5}$ chemical composition suggests a non-uniform source distribution and mass-specific health effects (Davidson et al., 2005). In the Eastern US, ammonium sulfate ($(NH_4)_2SO_4$) and organic matter (OM) are the most abundant species in $PM_{2.5}$, while in the Western US ammonium nitrate (NH_4NO_3) plays a bigger role than sulfate ($SO_4^=$). The OM contribution typically increases with urbanization due to mobile and industrial emissions (e.g., Chow et al., 2006a). Since the establishment of the National Ambient Air Quality Standards (NAAQS) under the Clean Air Act (Federal Register, 1970), a general decreasing trend in $PM_{2.5}$ concentrations has been observed across the US urban and rural areas (Murphy et al., 2011; Schichtel et al., 2001), particularly in the Eastern US, due to reductions in sulfur dioxide (SO_2) emission and $SO_4^=$ concentration.

The Truckee Meadows is a valley in Northern Nevada with the Sierra Nevada to its west and the Great Basin to its east. The valley floor is approximately 16 km square, containing the cities of Reno and Sparks with a population of ~315 000 (2010 census). It is isolated from major metropolitan areas by at least 200 km. Speciated $PM_{2.5}$ concentration in the valley has been monitored by the Washoe County Air Quality Management Division at the urban center since 2001. The measurements demonstrate compliance with the current NAAQS, which require the annual arithmetic mean $PM_{2.5}$ concentration, averaged over three years, to be less than 15 $\mu g\,m^{-3}$ and the 98th percentile of 24-h concentrations, averaged over three years, to be less than 35 $\mu g\,m^{-3}$ (Bachmann, 2007; Chow et al., 2007c). However, several 24-h $PM_{2.5}$ exceedances ($> 35\,\mu g\,m^{-3}$) were observed during 2008–2010 (Mendoza and Inouye, 2011), raising concerns of potential NAAQS non-attainment.

Most of the highest/unhealthy $PM_{2.5}$ concentrations were observed in winter, although there were sometimes excursions during late summer and fall when the smoke from large wildfires affected the region. The 2008 Truckee Meadows annual emission inventory (Ling-Barnes, 2010) showed that most primary $PM_{2.5}$ emissions are from

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area (non-point) sources associated with wintertime residential heating. Other important sources include motor vehicle emissions and fugitive dust. This study investigates meteorology, source emissions, and their interactions that lead to wintertime $PM_{2.5}$ episodes in the Truckee Meadows valley. The analysis is based on regulatory and auxiliary measurements. Twenty archived samples were also retrieved for analysis of organic markers and aerosol light absorption properties to facilitate source apportionment using an effective variance-chemical mass balance (EV-CMB) approach. Results of this study provide information for developing control strategies to reduce $PM_{2.5}$ levels in this and similar urban valleys.

2 Ambient monitoring data description and analysis

The central valley monitoring site in Reno (RENO_C: 39.525079° N, −119.807723° W, 1371 m above mean sea level, MSL) is located in a residential/commercial area south of the Truckee River and ∼2 km west of the US 395 north/south freeway and ∼1 km south of the I-80 east/west freeway. A Mexican restaurant is located ∼20 m east of the station. As part of the USEPA Speciation Trends Network (STN), $PM_{2.5}$ filters have been acquired every 3rd day with speciation samplers (Met One SASS + URG 3000N Carbon Sampler) for chemical characterization (Chow et al., 2010; Flanagan et al., 2006). Additional $PM_{2.5}$ and PM_{10} filter samples are taken with Federal Reference Method (FRM) samplers for gravimetric analysis of mass concentration. Continuous (hourly average) measurements in place include $PM_{2.5}$, PM_{10}, carbon monoxide (CO), reactive nitrogen oxides (NO_x), and ozone (O_3). The sampling probes are situated ∼4 m above ground level and ∼1 m above the rooftop of the shelter. Surface meteorological data are available onsite and from several valley floor and elevated weather monitoring stations as shown in Fig. 1.

Based on the FRM measurements, there were four $PM_{2.5}$ exceeding $> 35\,\mu g\,m^{-3}$ out of 20 measurements at the RENO_C site during December 2009 and January 2010 (i.e., 9 December 2009, 15 December 2009, 18 December 2009, and 5 January 2010).

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Daily beta attenuation monitor (BAM; MetOne E-BAM; Grants Pass, OR) mass reported five additional $PM_{2.5}$ exceedances (i.e., 10 December 2009, 11 December 2009, 14 December 2009, 19 December 2009, and 20 December 2009) during the period. Average two-month FRM $PM_{2.5}$ mass concentration was 17.9 $\mu g\,m^{-3}$, ~45 % higher than the corresponding period during 2008/2009 (12.3 $\mu g\,m^{-3}$) where no $PM_{2.5}$ exceedances were reported. $PM_{2.5}$ mass acquired by the continuous BAM and the speciation sampler showed good agreements with the FRM mass ($r^2 > 0.95$ and average differences within ±7 %; Watson et al., 2011).

2.1 Meteorological characteristics of $PM_{2.5}$ episodes

Urban air quality is strongly influenced by meteorology. Temperature inversions are usually associated with calm winds and low vertical dispersion that enhance accumulation of pollutants released from the surface. Horizontal dispersion is further limited by mountain ranges surrounding the valley leading to serious pollution episodes (e.g., Pope III, 1996). Valley-floor and elevated meteorological observations (Fig. 1) were used to characterize the strength of inversions in the Truckee Meadows area. The Reno rail yard site (39.5391° N 119.78605° W) is on the valley floor at an elevation of 1360 m MSL, ~1.3 km northeast of RENO_C, while the Galena Remote Automated Weather Station (RAWS) site (39.3794° N 119.8319° W) is at an elevation of 1710 m MSL, generally upwind of the Truckee Meadows, and at the top of the atmospheric boundary layer.

Good relationships were found between $PM_{2.5}$ mass at the RENO_C site and vertical temperature differences. For winter 2009/2010, Fig. 2 shows that there were three periods (i.e., 8–11 December 2009; 14–20 December 2009; and 3–6 January 2010) of persistent, multi-day inversions with maximum inversion strengths ($\Delta T = T_{Galena} - T_{Rail}$) > 5 °C and minimum $\Delta T > -2$ °C. During these periods, ΔT peaked at or just before midday. As surface heating increased during the afternoon, the inversion layer coupled to layers aloft near 1600 local standard time (LST), but re-instated itself soon after

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sunset. The highest $PM_{2.5}$ concentrations, including all 24-h exceedances, occurred near the middle of each inversion period. For other times during the winter, inversions were weak and short-lived, typically lasting no more than several hours. The region was hit by several snow storms during which no inversions occurred throughout a day. In contrast, there were no extended periods of strong inversions and fewer episodes with elevated $PM_{2.5}$ concentrations during winter 2008/2009 (Fig. 2b). Daily average ΔT is positively correlated with 24-h $PM_{2.5}$ measured by BAM (r^2 = 0.785 and 0.420 for winter 2009/2010 and winter 2008/2009, respectively).

December 2009 was the sixth coldest and fifth snowiest December (39.6 cm snowfall) recorded since 1931 at the Reno-Tahoe International Airport (RNO, see Fig. 1). Snowfall was low to moderate for the other three months (1.3–15.0 cm; December 2008, January 2009, and January 2010). Highly reflective snow cover reduces daytime surface heating, which allows the formation of persistent inversions throughout the day under stable synoptic conditions. Forty-eight out of 124 days in the two winter periods recorded snow cover of > 2.5 cm at RNO with an average daily ΔT of $0.1 \pm 3.6\,^{\circ}C$, which is significantly higher (p = 0.005) than the average daily ΔT of $-1.6 \pm 2.9\,^{\circ}C$ for the 76 days without snow cover. Certainly high ΔT can occur on days without snow cover, but heating in the afternoon on those days is usually strong enough to break the inversion completely, avoiding overnight accumulation. This was the case for most of winter 2008/2009 as shown in Fig. 2b. Snow cover also tended to increase relative humidity (RH), as RH averaged 78 % on snow-cover days and 66 % on no-snow-cover days.

Figure 3 compares BAM $PM_{2.5}$ in both winters as a function of ΔT and snow cover. All nine days with $PM_{2.5} > 35\,\mu g\,m^{-3}$ experienced 24-h ΔT of 1.5 to 4.5 °C and snow cover of 8–18 cm. There had been much less snow during winter 2008/2009 with surface snow cover always < 8 cm. No $PM_{2.5} > 35\,\mu g\,m^{-3}$ were recorded during winter 2008/2009 despite ΔT sometimes as high as the winter 2009/2010 exceedance days. On the other hand, days with deep snow cover but no inversion had only moderate $PM_{2.5}$ levels as well.

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It is apparent that $PM_{2.5}$ episodes are related to conditions of high 24-h ΔT and snow cover, which together increase the chance of prolonged primary aerosol accumaltion and secondary aerosol (e.g., NH_4NO_3 and secondary organic carbon, SOC) formation. In addition, snow cover necessitates snow plowing and blowing activities occurring both on-road and off-road. These activities increase the use of diesel and gasoline engines that may emit more primary $PM_{2.5}$ and NO_x (i.e., nitrate (NO_3^-) precursor) than during drier periods. More cold starts for commuters can also increase emissions over those found during warmer weather (Cadle et al., 2001; Chen et al., 2001; Nam et al., 2010; Weilenmann et al., 2009).

2.2 Chemical characteristics of $PM_{2.5}$ episodes

$PM_{2.5}$ mass (speciation mass hereafter unless mentioned otherwise) and speciation data were downloaded from the USEPA's Air Quality System database (AQS; http://www.epa.gov/ttn/airs/airsaqs/index.htm), which contains uncertainty estimates for each data, except for organic carbon (OC), elemental carbon (EC), and thermal carbon fractions by the IMPROVE_A protocol (Chow et al., 2007a). In addition to OC and EC, there are 48 elemental concentrations reported along with water soluble ammonium (NH_4^+), NO_3^-, $SO_4^=$, sodium (Na^+), and potassium (K^+). Mass closure for the $PM_{2.5}$ samples was calculated by summing NH_4^+, NO_3^-, $SO_4^=$, OM, EC, crustal material, and sea salt as the reconstructed mass, where:

$$\mathrm{OM} = 1.4 \times [\mathrm{OC}] \quad (1)$$

$$\text{Crustal Material} = 2.2 \times [\mathrm{Al}] + 2.49 \times [\mathrm{Si}] + 1.64 \times [\mathrm{Ca}] + 2.42 \times [\mathrm{Fe}] + 1.94 \times [\mathrm{Ti}] \quad (2)$$

$$\mathrm{Salt} = [\mathrm{Na}^+] + [\mathrm{Cl}^-] \quad (3)$$

Figure 4 shows the time series of measured and reconstructed $PM_{2.5}$ mass during the winter 2008/2009 and 2009/2010, while Fig. 5 compares concentrations of major constitutes between the two winter periods. Since $SO_4^=$ levels were low, NH_4^+ is mostly associated with NO_3^- as NH_4NO_3, which, along with OM, dominates the $PM_{2.5}$ mass. The

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sum of constituents exceeds the measured mass for samples from winter 2008/2009 except 8 December 2008 and 13 January 2009, leading to overall negative unidentified mass (UnID). For winter 2009/2010, however, UnID is generally positive. Negative UnID could result from overestimating OM. Using a multiplier of 1.4 for OC (Eq. 1) may be too high for sources such as biomass burning and mobile exhausts (Aiken et al., 2008; El-Zanan et al., 2005; Russell, 2003) and the organic sampling artifact may not be sufficiently subtracted for the STN (Chow et al., 2010; Watson et al., 2009). Positive UnID indicates unaccounted species such as water.

The higher average $PM_{2.5}$ concentration during winter 2009/2010 mainly results from increasing NH_4NO_3 and UnID contributions (Fig. 5). Despite high OM concentrations on episode days (i.e., 9 December 2009, 15 December 2009, 18 December 2009, and 5 January 2010), OM averaged lower for winter 2009/2010 than winter 2008/2009. For instance, the 5 January 2010 sample contained 3.2 times the NO_3^- concentration of 1 January 2009 (8.4 $\mu g\,m^{-3}$ versus 2.6 $\mu g\,m^{-3}$) and a high UnID (4.6 $\mu g\,m^{-3}$) but their OM was comparable (18.5 $\mu g\,m^{-3}$ versus 17.2 $\mu g\,m^{-3}$ on 1 January 2009 and 5 January 2010, respectively). The Teflon-membrane filters were weighed at 30–40 % RH but water strongly bound to NH_4NO_3 may not be removed completely due to a hysteresis effect (Speer et al., 2003). If so, NH_4NO_3 plays a critical role in $PM_{2.5}$ exceedances during winter 2009/2010. This is consistent with observations from the nearby, but much larger, San Joaquin Valley, California during winter (Chen et al., 2007b; Chow et al., 2006a; Watson and Chow, 2002).

Teflon-membrane filter samples and the remnants of quartz-fiber filter samples for winter 2009/2010 were retrieved from the CSN archive and submitted to the following analyses: (1) thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS; Chow et al., 2007d; Ho et al., 2008; Ho and Yu, 2004) for non-polar organic compounds, including ~ 120 polycyclic aromatic hydrocarbons (PAHs), hopanes, steranes, alkanes, and alkenes; (2) water extraction/total organic carbon (TOC; Yang et al., 2003) analysis for water-soluble organic carbon (WSOC); (3) ion chromatography-pulsed amperometric detection (IC-PAD; Engling et al., 2006) for levoglucosan; and (4) two-wavelength

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optical transmissometer (Ahmed et al., 2009; Chen et al., 2010b) for light absorption (b_{abs}) at 370 and 880 nm. The detailed analytical techniques are described in Watson et al. (2011). Twenty measurements were acquired for each of the species except for WSOC and levoglucosan on 18 December 2009 and 2 January 2010 where there were insufficient quartz-fiber filter remnants.

The temporal variations and relative abundances of organic species are presented in the Supplement, along with their two-month averages/signal-to-noise ratios (SNR; Fig. S1 and Table S1). n-Alkanes were the most abundant organic compounds with concentrations ranging from 6.1 ng m^{-3} (20 January 2010) to 79.1 ng m^{-3} (9 December 2009), with abundant n-tetracosane (tetcos), n-hentriacontane (htricont), and n-pentacosane (pencos). The most abundant cyclo-/branched alkanes are anteiso-dotriacontane (anteisoc32), iso-tritriactotane (isoc33), and iso-hentriacotane (isoc33). Particle-bound PAHs (p-PAHs) are air toxics that derive from many combustion sources. The sum of measured p-PAH concentrations ranges from 0.82 ng m^{-3} (2 January 2010) to 46.2 ng m^{-3} (9 December 2009). Abundant p-PAH species include cyclopenta[c,d]pyrene (cp-cdpyr), retene, and benzo[b,j,k]fluoranthene (bbjkfl). Retene, a known marker for coniferous wood combustion (Ramdahl, 1983), appears to be more enriched in Truckee Meadows (13 ± 5 % of total p-PAHs) than areas dominated by mobile sources (e.g., 1 ± 1 % in Chen et al., 2012). Hopanes and steranes originate from oil combustion or from vehicle lube oil (Zielinska et al., 2008), and are < 5 ng m^{-3} with the dominant species being $\alpha\alpha\alpha$ 20S 24R/S-ethylcholestane (ster12), 17α[H], 21β[H]-30-norhopane (hop17), and 17α[H], 21β[H]-hopane (hop19).

Both WSOC and levoglucosan concentrations were high, particularly during the episode days. On 9 December 2009, WSOC reached almost 7 µg m^{-3} while levoglucosan exceeded 1 µg m^{-3}. Levoglucosan has been considered as a primary marker for biomass burning (Chow et al., 2007b) and this supports the importance of residential wood combustion (RWC) over this episode.

Aerosol b_{abs} at 370 and 880 nm both correlate well with EC concentrations (r^2 = 0.9). The regression slopes are 21.3 m^2 g^{-1} for 370 nm and 13.6 m^2 g^{-1} for 880 nm. This

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confirms EC as the dominant light-absorbing component. The Ångström absorption exponent (AAE), determined from (Chen et al., 2006; Moosmüller et al., 2009):

$$\mathrm{AAE} = -\frac{\ln(b_{\mathrm{abs},370}) - \ln(b_{\mathrm{abs},880})}{\ln(370) - \ln(880)} \quad (4)$$

ranges from 0.61 to 1.32. Biomass burning aerosol from smoldering combustion generally shows AAE (> 1) higher than those from flaming combustion or motor vehicle exhausts with AAE < 1 (Chakrabarty et al., 2010; Chen et al., 2010b; Kirchstetter et al., 2004). In this study, AAE appears to be the lowest during $PM_{2.5}$ episodes (Fig. 6), suggesting contribution from flaming RWC and motor vehicles. The spectral characteristics of b_{abs} for the episode and non-episode periods are confirmed by in situ, continuous measurements (Gyawali et al., 2012). Emissions from smoldering combustion do not seem to be important.

3 Chemical mass balance source apportionment

The EV-CMB method (Chen et al., 2010a; Chow and Watson, 2002; Held et al., 2005; Watson et al., 1984, 2008) uses both source profiles and ambient concentrations as inputs to calculate source contribution estimates (SCEs) and associated uncertainties for individual samples. EV-CMB inputs and results are reported here.

3.1 Source profiles

Source profiles assembled for this study are identified and referenced in supplemental Table S2. Major source types include: (1) geological materials; (2) motor vehicles (gasoline and diesel); (3) biomass burning (RWC and open burning); (4) cooking; (5) utility combustion; and (6) secondary aerosol, corresponding to a local $PM_{2.5}$ emission inventory for 2008 (Ling-Barnes, 2010). Profiles most relevant to the region were selected. Two fugitive dust samples (i.e., paved road dust (RNOPVRD), surface soils

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from a vacant lot (RNOSOIL)) were obtained from representative locations around the RENO_C site along with two types of de-icing material (RNOSalt1 and RNOSalt2). These samples were dried, sieved, and resuspended in chamber, following a procedure in Chow et al. (1994), to create $PM_{2.5}$ source profiles for this study. Chemical analyses applied to these samples were identical to those for ambient samples, though WSOC and levoglucosan were not quantified and set to zero owing to low OC contents (1.1–14.9 %, see Table S3).

Mobile source profiles considered include those acquired from the National Renewable Energy Laboratory Gas/Diesel Split Study (Fujita et al., 2007a,b) and the Las Vegas Carbon Source Apportionment Study (LVCSAS; Green et al., 2004). These profiles are more recent and contain full organic speciation except for alkanes. They have been used in other CMB analyses (Chow et al., 2007b; Green et al., 2012). The gas/diesel split profiles were based on dynamometer tests of 57 gasoline and 32 diesel vehicles while LVSAS adopted an in-plume monitoring system (Nussbaum et al., 2009; Zhu et al., 2009) at traffic intersections where air was dominated by a mixture of motor vehicle exhausts. Both studies were conducted in Nevada or neighboring California and considered extrapolative to traffic fleets in Truckee Meadows.

The RWC source profiles resulted from tests during the Central California $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS; Fitz et al., 2003) and the Lake Tahoe Source Characterization Study (LTSCS; Kuhns et al., 2004). CRPAQS focused on fireplace emissions while LTSCS tested both fireplaces and woodstoves. Both studies examined hardwood (i.e., oak, almond, and eucalyptus) and softwood (i.e., pine, tamarack, and juniper) combustion separately, resulting in six composite profiles. Levoglucosan's abundance ranges from 0.1 % to 55.5 % among these six profiles. This suggests that RWC emissions are highly variable depending on fuel and combustion conditions, as indicated by Chen et al. (2007a, 2010b). Open burning including wildland fires are not expected to contribute significantly during winter months.

Due to the proximity of the RENO_C site to a Mexican restaurant, a meat cooking profile (BVCOOK, a composite of charbroiled chicken, chicken over propane, and

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charbroiled hamburger) as part of CRPAQS was included. Chow et al. (2007b) found meat cooking to be an important contributor at the Fresno supersite during winter. The markers for meat cooking are often associated with polar compounds such as cholesterol, palmitic acid, palmitoleic acid, stearic acid, and oleic acid (Fraser et al., 2003; Rinehart et al., 2006). However, the archived ambient samples were not amenable to analyses of these components.

Most of the point source profiles in the literature do not contain organic markers and eventually were not included in the CMB modeling. This is justified by the lack of major point sources, such as coal-fired power plants and other large industrial factories, in Truckee Meadows and low long-range transport potential in winter. Secondary NO_3^- and SO_4^{-2} sources are represented by pure NH_4NO_3 (AMNIT) and $(NH_4)_2SO_4$ (AMSUL) profiles, respectively. Secondary OC is represented by a profile (SOC) containing exclusively (100 %) OC (Watson, 1979). This is equivalent to using the OC/EC ratio method to estimate SOC.

Table S1 indicates the EV-CMB fitting species. Important source markers that are commonly detectable in ambient samples and their corresponding sources include (e.g., Chow et al., 2007b; Watson et al., 2008): (1) Al, Si, Ca, Fe, Mn, K, Ti, and Sr for geological material/minerals; (2) EC and hopanes for diesel exhaust; (3) indeno[1,2,3,cd]pyrene (incdpy), benzo[g,h,i]perylene (bghipe), and coronene (corone) for gasoline engine exhaust; (4) K^+, retene, and levoglucosan for biomass burning; (5) pristane, and phytane for cooking; (6) Cu, Zn, As, Se, Br, Pb for industrial/utility; (7) Na^+, Cl for de-icing, playas, and sea salt; and (8) S, and NO_3^- for secondary inorganics. OC is not a specific marker but it is a major $PM_{2.5}$ constituent. Temperature-resolved carbon fractions were not used as they were mostly determined by IMPROVE protocol in source profiles but by IMPROVE_A protocol in ambient samples acquired after 2007. The two protocols are known to yield comparable OC and EC measurements but different carbon fractions (Chow et al., 2005, 2007a).

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3.2 Sensitivity tests

As recommended by Watson (2004), sensitivity tests should be performed on several samples to evaluate the performance of different source profile combinations in terms of correlation (r^2), root mean square difference (χ^2), and percent of mass explained (%MASS). The initial source profile combination is modified in subsequent trials to examine changes in the SCEs and EV-CMB performance measures. Often, only one profile in each source type may be included since similar profiles result in collinearity, non-convergence, and/or negative source contributions. An acceptable solution requires %MASS between 0.9 and 1.1, $r^2 > 0.9$, and $\chi^2 < 2$. The modified pseudo-inverse normalized (MPIN) matrix would indicate the most influential species (e.g., MPIN value > 0.5) for each source type.

Table S4 illustrates two examples of sensitivity test (an episode day on 5 January 2010 and a median loading day on 17 January 2010). Better EV-CMB fits to the data result from combinations of paved road dust (RNOPVRD), road salt (RNOSALT2), mobile source (gasoline and diesel engine exhaust; GAS and DIESEL, respectively), RWC (fireplace and woodstove burning hardwoods; CRBURN_H and LTWS_H), and secondary (AMNIT and AMSUL) source profiles. Note that profile DIESEL may represent both on-road and off-road diesel engine emissions. Gasoline-engine exhaust contributions appear to be minor compared with those from diesel engines. Including softwood RWC profiles in the CMB model always lowered the overall model performance.

Including the cooking (BVCOOK) profile improves performance measures (e.g., lower χ^2 and higher %MASS). However, the cooking contribution would be comparable to or even greater than the combined contribution from gasoline and diesel engine exhaust (Table S4). The MPIN matrix suggests that OC is the only important species identifying the cooking source. Due to the lack of more specific cooking markers such as cholesterol and palmitoleic acid, BVCOOK was deselected. Adding SOC into the mix led to non-convergence in both tests.

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The MPIN matrices for the selected source combination (Table S5) indicates that the most important diesel engine exhaust marker is EC, followed by Zn while the gasoline engine exhaust contribution is marked by corone. Incdpy and bghipe are found to be more associated with the wood stove profile (i.e., LTWS_H), of which contribution is also sensitive to levoglucosan, OC, and 17α(H), 21β(H)-hopane. This explains the low gasoline engine exhaust SCEs by EV-CMB. The fireplace emission (i.e., CRBURN_H) is marked by retene and K^+. Si is the most influential species for paved road dust profile (i.e., RNOPVRD), followed by Al and Ca. Fe, however, is associated with a de-icing profile (i.e., RNOSalt2) along with Na^+ and Cl. Water-soluble iron cyanide compounds are widely used as anticaking agents in road salt. NO_3^- and S are unambiguous markers for secondary NH_4NO_3 and $(NH_4)_2SO_4$, respectively.

Figure 7 compares measured and calculated $PM_{2.5}$ species concentrations. For the 5 January 2010 sample, the EV-CMB solution explains measured species well except for the carbon fractions (EC1, EC2, and OP, not included in the fitting), Pb, As, 22R-17α(H), 21β(H)-30,31,32-Trishomohopane (hop27), and phytane. In addition, Cl, Ti, Br, Cu, Rb, and all hopanes were not fitted as well for the 17 January 2010 $PM_{2.5}$ sample. None of these species, however, are source markers. Removing these species does somewhat alter the SCEs but the changes are within the uncertainty intervals.

3.3 Source contribution estimates

Figure 8 shows the winter 2009/2010 SCEs for $PM_{2.5}$, OC, and EC. RWC is resolved for all samples, though the partition between fireplace and woodstove contributions varies. Woodstove contributions are missing for the 18 December 2009 and 2 January 2010 samples because levoglucosan data were not available on these two days. Diesel contributions show up every day except 26 January 2010 when only gasoline engine exhaust was detected. This abnormality is hard to explain but is a reminder of the uncertainty in separating diesel and gasoline source contributions even with organic markers. De-icing contributions are also resolved for every sample except 26 January 2010, while paved road dust contribution does not appear on 3–9 December

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2009, 15–18 December 2009, and 30 December 2009. De-icing material contributed more to $PM_{2.5}$ than paved road dust during December 2009, while the opposite was true during January 2010. This is consistent with higher snowfalls in December 2009 since snow covers reduce fugitive dust but increase salting and plowing activities. Secondary $(NH_4)_2SO_4$ is resolved for all samples except 2 January 2010, although its contribution never exceeded 0.25 $\mu g\,m^{-3}$. EV-CMB-calculated $PM_{2.5}$ mass concentrations are generally lower than measured $PM_{2.5}$. A strong correlation (r^2 = 0.89) between the unexplained $PM_{2.5}$ mass and secondary NH_4NO_3 (AMNIT) contribution supports water associated with NH_4NO_3 as a major component of unexplained mass (Fig. 9).

RWC, diesel engine exhaust, and secondary NH_4NO_3 are the major $PM_{2.5}$ contributors during NAAQS exceedances. The highest RWC contribution of 26.6 $\mu g\,m^{-3}$ or 51 % of $PM_{2.5}$ mass occurred on 9 December 2009. Most of the RWC was attributed to fireplace emissions. An intense and persistent inversion layer and deep snow cover, coupled with low temperatures during the day (daily mean: −13 °C), enhanced RWC emissions and accumulation. Secondary NH_4NO_3 accounted for 26.7 % of $PM_{2.5}$ mass on 9 December 2009. NH_4NO_3 is also favored by low temperatures and high RH (Chow et al., 2008; Watson et al., 1994; West et al., 1999). Diesel engine exhaust explained another 6.5 % of $PM_{2.5}$ while other sources were minor contributors (0–3 %). For the other episode days (15 December 2009, 18 December 2009, and 5 January 2010), RWC contributions were lower (11–39 %) while diesel contributions were higher (13–22 %). Higher ambient temperatures, i.e., daily mean: 0–1 °C, compared to those of 9 December 2009 may explain the difference. Nevertheless, ambient temperatures on the three days appear to be low enough for NH_4NO_3 formation–NH_4NO_3 fractions ranged from 27 % to 37 %. Paved road dust was an important contributor (5.7 %) only on 5 January 2010.

RWC from fireplaces also dominated the ambient OC concentrations (Fig. 8). On 15 December 2009 and 18 December 2009, diesel exhaust was almost as important as RWC as an OC source. The unexplained OC, up to 44 % of measured OC, may be in part attributed to a positive organic sampling artifact, which was not adequately

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corrected for the STN samples (Chow et al., 2010). Since OC was quantified on quartz-fiber filters and mass was measured on teflon-membrane filters, this artifact should not contribute to the unexplained $PM_{2.5}$ mass. Certainly the missing OC might also result from SOC and/or differences between the selected source profiles and the actual (but unknown) profiles typical of local RWC emissions. The EV-CMB model explains EC better than OC. There is no organic sampling artifact associated with EC. Diesel engine exhaust is found to be the dominant EC source.

3.4 Origins of secondary ammonium nitrate

Comparing $PM_{2.5}$ chemical speciation of winter 2009/2010 with winter 2008/2009 shows that the higher secondary NH_4NO_3 lifted $PM_{2.5}$ concentrations over the $35\,\mu g\,m^{-3}$ threshold. The formation of NH_4NO_3 may depend on gaseous ammonia (NH_3) or nitric acid (HNO_3; derived from NO_x emissions) concentrations and be influenced by ambient temperature and RH (Watson and Chow, 2002). Ion balance shows a full neutralization of NO_3^- and SO_4^{-2} by NH_4^+ during the $PM_{2.5}$ episodes and so NO_x emission and oxidation likely limits the NH_4NO_3 formation in the valley.

Most wintertime NO_x is generated from local sources, particularly mobile source and RWC emissions. Compression-ignition engines used in diesel vehicles have long been considered important NO_x sources owing to a high combustion temperature (Chow, 2001; Lloyd and Cackette, 2001). Biomass burning, especially high-temperature flaming combustion, may also generate substantial NO_x (Chen et al., 2007a; 2010b). Other Truckee Meadows NO_x sources include natural gas combustion in furnaces and boilers (Ling-Barnes, 2010), which have higher emissions during winter than other seasons. Coal-fired power plant contributions and other distant sources can be excluded as NO_x/NO_3^- contributors during winter.

To a first approximation, secondary NH_4NO_3 affiliated with mobile sources or RWC was estimated from regressing AMNIT contributions against mobile and RWC contributions. A robust regression method (Huber, 1981) was applied which involves iterative reweighting of the input data values to lessen the influence of extreme values. The two

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RWC profiles (i.e., CRBURN_H and LTWS_H) were combined to form an overall RWC contribution while the diesel and gasoline profiles (i.e., DIESEL and GAS) were pooled to represent the mobile source contribution. The regression of AMNIT against the RWC and mobile contributions together yielded a good correlation (r^2 = 0.81), better than the regression correlations against RWC or mobile contributions alone (r^2 = 0.45–0.65). The regression coefficients are 0.34 and 1.20 for RWC and mobile sources, respectively, suggesting that 0.34 and 1.2 $\mu g\,m^{-3}$ secondary NH_4NO_3 is produced per $\mu g\,m^{-3}$ of primary $PM_{2.5}$ emitted from the RWC and mobile sources, respectively.

Figure 10 shows mobile- and RWC-affiliated secondary NH_4NO_3, which explains total NH_4NO_3 (i.e., AMNIT) levels for three of four high $PM_{2.5}$ days: 9 December 2009, 15 December 2009, and 5 January 2010. (Note: RWC contribution on 18 December 2009 is underestimated due to missing levoglucosan measurement.) Although the mobile sources did not contribute to primary $PM_{2.5}$ as much as RWC during winter 2009/2010, the mobile-source contribution might be responsible for ~2/3 of secondary NH_4NO_3.

4 Conclusions

The Truckee Meadows is an urban valley in the arid west of the US with light-to-moderate snowfall and frequent subsidence in winter. Wintertime air quality in the valley was found to be highly influenced by RWC for heating (Chow et al., 1988). It has been improving through measures that reduced the number of low-efficiency woodburning appliances and improved fuels and burning practices. However, four FRM and nine BAM $PM_{2.5}$ samples have exceeded 35 $\mu g\,m^{-3}$ NAAQS at a central valley site during December 2009 and January 2010 (winter 2009/2010), while no exceedances were reported during the previous winter (2008/2009). The formation of $PM_{2.5}$ episodes show meteorological and chemical characteristics that may be experienced by similar urban areas.

First, the highest $PM_{2.5}$ concentrations were accompanied by intense and prolonged (multi-day) temperature inversions, snow on the ground, and low wind speeds. These

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variables are inter-related, as snow cover increases the reflectance of sunlight, thereby decreasing heating at the surface that would break up the inversion. Most of the surface heating that remains is absorbed as latent heat, melting the snow rather than raising the surface temperature. The prolonged inversion creates a stagnant condition that inhibits ventilation by wind.

Second, although carbonaceous material including OC and EC dominated the $PM_{2.5}$ mass, it is the much higher NH_4NO_3 and unidentified mass concentrations in winter 2009/2010 that lifted $PM_{2.5}$ levels over the 35 $\mu g\,m^{-3}$ threshold. The low temperatures and higher RH associated with snow cover and melting snow encourage a shift in equilibrium for gaseous HNO_3 and NH_3 to the particulate NH_4NO_3, thereby increasing its contribution to $PM_{2.5}$ mass. Liquid water associated with NH_4NO_3 explains significant unidentified mass in the samples, especially during the $PM_{2.5}$ episodes. The water may not completely leave these particles until RH decreases below 30 %.

The EV-CMB receptor model using locally-derived geological profiles and inorganic/organic markers found that RWC, diesel exhaust, and NH_4NO_3 were major contributors to $PM_{2.5}$. Paved road dust and de-icing materials were minor, but detectable contributors. Gasoline engine exhaust was a small contributor, as was secondary $(NH_4)_2SO_4$ that never exceeded a 0.25 $\mu g\,m^{-3}$ contribution to $PM_{2.5}$ mass. Contributions from large industrial sources (e.g., coal-fired power stations) were not determined, though they are expected to be minor with negligible long-range transport to and from the Truckee Meadows during winter stagnations. Cooking and SOC sources were not detected, either.

RWC contribution ranged from 11–51 % of $PM_{2.5}$ mass on four exceedance days identified by FRM (i.e., 9 December 2009, 15 December 2009, 18 December 2009, and 5 January 2010). Most of the RWC was attributed to fireplace emissions burning hardwoods. The wide range of RWC contribution may reflect different ambient temperatures, as lower temperatures increase home heating demand. Secondary NH_4NO_3 accounted for 27–37 % of $PM_{2.5}$ while diesel engine exhaust explained 7–22 % of $PM_{2.5}$. Paved road dust was an important contributor (5.7 %) only on 5 January 2010.

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A multiple linear regression of the NH_4NO_3 contribution on weighted sum of the mobile source and wood burning contributions suggested that about 2/3 of the NH_4NO_3 was associated with mobile source emissions and 1/3 with RWC emissions. This indicates that most of the NO_3^- derives from engine NO_x emissions, and therefore snow plowing and blowing activities with on-road and off-road diesel engines do provide a possible reason for the relationship between snow cover and elevated NH_4NO_3 and $PM_{2.5}$ concentrations. Reducing use of diesel-powered equipments and restricting domestic burning for unfavorable pollution meteorology forecasts should contribute to the prevention of future NAAQS exceedances.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/12/15801/2012/acpd-12-15801-2012-supplement.pdf.

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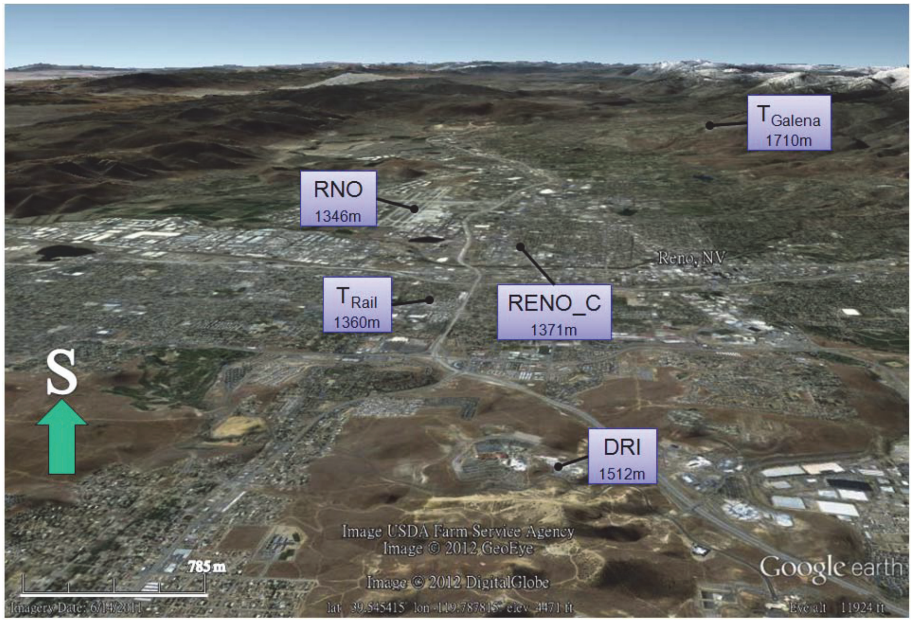

Fig. 1. Topography of the Truckee Meadows valley and locations/elevations of $PM_{2.5}$ monitoring site (RENO_C), valley-floor weather station (Reno Rail Yard, T_{Rail}), elevated weather station (Galena, T_{Galena}), Reno-Tahoe International Airport (RNO), and the Desert Research Institute (DRI).

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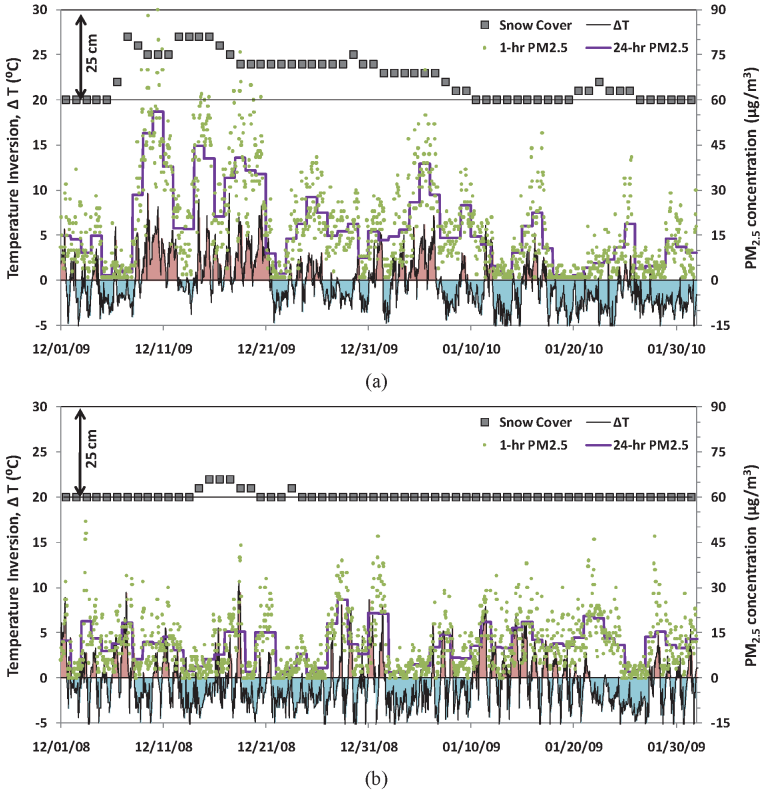

Fig. 2. Snow cover (daily), temperature inversion ($\Delta T = T_{\text{Galena}} - T_{\text{Rail}}$), and corresponding $PM_{2.5}$ mass concentrations by beta attenuation monitor (BAM) during: **(a)** December 2009–January 2010, and **(b)** December 2008–January 2009. $\Delta T > 0$ (i.e., with inversion) and $\Delta T < 0$ are marked by red and blue, respectively.

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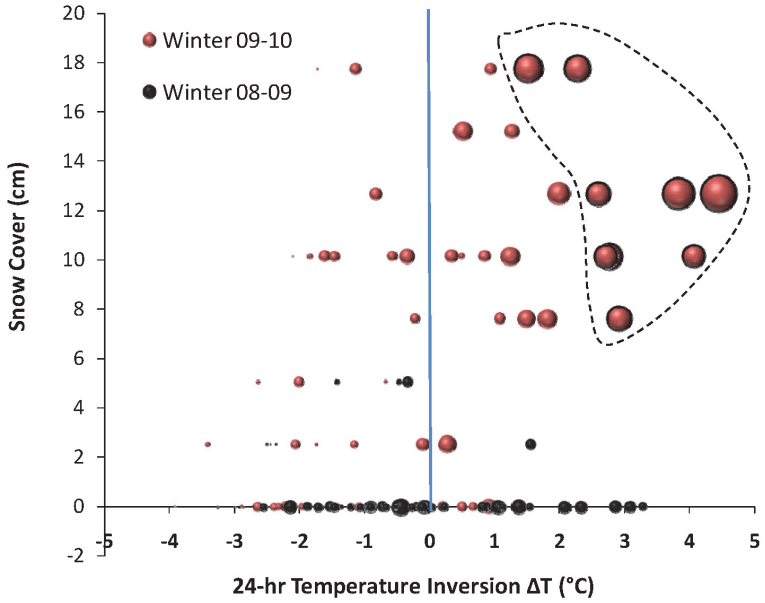

Fig. 3. Average 24-h $PM_{2.5}$ mass concentration (bubble diameter) by beta attenuation monitor (BAM) as a function of temperature inversion ($\Delta T = T_{Galena} - T_{Rail}$) and snow cover. The largest bubble corresponds to 56.1 $\mu g\,m^{-3}$ of $PM_{2.5}$. The dashed circle encloses all nine days that exceed the USEPA 24-h $PM_{2.5}$ National Ambient Air Quality Standard (NAAQS) of 35 $\mu g\,m^{-3}$.

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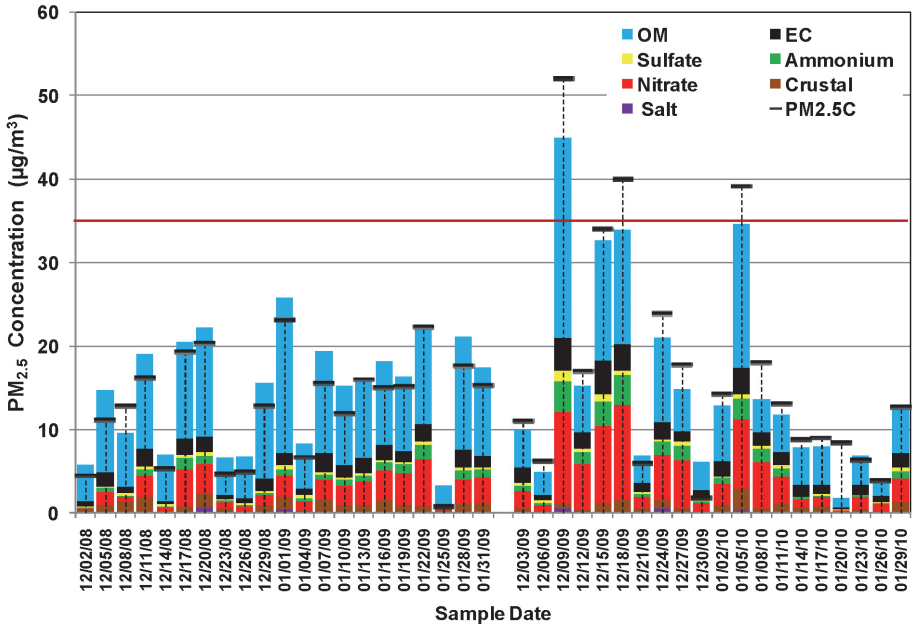

Fig. 4. $PM_{2.5}$ mass reconstruction as compared to speciation mass ($PM_{2.5}C$) during winter 2008/2009 and 2009/2010. The red line indicates the USEPA 24-h $PM_{2.5}$ National Ambient Air Quality Standard (NAAQS) of 35 µg m^{-3}. The 15 December 2009 sample exceeds the NAAQS by FRM mass but not by speciation mass (34 µg m^{-3}). Reconstructed mass is calculated as: OM = 1.4 × [OC]; Crustal Material = 2.2 × [Al] + 2.49 × [Si] + 1.64 × [Ca] + 2.42 × [Fe] + 1.94 × [Ti]; and Salt = [Na^+] + [Cl^-].

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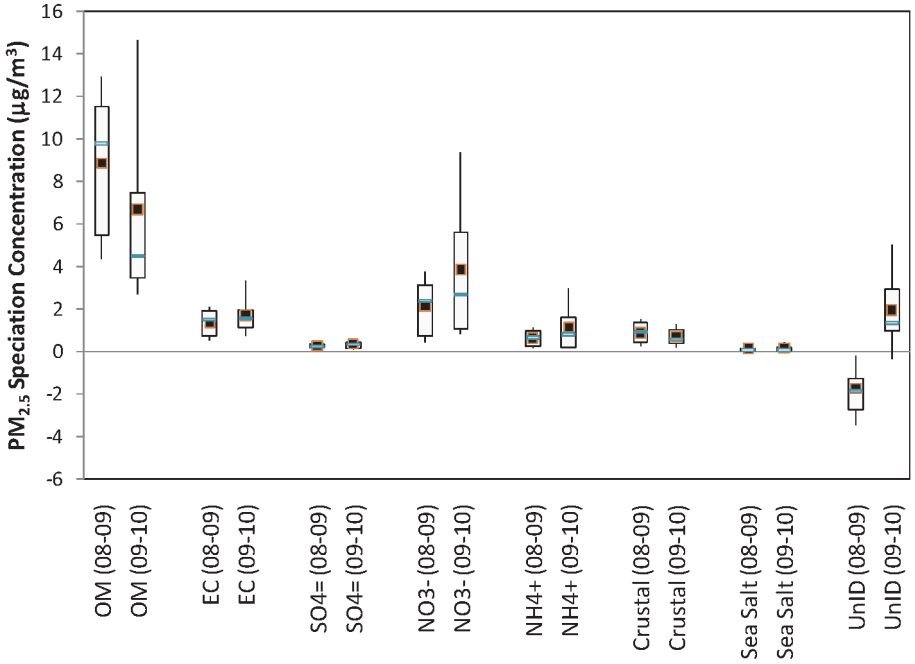

Fig. 5. Concentrations of major $PM_{2.5}$ constituents (i.e., square: average; bar: median; box: 25th and 75th percentiles; whiskers: 10th and 90th percentiles) during winter 2008/2009 and 2009/2010. UnID is the unidentified mass (i.e., measured minus reconstructed $PM_{2.5}$ mass).

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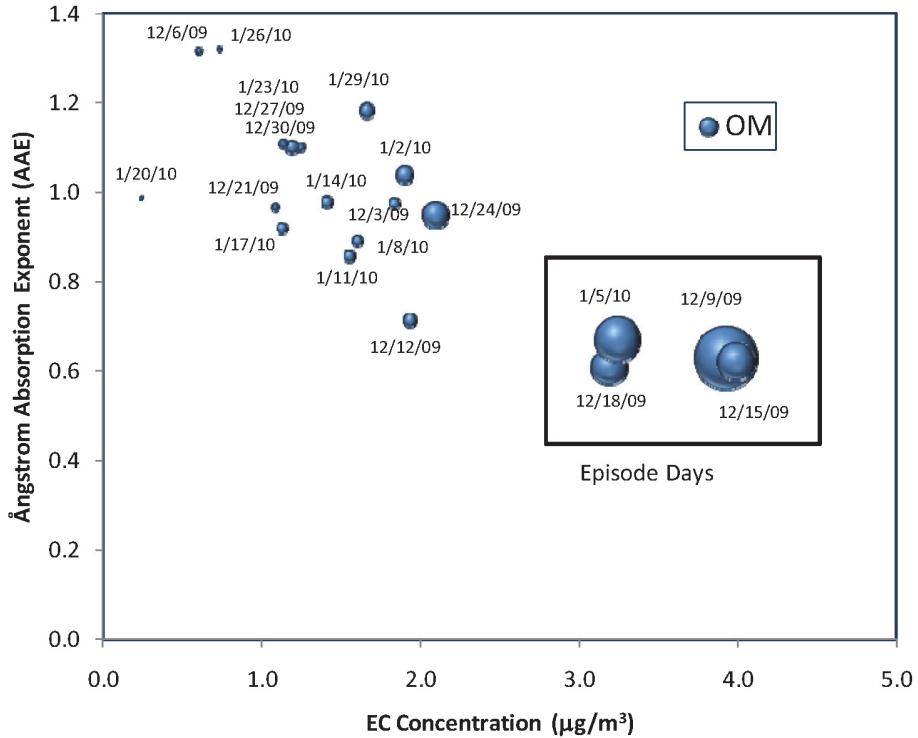

Fig. 6. Ångstrom Absorption Exponent (AAE) as a function of elemental carbon (EC) and organic material (OM) concentration. Diameter of the spheres is proportional to the OM concentration where OM = 1.4 × OC. Days exceeding the USEPA 24-h $PM_{2.5}$ National Ambient Air Quality Standard (NAAQS) of 35 µg m^{-3} are identified.

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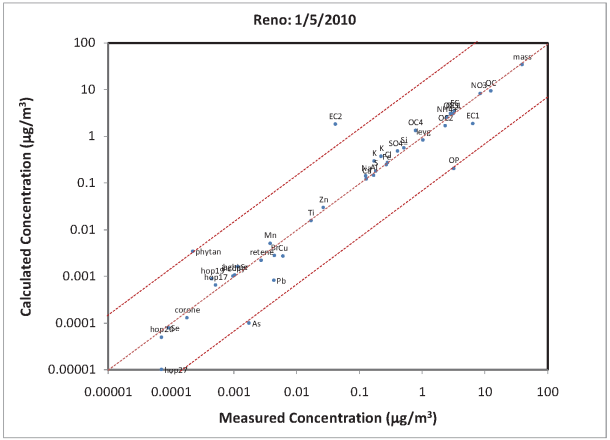
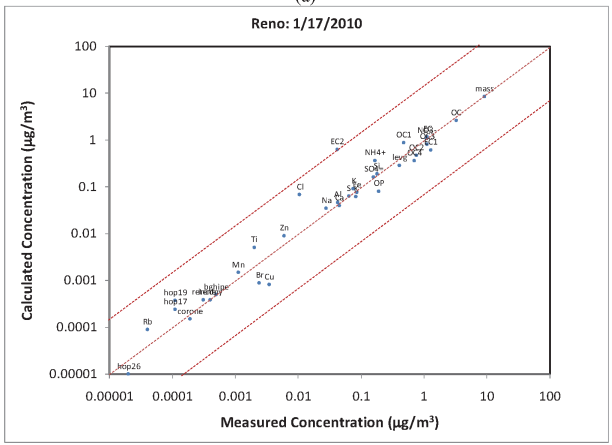


(a)



(b)

Fig. 7. Comparisons of EV-CMB calculated versus measured $PM_{2.5}$ species for: **(a)** 5 January 2010 and **(b)** 17 January 2010 samples from the Reno monitoring site (RENO_C).

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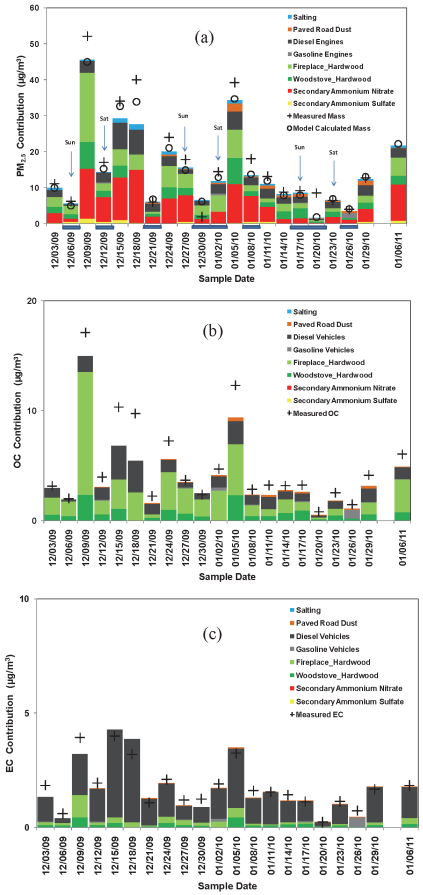

Fig. 8. Effective Variance-Chemical Mass Balance (EV-CMB) $PM_{2.5}$ source apportionment for: **(a)** mass, **(b)** OC, and **(c)** EC. Measured and model calculated mass are compared. Sundays and Saturdays are noted in **(a)**.

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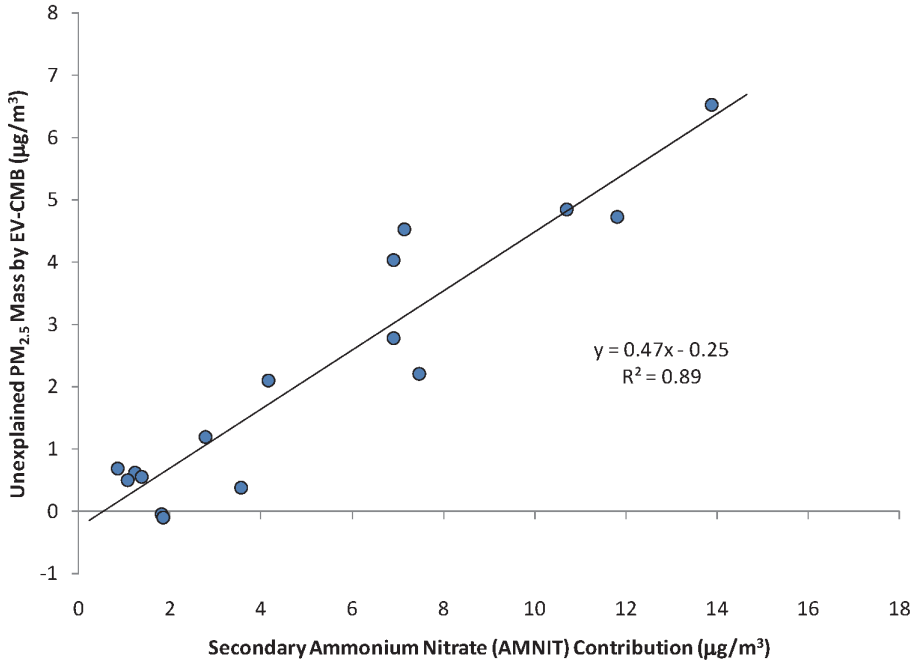

Fig. 9. Relationship between unexplained $PM_{2.5}$ mass and secondary ammonium nitrate contribution by EV-CMB analysis. Four data points were excluded due to either missing levoglucosan measurements (18 December 2009 and 2 January 2009) or very poor mass closure (30 December 2009 and 20 January 2010).

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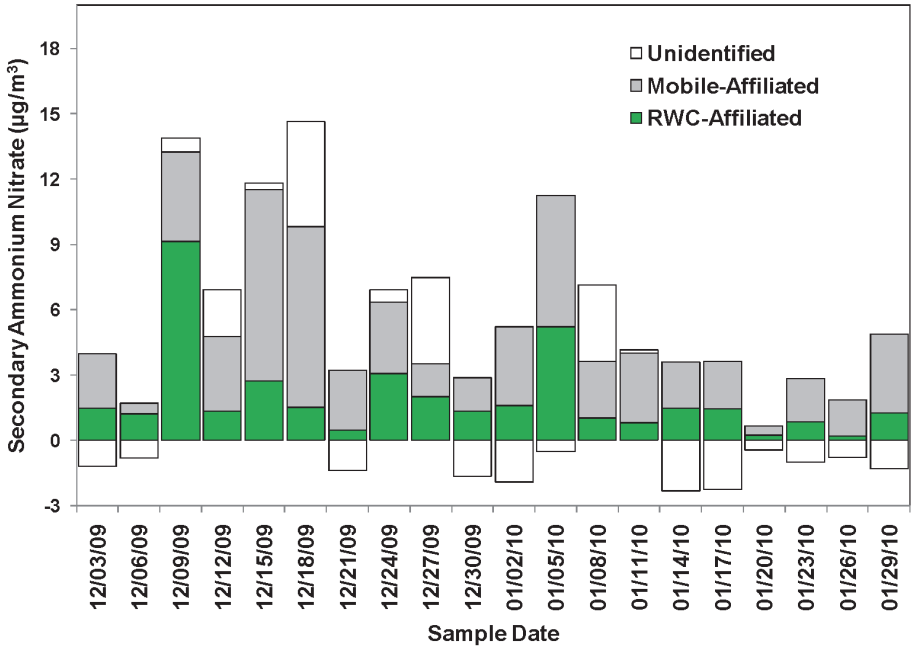

Fig. 10. Source apportionment of secondary ammonium nitrate by robust linear regression.

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