

Enhanced PM_{2.5} Source Apportionment Using Chemical Mass Balance Receptor Modeling and Scanning Electron Microscopy

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Abstract

One of the weaknesses of using receptor models to apportion the sources of ambient particulate matter is their inability to separate collinear sources such as different types of geological material. In order to develop a methodology to separate the different geological source contributions an ambient monitoring and source apportionment study was carried out for the cities of Reno and Sparks, NV during summer 1998. Chemical Mass Balance (CMB) receptor modeling was performed to estimate the contributions of both anthropogenic and natural sources to the observed ambient concentrations. Scanning electron microscopy was used to examine the geological component of the PM_{2.5} to determine the sources of that component. Chemical mass balance receptor modeling showed the dominant contribution to summertime PM_{2.5} mass in Reno and Sparks to be motor vehicle sources (~68%). Geological material was the second most abundant component of the PM_{2.5} (~14.5%). Sulfate was the predominant secondary species during the measurement period (~11%). The remaining components of significance were vegetative burning (~4%), secondary nitrates (~2%), and salt (NaCl) (0.6%). Scanning electron microscopy of selected ambient samples on a particle-by-particle basis showed the mineral component of the PM_{2.5} was predominantly aluminum-silicate in nature with a wide range of composition percentages for the major aluminum-silicate minerals (Na, Mg, Al, Si, K, and Ca). Virtually all of the particles examined had P and S in the typical aluminum-silicate spectra, which is attributed to contact with mobile source emissions. In approximately 10% of the examined particles were metallic in nature. Barium was also noted as a minor constituent of some particles, suggesting incorporation of diesel vehicle emissions. This evidence suggests that the source of the majority of the PM_{2.5} of geological origin in Reno and Sparks during the study period was from the resuspension of paved road dust. Thus, the amount of PM_{2.5} attributed to mobile source activity was in excess of 80%.

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1. Introduction

In northern Nevada, particulate and gaseous emissions from anthropogenic and natural sources often combine with meteorology to create high levels of air pollution. The Truckee Meadows, in which the urban centers of Reno and Sparks are located, was designated as moderate non-attainment for CO (carbon monoxide) and PM₁₀ (particulate matter with aerodynamic diameter of 10 μm or less) in 1990 (non-compliant for both the 24-hour and annual federal standard) and marginal for O₃ (ozone) in 1992 (U.S. EPA 1997). Washoe County has not violated the National Ambient Air Quality Standard (NAAQS) for ozone since 1990 or for CO since 1991 and was redesignated

as attainment for O₃ in 1998. However, the 24-hour PM₁₀ standard ($\geq 150 \mu\text{g m}^{-3}$) was exceeded on January 6, 1999. This is the first violation for PM₁₀ since 1993, and indicates that PM is still an important pollutant that affects air quality in the Truckee Meadows. Despite general improvement in the reduction of PM₁₀ violations, there is still a need to understand the various emission sources in the Truckee Meadows, especially their contributions to ambient PM concentrations. This is especially true for PM_{2.5}, the pending and potentially more stringent NAAQS standard for PM (U.S. EPA 1997).

There are several different sources of particulate matter in the Reno-Sparks area. These include but are not limited to motor vehicle exhaust, residential wood combustion, resuspended geological material, industrial processes, and secondary species such as ammonium nitrate and

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ammonium sulfate. The apportionment of ambient aerosol mass to different sources of geological particles is a difficult problem because of the similarity of the chemical composition of these sources. The goal of this study was to characterize the current summer $PM_{2.5}$ levels in Reno and Sparks and to identify and apportion the contributing sources, including the fugitive dust. To achieve this goal, twenty-four-hour $PM_{2.5}$ samples on filters were taken at two sites in Reno and Sparks, NV. Sampling for $PM_{2.5}$ took place every third day. The sampling period began on 07-17-98 and ended on 09-11-98. The chemical mass balance (CMB) receptor model (Watson et al. 1990) was used to apportion the $PM_{2.5}$ to its sources. In addition, manual scanning electron microscopy was used to examine the $PM_{2.5}$ particles (Mamane 1988, Mamane et al. 1998) to aid in the identification of the source of the mineral particles.

2. Methodology

2.1. Ambient Measurements

Particulate matter samples were collected using $PM_{2.5}$ medium-volume (MedVol) samplers designed to collect samples for chemical analyses (Gertler et al. 1993). This type of sampler employs a Bendix $PM_{2.5}$ cyclone to determine the size fractions collected. The ambient air is transmitted through the size-selective inlet and into a plenum. The flow rate is controlled by maintaining a constant pressure across a valve with a differential pressure regulator. For the size-selective inlet to work properly, a flow rate of 113 lpm must be maintained through the sampler. Two Savillex filter packs, one with a ringed 47 mm Teflon-membrane filter (Gelman Scientific, Ann Arbor, MI) and one with a 47 mm quartz-fiber filter (Pallflex Corp., Putnam, CT) draw air from the plenum each with flow rates of 20 lpm to collect samples for gravimetric and chemical analyses. The remaining 73 lpm was drawn through a makeup airport. The flow rates were set with a calibrated rotometer and monitored with the same rotometer at each sample change. This type of sampler has been used in many aerosol and visibility studies over the past decade (e.g., Chow et al. 1992, Chow et al. 1997, Watson et al. 1998).

The AirMetrics (AirMetrics, Springfield, OR) Minivol was used to collect $PM_{2.5}$ samples for analysis by scanning electron microscopy (SEM). This type of sampler draws ambient air at a rate of 5 lpm through an impaction plate designed to remove particles greater than $PM_{2.5}$. A 24-hour sample was collected on 47-mm polycarbonate filters (Poretics Products, Livermore, CA).

The Teflon-membrane and polycarbonate filters were weighed on a Cahn 31 Electro-microbalance before and after sampling to determine mass concentrations. Chemical analyses were performed on both the Teflon-membrane and quartz-fiber filters following the methodology described by Watson and Chow (1994). Briefly, the Teflon-membrane filters were analyzed for elements by x-ray fluorescence. One-half of the quartz filter was extracted with distilled-deionizer water and the extract analyzed for chloride, nitrate, and sulfate ions by ion

chromatography, for ammonium by automated colorimetry, and for sodium and potassium by atomic absorption spectrometry. Organic and elemental carbon were measured by thermal-optical reflectance on 0.5 cm^2 punches taken from the remaining half of the quartz-fiber filter (Chow et al. 1993).

For scanning electron microscopy analysis of the $PM_{2.5}$, small ($\sim 0.4 cm^2$) samples were cut from the polycarbonate filters and mounted with conductive adhesive to 10 mm \times 14 mm carbon rods. The sample rods were then coated with a fine layer of carbon to allow for analysis of the elemental composition of the particles using the energy dispersive x-ray (EDX) capability of the SEM (JEOL Model JSM-840 A). The samples were loaded into the SEM and for each sample; a randomly selected image field at 3000 magnification was centered on the viewing screen. The image is captured as a bitmap file and formed the basis of the analysis. The particles on the captured image were numbered and then analyzed one by one using the EDX capability and to note characteristic features such as size and shape. The EDX analysis provides a spectrum indicating the elemental composition of the selected particle and a normalized weight fraction for each selected element.

2.2. Chemical Mass Balance

The Chemical Mass Balance (CMB) receptor model was used to apportion PM and its chemical constituents to their sources. CMB steps, model outputs, performance measures, and deviations from model assumptions are discussed elsewhere (Watson et al., 1984; Pace and Watson, 1987; Watson et al., 1990; and Lowenthal et al., 1992).

2.3. Scanning Electron Microscopy

Another method for estimating the contribution of different sources to the observed ambient PM concentrations is to apply SEM analytical techniques to characterize the collected particulates. The SEM is useful in distinguishing particles originating from different sources based on their composition and morphological characteristics. This feature makes the SEM technique especially useful in distinguishing between aerosols that have similar chemical compositions, but differ in their morphologies.

3. Results

3.1. Ambient $PM_{2.5}$ Data

38 samples (36 ambient and 2 field blanks) were subjected to full chemical analysis to determine the composition of the collected particulate. Validation of the collected ambient data requires evaluation of the chemical data for internal consistency. In this study data, validations were made for sum of species versus $PM_{2.5}$ mass; physical consistency, including examination of the relationships between sulfate and total sulfur, soluble potassium and total potassium; ammonium balance; and anion and cation

balance. Ratios, correlations, and linear regression statistics were computed and scatter plots prepared to examine the data. Suspect data were flagged and their validity examined.

Because soluble potassium (K^+) concentrations are often used as an indicator of vegetative burning, it is important to assure the validity of this measurement. The average ratio of K^+ : K for Reno is $0.47 (\pm 0.11)$ and $0.43 (\pm 0.11)$ for Sparks; this indicates a non-crystal source for the K^+ . This ratio for a pure vegetative burn source or a crystal source would be around 0.9 and 0.2, respectively (Calloway et al., 1989). Ammonium nitrate (NH_4NO_3), ammonium sulfate ($[NH_4]_2SO_4$), and ammonium bisulfate (NH_4HSO_4), are the most likely nitrate and sulfate compounds to be found in Reno and Sparks. Some sodium nitrate ($NaNO_3$) and/or sodium sulfate (Na_2SO_4) may also be present. Ammonium (NH_4) can be calculated based on the stoichiometric ratios of the compounds and compared with that which was measured. Comparing the calculated and measured values revealed that a majority of the sulfate was neutralized and in the form of ammonium sulfate during the study period. However, there were days when ammonium bisulfate predominated. The data for Sparks indicated that for approximately 60% of the days sampled, ammonium bisulfate was the more common ammonium compound, indicating a slightly more acidic environment (Watson et al., 1994).

The calculated mass concentration data are presented in Table 1. Data from both the MedVol and MiniVol samplers are shown. The ambient $PM_{2.5}$ ranges from a low of $4.71 \pm 0.38 \mu g m^{-3}$ measured in Sparks on August 11 to a high of $14.46 \pm 0.78 \mu g m^{-3}$ measured in Sparks on 8/2/98. The average 24-hour concentration observed in Reno was $7.85 \pm 1.84 \mu g m^{-3}$ and $7.80 \pm 2.22 \mu g m^{-3}$ in Sparks. These data are drawn from the higher precision measurements obtained with the MedVol sampler. More data will be needed to test compliance with the pending NAAQS for $PM_{2.5}$.

The variation in $PM_{2.5}$ throughout the sampling period and between Reno and Sparks is shown in Figure 1. Data are shown for both the MedVol and the MiniVol samplers. The relationship between the MedVol and MiniVol samplers for the measurement of $PM_{2.5}$ at both sites is shown in Figure 2. In general, the agreement is good ($R^2=0.70$), and in a pair-wise t-test the means of the two samplers were not statistically different. It follows that the change in $PM_{2.5}$ levels on a day-to-day basis between the two sites shows about the same degree of correlation ($R^2=0.74$) (Figure 3). This is indicative of the more spatially independent nature of $PM_{2.5}$, unlike PM_{10} , which can show higher inter-site variability due to the effects of local emission sources and their smaller zone of influence (Chow et al. 1999).

3.2. $PM_{2.5}$ Chemical Composition

The mass and chemical composition measurements for all of the chemically speciated samples are summarized in Table 2. The most abundant species were organic carbon (OC), elemental carbon (EC), sulfate (SO_4^{2-}), and

ammonium (NH_4^+). These species accounted for 82.4%, on average, of the $PM_{2.5}$ mass. Soil-related species (Al, Si, K, Ca, Ti, Fe, and Zn), without accounting for their oxide forms, accounted for about 9.6% of the mass.

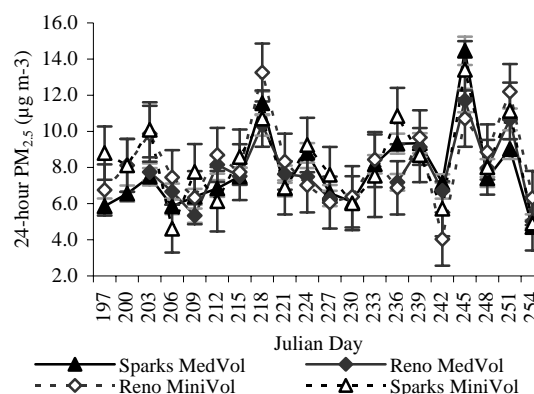


Figure 1. Time series plot of the $PM_{2.5}$ measured in Reno and Sparks, NV, from July 16 (day 197), 1998 to September 11 (day 254), 1998.

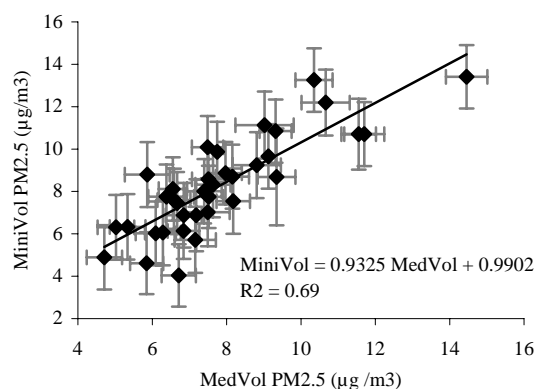


Figure 2. The relationship between $PM_{2.5}$ measured with the MedVol and the MiniVol samplers for Reno and Sparks.

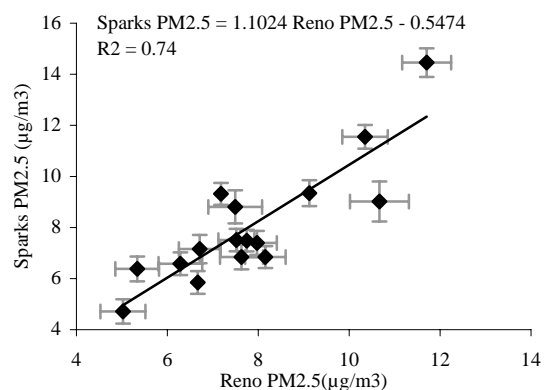


Figure 3. The relationship between $PM_{2.5}$ measured at Reno and Sparks for the MedVol data.

Table 1. Summary statistics for PM_{2.5} measured in Sparks and Reno

Date	DRI MedVol		AirMetrics Minivol	
	Reno PM _{2.5}	Sparks PM _{2.5}	Reno PM _{2.5}	Sparks PM _{2.5}
	($\mu\text{g m}^{-3}$)	($\mu\text{g m}^{-3}$)	($\mu\text{g m}^{-3}$)	($\mu\text{g m}^{-3}$)
7/16/1998		5.86±0.42	6.76±1.42	8.80±1.47
7/19/1998		6.55±0.45	8.12±1.46	8.12±1.46
7/22/1998	7.75±0.48	7.49±0.49	9.87±1.54	10.09±1.52
7/25/1998	6.67±0.45	5.85±0.43	7.45±1.51	4.62±1.32
7/28/1998	5.34±0.40	6.38±0.44	6.33±1.47	7.75±1.54
7/31/1998	8.16±0.50	6.84±0.46	8.70±1.50	6.14±1.67
8/3/1998	7.52±0.47	7.51±0.48	7.74±1.54	8.58±1.52
8/6/1998	10.35±0.59	11.55±0.65	13.26±1.61	10.70±1.56
8/9/1998	7.63±0.48	6.85±0.44	8.32±1.55	6.88±1.47
8/12/1998	7.49±0.48	8.81±0.54	7.02±1.50	9.24±1.51
8/15/1998	6.29±0.42	6.58±0.45	6.06±1.44	7.60±1.54
8/18/1998		6.09±0.43	6.38±1.70	6.02±1.49
8/21/1998		8.18±0.51	8.44±1.52	7.54±2.29
8/24/1998	7.18±0.46	9.32±0.56	6.88±1.47	10.85±1.56
8/27/1998	9.12±0.54	9.34±0.56	9.66±1.51	8.68±1.50
8/30/1998	6.71±0.44	7.16±0.47	4.04±1.48	5.72±1.52
9/2/1998	11.70±0.65	14.46±0.78	10.70±1.56	13.41±1.58
9/5/1998	7.97±0.49	7.40±0.48	8.86±1.53	8.01±1.52
9/8/1998	10.66±0.60	9.02±0.55	12.19±1.53	11.13±1.56
9/11/1998	5.02±0.38	4.71±0.38	6.31±1.50	4.89±1.48
Mean	7.85	7.80	8.15	8.24
Std. Dev.	1.84	2.22	2.20	2.25

Table 2. Average mass concentrations and standard deviations for the measured species.

Species	Reno PM _{2.5} ($\mu\text{g m}^{-3}$)	Sparks PM _{2.5} ($\mu\text{g m}^{-3}$)	Species	Reno PM _{2.5} ($\mu\text{g m}^{-3}$)	Sparks PM _{2.5} ($\mu\text{g m}^{-3}$)
Mass	7.850±1.843	7.797±2.217	Calcium (Ca)	0.067±0.036	0.084±0.058
Chloride (Cl ⁻)	0.020±0.032	0.011±0.023	Vanadium (V)	0.001±0.001	0.001±0.001
Nitrate (NO ₃ ⁻)	0.126±0.050	0.149±0.076	Manganese (Mn)	0.004±0.004	0.003±0.003
Sulfate (SO ₄ ⁻)	0.811±0.396	0.794±0.342	Iron (Fe)	0.133±0.073	0.132±0.080
Ammonium (NH ₄ ⁺)	0.290±0.149	0.270±0.124	Cobalt (Co)	0.000±0.000	0.000±0.000
Soluble Sodium (Na ⁺)	0.026±0.021	0.034±0.023	Nickel (ni)	0.000±0.000	0.000±0.001
Soluble Potassium (K ⁺)	0.051±0.099	0.038±0.068	Copper (Cu)	0.012±0.009	0.024±0.017
Organic Carbon	3.379±0.561	3.382±0.534	Zinc (Zn)	0.009±0.008	0.010±0.008
Elemental Carbon	1.514±0.437	1.499±0.450	Gallium (Ga)	0.001±0.000	0.001±0.000
Total Carbon	4.881±0.877	4.869±0.870	Selenium (Se)	0.000±0.000	0.000±0.000
Sodium (Na)	0.029±0.025	0.032±0.026	Bromine (Br)	0.003±0.002	0.003±0.001
Magnesium (Mg)	0.024±0.015	0.026±0.016	Strontium (Sr)	0.003±0.003	0.002±0.002
Aluminum (Al)	0.087±0.055	0.095±0.067	Zirconium (Zr)	0.000±0.000	0.000±0.000
Silicon (Si)	0.277±0.169	0.312±0.212	Molybdenum (mo)	0.002±0.001	0.002±0.001
Sulfur (S)	0.338±0.157	0.328±0.146	Palladium (Pd)	0.003±0.002	0.003±0.001
Chlorine (Cl)	0.011±0.036	0.008±0.024	Silver (Ag)	0.000±0.000	0.001±0.001
Potassium (K)	0.090±0.124	0.075±0.088	Cadmium (Cd)	0.003±0.002	0.003±0.002

The average PM_{2.5} SO₄⁼ for Reno and Sparks was 0.79 ±0.34 $\mu\text{g m}^{-3}$. On average, SO₄⁼ accounts for about 11.1% of the PM_{2.5}. The average PM_{2.5} NH₄⁺ for Reno and Sparks was 0.27 ±0.12 $\mu\text{g m}^{-3}$ that is about 3.9% of the PM_{2.5}. The average PM_{2.5} NO₃⁻ for Reno and Sparks was 0.15 ±0.07 $\mu\text{g m}^{-3}$ or 1.9% of the PM_{2.5}.

Total carbon (OC + EC) was the largest component of PM_{2.5} in Reno and Sparks, accounting for 70.0 ±12.2% of the mass, on average. The ratios of OC to TC (sum of OC and EC) averaged 0.70 ±0.05. Elemental carbon originates primarily from direct emissions of particles, whereas

organic carbon may originate either from direct primary emissions or from atmospheric transformations of organic gases. The OC/TC ratio has been used to identify the presence of secondary organic aerosol when the OC to EC ratio exceeds ~2 (i.e., OC/TC > 0.67) (Turpin et al. 1990, Hildemann et al. 1991). The proximity of combustion sources to the monitoring sites might have a direct effect on the higher OC/TC ratios. Within the measurement uncertainty, it is not possible to state whether there is a large fraction of secondary organic aerosol in the carbonaceous PM_{2.5} component.

3.3. Scanning Electron Microscopy Results

Manual SEM analysis is a time-intensive analytical methodology. For this reason, a set of samples from the ambient data was selected for analysis. Mamane et al. (1998) recommended filter loadings around 100-300 μg per filter for SEM analysis. Observed mass loadings were between 40 and 93 μg per filter so three samples of the highest mass loadings were selected for analysis: 07-22-98 (69.5 μg), 08-06-98 (93.5 μg), and 09-02-98 (75.5 μg).

The chemical speciation data indicated that carbonaceous material, sulfate, ammonium dominated the ambient samples, and soil-related crustal species (Al, Si, K, Ca, Ti, Fe, and Zn) (Table 2). The SEM analysis also revealed that the majority of particles on the polycarbonate filters were carbonaceous. The size of these particles were, for the most part, $\leq 1 \mu\text{m}$ in diameter. Unfortunately, $1 \mu\text{m}$ is the minimum size of resolution for chemical analysis using the EDX capability of this SEM. Therefore, the SEM analysis had to focus on the particles that were greater than $1 \mu\text{m}$ diameter. These particles proved to be mostly mineral in nature (i.e., non-organic).

EDX analysis of the individual particles showed that for the most part the particles tended to be aluminum-silicates usually with Fe present. Based upon the observed spectra for the particles sampled, 12 different classes of particle type were arbitrarily established for aluminum-silicate types of particles based on the relative amounts of Na, Mg, Si, K, and Ca. The characteristic relationships for these elements and their average relative proportions observed are shown in Table 3. The greatest variability is observed in the Na: Mg and K: Ca ratios, with the Al: Si and Fe: Si ratios being fairly similar (Table 3).

Table 3. Typical relationships observed between the major aluminum-silicate elements observed in the mineral particles collected in Reno and Sparks, NV.

Spectra Form	Al:Si	Na:Mg	K:Ca	Fe:Si	% Occurrence ¹
Si	0.14	0.84			1 \pm 1
Na~Mg, K~Ca, Fe	0.38	0.96	1.32	0.19	15 \pm 10
Na~Mg, K>Ca, Fe	0.39	1.01	12.51	0.12	16 \pm 5
Na~Mg, Ca>K, Fe	0.17	0.9	0.12	0.07	9 \pm 7
Na>Mg, K~Ca, Fe	0.16	2.34	0.57	0.02	3 \pm 3
Na>Mg, K>Ca, Fe	0.23	2.24	2.61	0.01	4 \pm 2
Na>Mg, Ca>K, Fe	0.37	3.42	0.2	0.04	12 \pm 7
Mg>Na, K~Ca, Fe	0.31	0.24	0.51	0.21	4 \pm 1
Mg>Na, K>Ca, Fe	0.38	0.39	17.8	0.23	18 \pm 12
Mg>Na, Ca>K, Fe	0.22	0.21	0.19	0.31	7 \pm 7
Ca>Si	0.31	1.03	0.03	0.00	6 \pm 2
Fe (+ other metals)	0.41	0.69	0.54	0.03	10 \pm 5

¹ total number particles analyzed = 400

The Fe comprised, on average, 8% of the particle mass considering only the ten spectra types that have Na, Mg, K, Ca, and Fe present. For most aluminum-silicate particles, a distinctive spike of S, P, or Ba was observed in the EDX spectrum. The average percent of mass attributable to S and P for all the particles analyzed was 6.2% and 3.3%, respectively. In addition to the typical

aluminum-silicate particles in the samples, particles showing distinctly metallic characteristics were observed. Iron-rich particles accounted for 10 \pm 5% of all particles examined. The Fe content of these particles ranged between 31 and 87.5% with an average content of 55.9%.

4. Chemical Mass Balance Receptor Modeling

The Chemical Mass Balance (CMB) receptor model (Watson et al. 1990) was used to estimate source contributions to $\text{PM}_{2.5}$. In order to ensure reasonable model estimates the CMB applications and validation protocols described by Watson et al. (1991) were applied in this study.

The chemically speciated 24-hour samples collected with the MedVol samplers expressed as mass concentrations with uncertainties formed the database for the CMB receptor modeling exercise. Site-specific source profiles were not determined for this study, so profiles from other studies that represent the major sources in Reno and Sparks were utilized.

Initial tests with different combinations of source profiles were performed to determine which profiles best explain the ambient data and the robustness of the results with respect to choice of source profiles. The tests were done using the average mass concentrations of each species based on the 18 samples collected in Reno and their root mean squared uncertainties. CMB performance measurements were examined to determine how well the ambient concentrations were explained by the CMB source contribution estimates. The results of these initial trials were used as guidance in CMB analysis of the entire sample set. Primary motor vehicle, primary geological material, and secondary sulfate sources were expected to be important contributors at both sites. The results of the test source apportionments are presented as a series of trials representing different combinations of source profiles in Table 4.

For the first trial run, the source profiles used for the CMB modeling were: 1) Mammoth Lakes, CA, road dust (Houck et al. 1989); 2) Northern Front Range Air Quality Study, Denver, CO, dynamometer low emitting gasoline vehicle composite, (Watson et al. 1998); 3) El Centro, CA, agricultural burning (Houck et al. 1989); 4) pure ammonium sulfate; 5) pure ammonium nitrate; and 6) pure sodium chloride. Common sources for sodium chloride include dry lakebeds during summer and road salting during winter. Three performance measures generated by the CMB model, the R SQUARE, the CHI SQUARE, and the PERCENT MASS were examined from each CMB model run to assess the applicability of the chosen source profiles.

The R SQUARE is the fraction of the variance in the measured concentrations accounted for by the variance in the calculated species concentrations. Values of R SQUARE greater than 0.9 indicate a good fit to the measured data. CHI SQUARE represents the weighted sum of the squares of the differences between calculated and measured species concentrations.

Table 4. Sensitivity of source contribution estimates to changes in source profiles for the average Reno sample.

PROFILE	BEST FIT	CASE 1	CASE 2	CASE 3	CASE 4	CASE 5	CASE 6
FGEOL ¹	1.13 ± 0.14	1.39 ± 0.15	1.16 ± 0.14	1.24 ± 0.13	1.57 ± 0.17	1.84 ± 0.15	
PLAYA ²							0.42 ± 0.1
NWLCP ³	5.75 ± 0.86	5.78 ± 0.86	5.22 ± 0.85	3.83 ± 0.89			7.81 ± 1.04
MTRV ⁴					4.15 ± 0.9		
FMT10 ⁵						5.71 ± 1.62	
VELAGBC ⁶	0.41 ± 0.15				0.31 ± 0.1	0.3 ± 0.14	0.5 ± 0.18
VEGB1 ⁷			1.1 ± 0.38				
VEGB7 ⁸				3.34 ± 0.72			
AMSLF ⁹	0.93 ± 0.11	0.95 ± 0.12	0.94 ± 0.11	0.96 ± 0.11	0.98 ± 0.12	1.02 ± 0.2	0.91 ± 0.12
AMNIT ¹⁰	0.17 ± 0.04	0.18 ± 0.04	0.17 ± 0.04	0.18 ± 0.04	0.18 ± 0.06	0.17 ± 0.14	0.17 ± 0.04
NACL1 ¹¹	0.05 ± 0.01	0.08 ± 0.01	0.07 ± 0.01	0.05 ± 0.02	0.06 ± 0.01	0.05 ± 0.01	0.06 ± 0.01
CHI SQUARE	0.19	0.95	0.82	0.3	0.6	0.88	1.44
R SQUARE	0.98	0.93	0.92	0.98	0.94	0.91	0.86
PERC MASS CLUSTERS	108.6	107.5	97.4	123.5	93.1	116.7	126.7

¹FGEOL9 Mammoth Lakes road dust (Houck et al., 1989).

²PLAYA Playa composite (Gillies et al., 1999).

³NWLCP2 NFRAQS low emitting gasoline vehicle composite (Watson et al., 1998).

⁴MTRV3 Las Vegas, NV, motor vehicle composite (Chow et al., 1997).

⁵FMT10 Las Vegas, NV, motor vehicle composite (Chow et al., 1997).

⁶VELAGBC El Centro, CA, agricultural burning (Houck et al., 1889).

⁷VEGB1 Bakersfield, CA, vegetative burning (Houck et al., 1989).

⁸VEGB7 Las Vegas, NV, residential wood combustion composite (Chow et al., 1997).

⁹AMSLF pure ammonium sulfate.

¹⁰AMNIT pure ammonium nitrate.

¹¹NACL1 pure sodium chloride.

Values between one and two indicate acceptable fits; values less than one indicates very good fits to the data. PERCENT MASS is the total mass accounted for by the source contribution estimates.

Values between 80 and 120% are considered acceptable. For the "best fit" profile selection (Table 4), the major contributor to the average Reno aerosol in the summer was motor vehicle emissions (5.75 $\mu\text{g m}^{-3}$, 68%). The percent of mass accounted for was 108.6%. For Case 1, the vegetative burning profile was removed resulting in a decrease in the R-SQUARE parameter from 0.98 to 0.93 and an increase in the CHI-SQUARE from 0.19 to 0.95 because the soluble and total potassium could not be accounted for without a vegetative burning profile. It is clear that the fraction of soluble to total potassium is too high in both the Reno and Sparks samples to have come solely from geological material. However, it is unlikely that the source of soluble potassium during summer is residential wood combustion, which is commonly used during winter for heating. More likely sources include cooking (barbecuing) and forest fires.

In Case 2, a vegetative burning profile (Bakersfield Majestic fireplace, Houck et al. 1989) was substituted for El Centro, CA, agricultural burning (Houck et al. 1989). The fit was nearly as good as that of the base case. In Case 3, a different residential wood combustion profile (Chow et al. 1997) was introduced. This resulted in an over-prediction of mass by 23.5%, because the soluble potassium content of this profile (1.1%) was lower than that of the El Centro, CA, agricultural burning (Houck et al. 1989) (12.5%) and Bakersfield Majestic fireplace (Houck et al. 1989) (4.1%) profiles. In Case 4, a Las

Vegas motor vehicle profile (Chow et al. 1997) was substituted for the NFRAQS profile composite (Watson et al. 1998). This resulted in a lower motor vehicle contribution (4.1 $\mu\text{g m}^{-3}$, 57%) and a higher CHI-SQUARE (0.60). This profile was not able to fit organic and elemental carbon, the two most prevalent species in motor vehicle emissions. In Case 5, a different Las Vegas motor vehicle profile (Chow et al. 1997) was substituted for the NFRAQS profile composite (Watson et al. 1998). This resulted in a lower R-SQUARE (0.91) and a higher CHI-SQUARE (0.88) than those of the "best fit". Finally, in Case six a profile developed from local playa sediments was substituted for the Mammoth Lakes road dust (Houck et al. 1989). The fit in this case was considerably worse than the "best fit" case, with an R-SQUARE of 0.86 and a CHI-SQUARE of 1.44.

The sensitivity analysis demonstrates that in the summer, motor vehicles, geological material, and secondary sulfate were the major contributors to the average Reno PM_{2.5} aerosol. It also shows that a vegetative burning profile is required to account for soluble and total potassium. The choice of motor vehicle profile had a significant effect on the ability of the CMB to account for elemental and organic carbon and on the magnitude of the motor vehicle source contribution.

One of the most important assumptions of the CMB model (Watson et al. 1984) is that the source profiles are linearly independent (i.e., they are statistically different). The degree to which this assumption can be met in practice depends to a large extent on the types and quality of chemical measurements made at the sources and receptor. The CMB model has been subjected to a number of tests to

determine its ability to tolerate deviations from the model assumptions (e.g., Watson 1979, Gordon et al. 1981, Henry 1982 1992, Currie et al. 1984, Dzubay et al. 1984, DeCesar et al. 1985, Javitz et al. 1988, Lowenthal et al. 1992). The impacts of collinearities among the source profiles vary from case to case. These collinearities tend to inflate the variances of the source contribution estimates. The sensitivity analysis did not indicate any significant collinearity problems.

CMB source apportionments were performed for each valid MedVol PM_{2.5} sample. The same geological, motor vehicle, and vegetative burning profiles were used for all samples. The sodium chloride profile was used in all cases to account for soluble sodium, but the contribution to mass was very small. The choice of secondary sulfate profile, ammonium sulfate, or ammonium bisulfate was based on which profile produced the best fits for ammonium and sulfate. A secondary ammonium nitrate profile was also used in all cases. The average R-SQUARE, CHI-SQUARE, and PERCENT MASS were 0.97, 0.41, and 106%, respectively. Most of the source apportionments experienced no collinearity clusters, with a few exceptions involving the geological and vegetative burning profiles. This resulted from very low source contribution estimates (SCEs) with relatively large uncertainties.

On average, the source contributions were similar at the two sites, with motor vehicles, geological material, secondary sulfates, vegetative burning, secondary nitrate, and salt accounting for 68 and 67%, 13 and 16%, 12 and 10%, 5 and 3%, 2 and 2%, and 0.5 and 1% of predicted mass at Reno and Sparks, respectively. T-tests demonstrated that differences between the major source contributions (motor vehicle, geological, secondary sulfate, and vegetative burning) at Reno and Sparks were not statistically significant. This demonstrates the spatially homogeneous nature of PM_{2.5}.

The Sparks summer 1998 results can be compared with CMB results previously reported for Sparks PM_{2.5} for the summer of 1997 (Gofa et al. 1998). In that case, the average motor vehicle contributions were somewhat lower (4.1 versus 5.7 $\mu\text{g m}^{-3}$) while the average geological contribution was over two times higher (3.0 versus 1.3 $\mu\text{g m}^{-3}$). These differences are due to the use of different motor vehicle profiles in the CMB for the summer, 1997 data. As demonstrated by the results of CMB sensitivity tests presented in Table 4, the Denver NFRAQS motor vehicle profile produced a better fit to the 1998 data, especially elemental and organic carbon, than did the Las Vegas profiles used by Gofa et al. (1998) in their study. Further, a vegetative contribution was not presented for the 1997 case, even though the same soluble potassium enrichment was observed.

To check for consistency of the source apportionment between 1997 and 1998, CMB model runs were carried out on the summer, 1997 data of Gofa et al. (1998) using the current "best fit" profiles. The results for the summers of 1997 and 1998 are remarkably similar, differing by no more than 3% for any source. In 1997 the dominant source was motor vehicle emissions (61%), followed by geological (17%), secondary sulfate (11%), and vegetative burning (6%).

5. Discussion

The CMB source apportionment of the Reno and Sparks ambient data defined the major source categories for the PM_{2.5} affecting the air quality in northern Nevada. Based on the SEM analysis some qualification of the source of the geological component can be advanced. The SEM analysis indicated that the non-carbonaceous PM_{2.5} was composed of aluminum-silicate mineral particles, many of which show a distinct signature in their spectra of S and P. In addition, metallic particles rich in Fe, Ti, and Cu, were observed. These characteristics are consistent with resuspended road dust as opposed to fugitive emissions from construction and playas.

Recent studies by Mamane et al. (1998) and Gillies et al. (1999) have examined the chemical and physical characteristics of fugitive dust types that could affect air quality in Reno and Sparks, NV. These studies examined PM₁₀ and PM_{2.5} samples from playas, construction sites, and paved roads that they assumed were the most likely sources of PM of geological origin. These samples were collected on filter media using a resuspension technique (Gillies et al. 1999) and examined using SEM, computer-controlled SEM, as well as other analytical methods (XRF, instrumental neutron activation analysis) in order to develop chemical and morphological marker for separating the geological sources. Mamane et al. (1998) reported that in the fine particle component of road dust collected from streets in Reno and Sparks the mineral particles were predominantly aluminum-silicates (>80%) with a wide range in the relative proportions of the typical aluminum-silicate elements (Na, Mg, Al, Si, K, and Ca). This was also observed in the ambient samples in this study. The variability in the samples could be a reflection of the wide range of aggregate source material used in the construction of paved roads. Several other physical and chemical characteristics of paved road dust in Reno and Sparks observed by Mamane et al. (1998) are mirrored in the ambient samples taken in this study. For example, Mamane et al. (1998) observed that only a small portion of the particles in road dust samples showed enrichment in Ca as compared to Si. This was also observed for the particles collected for the ambient samples. Playa dusts were observed by Mamane et al. (1998) to have more Ca-rich particles (17%). The low percentage of Ca-rich particles in the ambient samples (6%) suggests that this source type did not contribute significantly to the ambient samples during the sampling period.

The presence of P and S in the spectra of the particles from the road dust collected from paved roads in Reno and Sparks was considered by Mamane et al. (1998) to be indicative of an anthropogenic influence. They suggested that these elements, whose source may be fuel-derived, become incorporated or coated onto the mineral particles, thus creating a "marker" species for road dust when it is found in association with mineral particles. Mamane et al. (1998) reported that S and P were seen as small peaks in many of the spectra for road dust source material and reached significant proportions in about 5% to 2% for S and P, respectively. For the ambient samples taken in this study the average percent of mass attributable to S and P, considering all the particles analyzed were 6.2% and 3.3%, respectively. In addition to S and P in paved road dust

particles, Mamane et al. (1998) also noted there was a noticeable presence of Ba. Ba was also found in some of the ambient particles examined in this study and its presence can be linked to its emission from diesel-fueled vehicles (Truex et al. 1980).

The metallic particles in the ambient samples also suggest a roadway source. Mamane et al. (1998) reported that about 3% of the road dust particles they examined with SEM were predominantly composed of Fe. Gillies et al. (1998) reported Fe contributed ~5% to the total PM_{2.5} in ambient samples taken in the Sepulveda Tunnel in Los Angeles, CA, where mobile source emissions and resuspended road dust can be expected to dominate the particulate matter composition due to the confined space. In the ambient samples taken in this study, the metallic particles made up around 10% ($\pm 5\%$) of the non-carbonaceous particles with Fe being the dominant metal, but Ti and Cu were commonly observed. The sources of these metallic particles are likely wear processes acting on vehicles. As the primary mechanism of resuspension of road dust is by entrainment in the turbulent wakes of vehicles and by injection due to the tires (Nicholson et al. 1989), the contribution of road dust to ambient PM_{2.5} in Reno and Sparks can be attributed to the mobile sources. The inclusion of resuspended road dust in the mobile source category raises the contribution from mobile sources to ~84% of the total ambient PM_{2.5}.

6. Conclusions

Summertime monitoring of PM_{2.5} during a period from 07-17-98 through 09-11-98 on an every third day sampling schedule showed average levels in Reno and Sparks, NV, to be $7.85 \pm 1.84 \mu\text{g m}^{-3}$ and $7.80 \pm 2.22 \mu\text{g m}^{-3}$, respectively. Within measurement uncertainties, these values are the same and indicate that the PM_{2.5} levels in this area appear to be relatively homogeneous.

The CMB modeling efforts carried out for this study suggest that the most important contributors to the ambient PM_{2.5} in Reno and Sparks, NV, in summer 1998, are in order of importance: motor vehicle emissions (67-68%), geological (13-16%), secondary sulfate (10-12%), and vegetative burning (3-5%).

One of the deficiencies of standard CMB analysis is the inability to separate the different sources of geological material. This study demonstrated that adding SEM analysis methods to the standard suite of analyses allowed for the attribution of the source of geological material. The similarity of the elemental composition for PM_{2.5} mineral particles in this area, as determined by SEM analysis, in both the paved road dust (Mamane et al. 1998) and the ambient samples collected for this study indicates that this type of PM_{2.5} is road dust resuspended by vehicle activity. That potentially 13 to 16% of the PM_{2.5} that the CMB attributed to geological material could have a road dust source indicates that the PM_{2.5} levels could be reduced with a strategy to limit this emission source.

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