



PM_{2.5} chemical source profiles for vehicle exhaust, vegetative burning, geological material, and coal burning in Northwestern Colorado during 1995

John G. Watson^{a,*}, Judith C. Chow^a, James E. Houck^b

^a Desert Research Institute, 2215 Raggio Parkway, Reno, NV 89512, USA

^b Omni Environmental Services, 5465 SW Western Ave., Beaverton OR 97005, USA

Received 6 March 2000; accepted 2 May 2000

Abstract

PM_{2.5} (particles with aerodynamic diameters less than 2.5 μm) chemical source profiles applicable to speciated emissions inventories and receptor model source apportionment are reported for geological material, motor vehicle exhaust, residential coal (RCC) and wood combustion (RWC), forest fires, geothermal hot springs; and coal-fired power generation units from northwestern Colorado during 1995. Fuels and combustion conditions are similar to those of other communities of the inland western US. Coal-fired power station profiles differed substantially between different units using similar coals, with the major difference being lack of selenium in emissions from the only unit that was equipped with a dry limestone sulfur dioxide (SO₂) scrubber. SO₂ abundances relative to fine particle mass emissions in power plant emissions were seven to nine times higher than hydrogen sulfide (H₂S) abundances from geothermal springs, and one to two orders of magnitude higher than SO₂ abundances in RCC emissions, implying that the SO₂ abundance is an important marker for primary particle contributions of non-aged coal-fired power station contributions. The sum of organic and elemental carbon ranged from 1% to 10% of fine particle mass in coal-fired power plant emissions, from 5% to 10% in geological material, >50% in forest fire emissions, >60% in RWC emissions, and >95% in RCC and vehicle exhaust emissions. Water-soluble potassium (K⁺) was most abundant in vegetative burning profiles. K⁺/K ratios ranged from 0.1 in geological material profiles to 0.9 in vegetative burning emissions, confirming previous observations that soluble potassium is a good marker for vegetative burning. © 2001 Published by Elsevier Science Ltd.

Keywords: PM_{2.5}; Source profile; Chemical mass balance; Coal-fired power plant; Receptor model

1. Introduction

Chemical source profiles are the fractional mass abundances of measured chemical species relative to primary PM_{2.5} mass in source emissions. These profiles are used to create chemically speciated emissions in-

ventories (Cass and McRae, 1983; Kuykendal et al., 1990) and to apportion ambient concentrations to sources using the chemical mass balance (CMB) receptor model (Watson et al., 1984, 1990a, 1991). Like emissions factors (US EPA, 1999) used to construct emissions inventories, source profiles are determined by taking several samples from representative sources. Unlike emissions factors, the chemical abundances in source profiles are normalized to PM_{2.5} or PM₁₀ mass emissions, constraining these abundances to values between 0% and 100%. Also unlike emissions factors, each chemical abundance in a profile is accompanied by a

* Corresponding author. Tel.: +1-775-674-7046, fax: +1-775-674-7009.

E-mail address: johnw@dri.edu (J.G. Watson).

standard deviation that intends to represent the variability of that abundance resulting from differences among separate emitters and between samples taken at different times from the same emitters.

Hundreds of particulate source profiles have been compiled (Cooper et al., 1987; Core and Houck, 1987; Shareef et al., 1988a,b; Houck et al., 1989a,b; Kuykendal et al., 1990; Chow and Watson, 1994; Watson et al., 1994a) and used in source apportionment studies (Watson et al., 1989; Chow and Ono, 1992). These profiles represent emissions for fugitive dust (e.g., paved and unpaved road dust, soil dust, storage pile), motor vehicle exhaust (e.g., diesel-, leaded-gasoline-, and unleaded-gasoline-fueled vehicles), vegetative burning (e.g., wood stoves, fireplaces, forest fires, and prescribed burning), industrial emissions (e.g., smelters, cement production, oil- and coal-fired power plants, steel mills), and other aerosol sources. Since these profiles differ with respect to location and time, additional profiles are always needed for contemporary inventories and source apportionment studies.

The profiles presented here represent sources in and near the Yampa Valley in northwestern Colorado during 1995 for:

1. geological material from paved and unpaved roads and open land,
2. motor vehicle exhaust from light- and heavy-duty gasoline- and diesel-fueled vehicles in Yampa Valley towns,
3. RCC and RWC chimneys,
4. simulated forest fires,
5. geothermal hot springs,
6. coal-fired power generation units.

The Yampa Valley is at an elevation of ~2000 m above mean sea level and ~300 km northwest of Denver, Colorado. Northwestern Colorado coal is exported to many other states and Mexico. Fuels and combustion conditions are similar to those of other communities of the inland western US.

Regional PM_{2.5} emissions estimates (Watson et al., 1996) showed that motor vehicles accounted for ~46% of primary PM_{2.5}, with summer emissions distributed among vehicle exhaust, paved road dust, and unpaved road dust. Another 21% of PM_{2.5} in the summer was emitted from natural dust sources, while 11% was emitted from agricultural tilling. During the winter months, residential wood (RWC) and coal combustion (RCC) were significant PM_{2.5} sources, constituting 11% of the emissions.

Profiles for geothermal hot springs and a coal-fired power station with a limestone SO₂ scrubber are original to this work. The remaining profiles supplement the existing profile data base and are applicable to similar sources and fuels found elsewhere. These profiles were used to attribute light extinction to its sources in the Mt. Zirkel Visibility Study (Watson

et al., 1996), but they have wider applicability to other times and places.

2. Experimental methods

Table 1 summarizes the profiles taken in this study. Two Yampa Valley coal-fired power stations were tested. The Hayden station, near Hayden, CO, consists of Unit 1 with a 184 MW capacity and a 76 m stack of 7.6 m diameter and Unit 2 with a 262 MW capacity and a 120 m stack of 9.4 m diameter. Hot-side electrostatic precipitators process emissions for both units. Bituminous coal with a nominal average sulfur content of 0.46% is obtained from the Seneca mine near the power station. Ammonia (NH₃) is periodically injected after combustion but prior to the precipitator to increase particle conductivity in the stack effluent.

The Craig station, near Craig, CO, consists of three units, each with a 180 m stack of 8.6 m diameter. The 428 MW Units 1 and 2 are equipped with electrostatic precipitators and wet scrubbers that remove SO₂ with ~67% efficiency. The 408 MW Unit 3 is equipped with a dry limestone SO₂ scrubber with ~85% efficiency followed by a baghouse. During the study period, Units 1 and 2 burned bituminous coal from the Trapper Mine with <0.4% sulfur content, while Unit 3 used coal from the Colowyo Mine with <0.4% sulfur content.

Measurements from continuous SO₂ and oxides of nitrogen (NO_x) emissions and load were examined to determine test periods. The Hayden station's daily SO₂ emissions ranged from 19.6 to 56.8 tons/day and typically averaged ~46 tons/day. Load and emissions at the Craig station were more variable than those at Hayden, both in terms of 24 h and hourly averages; Craig emissions showed a diurnal cycle that peaked during the daytime and dropped to nearly half of maximum load at night. Daily SO₂ emissions ranged from 18.3 to 37 tons/day with an average of 26.4 tons/day.

Diluted stack samples were taken from Units 1 and 2 at the Hayden station and Units 2 and 3 at the Craig station. Craig Units 1 and 2 are identical and there is no reason to believe that compositions differ between these two stacks. Emissions were drawn from the stack into a dilution sampler (Houck et al., 1989a,b, 1990) by maintaining a lower pressure within the sampler's dilution chamber. Dilution ratios were adjusted to obtain an effluent temperature within ±10°C of ambient temperature, with typical dilutions of ~10:1.

Three sets of three parallel samples were taken at the power stations. The first parallel filter pack consisted of a 47 mm Teflon-membrane filter followed by three potassium-carbonate-impregnated cellulose-fiber filters. The second parallel filter pack contained a quartz-fiber filter, and the third contained a citric-acid-impregnated

Table 1
Descriptions of Yampa Valley, CO, PM_{2.5} source profiles

Profile ID	Description
<i>Coal-fired power generation</i>	
MZCG2PPC	Composite of four Craig Unit 2 samples with coal from the Trapper Mine, SO ₂ wet scrubber, and electrostatic precipitator
MZCG3PPC	Composite of three Craig Unit 3 samples with coal from the Colowyo Mine, dry lime SO ₂ scrubber, and fabric baghouse
MZHD2PPC	Composite of two Hayden Unit 2 samples with coal from the Seneca Mine, ammonia injection, and electrostatic precipitator
MZHD1PP1	One sample collected from Hayden Unit 1
MZHDPPC	Composite of one Hayden Unit 1 and two Hayden Unit 2 samples with coal from the Seneca Mine, ammonia injection, and electrostatic precipitator
MZPPC	Composite of four Craig Unit 2, three Craig Unit 3, two Hayden Unit 2, and one Hayden Unit 1 samples
<i>Residential wood combustion</i>	
MZRWCC	Composite of three samples from: (1) a fireplace and stove burning lodgepole pine, spruce/aspen, spruce/firewood; (2) a fireplace and stove burning lodgepole pine; and (3) a single stove burning lodgepole pine and spruce
<i>Residential coal combustion</i>	
MZRCCC	Composite of two samples from a stove burning coal from the Trapper Mine and two samples from a fireplace and stove burning coal from the Seneca Mine
<i>Wildfire</i>	
MZFFIREC	Composite of four sample burns of pinion and juniper near Dinosaur, CO
<i>Geothermal hot springs</i>	
MZGSC	Composite of three samples from the Lithia, Iron, Sulfur, Black Sulfur, and Steamboat geothermal springs when no odors were detected
MZGS2C	Composite of two samples from the Lithia, Iron, Sulfur, Black Sulfur, and Steamboat geothermal springs when odors were detected
<i>Motor vehicle exhaust</i>	
MZMVCG1C	Composite of three early morning (0800–0900 MST) samples collected at the intersection of Victory Way and Ranney Avenue, Craig, CO, during July 1995
MZMVCG2C	Composite of three morning (0900–1300 MST) samples collected at the intersection of Victory Way and Ranney Avenue, Craig, CO, during July 1995
MZMVCG3C	Composite of three afternoon (1400–1800 MST) samples collected at the intersection of Victory Way and Ranney Avenue, Craig, CO, during July 1995.
MZMVCGC	Composite of all nine early morning, morning, and afternoon samples collected from Craig, CO
MZMVSBC	Composite of three morning (0800–1200 MST) samples collected at the intersection of Highway 40 and Elk River Road, Steamboat Springs, CO
MZMVC	Composite of all 12 motor vehicle samples (nine Craig and three Steamboat Springs samples)
<i>Geological material</i>	
MZCPVRDC	Composite of three paved road dust samples collected near vehicle exhaust sampling locations in the town of Craig, CO
MZSPVRDC	Composite of three paved road dust samples collected near vehicle exhaust sampling locations in the town of Steamboat Springs, CO
MZPVRDC	Composite of all six paved road dust samples (three from Craig and three from Steamboat Springs, CO)
MZUPRDC	Composite of two unpaved road dust samples from the Buffalo Pass (BP) and Hayden VOR (HV) access roads
MZSOILC	Composite of four soil samples in the vicinity of BP, Juniper Mountain (JU), Baggs (BB), and Hayden Waste Water (HS) receptor sites
MZGEOLC	Composite of all 12 geological samples (six paved road dust, two unpaved road dust, and four soil samples)

cellulose-fiber filter. Sampling times of a few hours were sufficient to obtain filter deposits in excess of 1 mg on each substrate.

Residential coal burning samples were acquired with the same configuration as that applied to woodburning, with samples described in Table 1. Coal from the Seneca

Mine, which is burned in some homes, is the same as that burned in the Hayden power station.

Wood- and coal-burning stoves were recruited from local homeowners and sampled from ~2100 to 2400 MST with 13–23 min sample durations during cold winter nights, especially during the holiday season, when radiation inversions are intense, local traffic and industrial source emissions are low, and people are likely to burn wood or coal. Samples were taken by drawing the diluted plume through a ~4 m stainless steel pipe equipped with a PM_{2.5} inlet into a mixing chamber where the filters packs were attached. The sample probe was moved to keep it within the visible portion of the plume after it exited the appliance chimney, and it was held about 1 m above the top of the stack to allow the plume to cool. Samples consisted of parallel Teflon-membrane/potassium-carbonate-impregnated cellulose-fiber filter and quartz-fiber filter packs.

Samples from five of the major hot springs in downtown Steamboat Springs (Lithia, Iron, Sulfur, Black Sulfur, and Steamboat Springs) were taken at night for 7.5–30 min intervals when vehicular emissions were low. One of the integrated samples was from geothermal springs with no odor, and the other was from springs with a characteristic H₂S smell. The sample configuration consisted of a Teflon-membrane/silver-nitrate-impregnated cellulose-fiber/potassium-carbonate-impregnated cellulose-fiber filter pack and a quartz-fiber filter pack in parallel.

According to the Craig Interagency Dispatch Center, wildfires in the region consist of approximately 80% pinion pine and juniper. To simulate these burns, short-duration (2–8 min) samples of forest fire emissions were taken of burning pinion pines and junipers in an area ~8 km north of Dinosaur, CO. Samples were collected onto parallel Teflon-membrane/quartz-fiber filter and quartz-fiber/potassium-carbonate-impregnated cellulose-fiber filter packs.

Motor vehicle exhaust samples were taken in source-dominated environments next to major highway intersections and diesel bus terminals to represent different mixtures of vehicles. Samples were acquired during the summer when residential burning emissions were low and before the wildfire season. Samples were taken on downwind curbs when contributions from other sources were minimal. Sample sets consisted of parallel Teflon-membrane/quartz-fiber filter and quartz-fiber/potassium carbonate impregnated cellulose-fiber filter packs. Samples of 60–120 min duration were acquired during the morning and evening rush-hours and during mid-day to represent different driving conditions (i.e., stop and go vs. continuous flow) and traffic volumes. Since the majority of motor vehicle exhaust is emitted in the PM_{2.5} size fraction, a PM_{2.5} inlet was used on the sampling system to minimize contamination of the sample from suspended road dust. Road dust was also sampled,

resuspended, and analyzed. CMB was used with geological fitting species to determine the road dust contribution to these samples, and this contribution was subtracted from all chemical components prior to calculating chemical abundances.

Geological material was acquired from areas identified in receptor site surveys, on streets adjacent to motor vehicle samples, and soil conservation surveys as shown in Table 1. Several fugitive dust samples were taken and mixed to obtain a representative composition for road dust and erodible soil. One-half to 1.0 kg of material in storage piles was swept from the surface and stored in zipped polyethylene bags. These samples were dried, sieved, and resuspended in a laboratory chamber and sampled through PM_{2.5} inlets onto Teflon-membrane and quartz-fiber filters (Chow et al., 1994).

Teflon-membrane filters were analyzed for mass by gravimetry and elements (Na to U) by X-ray fluorescence (Watson et al., 1999). Half of each quartz-fiber filter was extracted in deionized distilled water and analyzed for anions by ion chromatography (chloride [Cl⁻], nitrate [NO₃⁻], sulfate [SO₄⁻]) (Chow and Watson, 1999), and for cations by atomic absorption spectrophotometry (soluble sodium [Na⁺], K⁺) and automated colorimetry (ammonium [NH₄⁺]). The other half of each quartz-fiber filter was used to quantify organic and elemental carbon (OC and EC) by the IMPROVE thermal/optical reflectance method (Chow et al., 1993, 2000). Potassium carbonate backup filters were extracted in a sodium carbonate solution and analyzed for absorbed SO₂ as SO₄⁻ by ion chromatography. Citric-acid-impregnated cellulose-fiber filters were analyzed for absorbed NH₃ as NH₄⁺ by automated colorimetry. Silver-nitrate-impregnated cellulose-fiber filters were analyzed for H₂S as SO₄⁻ by ion chromatography.

Each substrate followed an established laboratory sample chain-of-custody and data validation process. Blank and replicate analyses were performed for ~10% of all samples according to standard operating procedures. Results from quality audits and laboratory intercomparisons demonstrated good accuracy and precision (Watson et al., 1996). Field blank standard deviations were combined with the flow rate and chemical analysis precisions to estimate the precision of each chemical concentration (Watson et al., 2000).

3. Source profile results

Composite source profiles were created by analyzing the individual samples for each source type and dividing the resulting chemical concentration by the mass concentration. Abundances in these individual profiles were averaged and their standard deviations calculated to obtain representative distributions of chemical abundances and their variabilities. Table 1 identifies the

composite profile names and the samples they include. Table 2 summarizes the composite profiles that are discussed in greater detail below.

3.1. Coal-fired boilers

The Craig Unit 2 (MZCG2PPC) and Unit 3 (MZCG3PPC) profiles differ significantly. Sulfate is the most abundant constituent in the particle phase, at $12.7 \pm 3.1\%$ for Unit 3 and $22.7 \pm 6.3\%$ for Unit 2. Total carbon (TC = OC + EC; carbonate carbon was not quantified) varies from 1% to 10%. EC for Unit 2 ($8.1 \pm 4.3\%$) is much higher than for Unit 3 ($1.2 \pm 1.2\%$). Since abundances of OC are similar ($\sim 2\%$ to 3%), the average OC/TC ratio varies from 0.22 for Unit 2 to 0.69 for Unit 3. For Craig Unit 2, abundances of aluminum (Al) ($4.2 \pm 0.3\%$) and calcium (Ca) ($3.5 \pm 0.3\%$) are similar to those found in the MZGE-OLC geological profile ($4.5 \pm 0.7\%$ for Al and $3.2 \pm 1.0\%$ for Ca), whereas silicon (Si) ($8.0 \pm 0.6\%$) and iron (Fe) ($3.1 \pm 0.2\%$) are present at 45–75% of the corresponding levels in geological material. Na, magnesium (Mg), and NH_4^+ are also present at 1–3% level for Craig Unit 2. The abundances of these components in Craig Unit 3 are commonly 5–10% of those found for Craig Unit 2. Other elements such as phosphorus (P), K, titanium (Ti), manganese (Mn), and barium (Ba) are present in Unit 2 emissions at levels of 0.1–1.0% and in Craig Unit 3 emissions at levels of 0.02–0.2%.

Selenium (Se) is usually in the gaseous phase in hot stack emissions; it condenses on particles when air is cooled in the dilution chamber. Se is in Craig Unit 2 emissions at $0.34 \pm 0.08\%$, but it is not found in $\text{PM}_{2.5}$ samples from Craig Unit 3. Abundances of Ca ($14.7 \pm 6.8\%$), Cl ($1.3 \pm 0.4\%$), and NO_3^- ($0.79 \pm 0.72\%$) for Craig Unit 3 are four times those measured for Craig Unit 2. These differences may have resulted from the dry limestone scrubber present in Unit 3.

The abundance of SO_2 for Craig Unit 2 ($21\,297 \pm 12\,557\%$ in MZCG2PPC) is three to four times higher than the Craig Unit 3 abundance ($6100 \pm 3330\%$ in MZCG3PPC), seven to nine times higher than the geothermal springs abundance (H_2S equivalent), and more than two orders of magnitude higher than the SO_2 abundance from RCC. NH_3 is detectable in Craig boiler emissions, ranging from 7% to 10% of primary $\text{PM}_{2.5}$ mass.

For most elements, Hayden Unit 1 (MZHD1PP1) exhibits higher chemical abundances than Hayden Unit 2 (MZHD2PPC). The largest difference is found for OC, with $0.49 \pm 0.20\%$ in Unit 2 emissions and $34.1 \pm 3.6\%$ in Unit 1. EC differences are also large, with $0.40 \pm 0.22\%$ in Unit 2 emissions and $4.3 \pm 0.8\%$ in Unit 1. The average OC/TC ratio is 0.56 for Unit 2 and 0.89 for Unit 1.

The Al abundance for Hayden Unit 1 of $10.3 \pm 0.67\%$ is approximately three times that of Unit 2. The Si abundance for Unit 1 of $16.0 \pm 1.0\%$ is similar to that found in geological profiles; it is also three times the Al abundance in Unit 2 emissions. Ca and Fe are present at 1–4% levels. Other elements such as P, K, Ti, Mn, strontium (Sr), and zirconium (Zr) show 0.1–1% abundances for Unit 1, two to three times higher than their abundances in Unit 2 emissions.

Se constitutes $0.22 \pm 0.02\%$ of $\text{PM}_{2.5}$ emissions from Hayden Unit 1 (MZHD1PP1) and $0.38 \pm 0.06\%$ from Hayden Unit 2 (MZHD2PPC). These are similar to those for Craig Unit 2, but not for Craig Unit 3. The abundances of SO_4^{2-} ($10.0 \pm 4.9\%$), NH_4^+ ($9.2 \pm 2.4\%$), and Cl^- ($1.9 \pm 0.12\%$) from Hayden Unit 2 (MZHD2PPC) are two to six times higher than those from Hayden Unit 1. NO_3^- and Ba are also detectable at $\sim 0.1\%$ from Hayden Unit 2.

The SO_2 abundance for Hayden Unit 1 ($5721 \pm 348\%$) is similar to that for Craig Unit 3 ($6100 \pm 3330\%$), but it is almost three times higher than that for Hayden Unit 2 ($2075 \pm 199\%$). These levels are 10–25% of the $21\,297 \pm 12\,558\%$ abundance for Craig Unit 2.

NH_3 abundances are $491 \pm 384\%$ for Hayden Unit 2 and $3365 \pm 265\%$ for Hayden Unit 3, compared to 7–10% at Craig Units 2 and 3. This is indicative of NH_3 injection at Hayden. SO_4^{2-} abundances vary from 3% to 22% among the different units, with an average of $7.7 \pm 5.3\%$ for Hayden and $15.2 \pm 8.3\%$ for Craig.

Elemental abundances in the composite coal-fired boiler profile (MZPPC) differ from those summarized by Sheffield and Gordon, (1986)'s 21-study averages and from Han (1992)'s average emissions from 15 eastern coal boilers equipped with different pollution control devices. Abundances of Al, Si, and Fe in Hayden and Craig emissions are 30–50% of the average Sheffield and Gordon, (1986) abundances; they are three to four times higher than the Han (1992) abundances. The Ca abundances also differ, with averages of 6.5% in Hayden and Craig emissions (western coal), $0.7 \pm 0.7\%$ from Sheffield and Gordon, (1986), and $0.15 \pm 0.12\%$ from Han (1992). Sulfur (S) abundances in Table 2 range from 1.7% to 8.8%, compared to 0.15–142% from Sheffield and Gordon, (1986) and an average of $1.8 \pm 1.0\%$ from Han (1992). The average Se abundance of 0.24 ± 0.18 (MZPPC) is much larger than the average from Sheffield and Gordon, (1986) ($0.0024 \pm 0.0017\%$) and Han (1992) ($0.065 \pm 0.15\%$). Arsenic (As) was not detectable in any of the Table 2 profiles, compared to averages of 0.004–0.05% for Sheffield and Gordon, (1986) and $0.0037 \pm 0.0026\%$ for Han (1992).

These differences demonstrate the need to obtain profiles that represent a study area, and especially the use of eastern or western coals. Fluctuations in chemical abundances from coal-fired boiler emissions may be due

Table 2 (Continued)

Table with columns for elements (Cl, CO2, SO2, etc.) and data columns for various monitoring stations: MZMVG1C, MZMVG2C, MZMVG3C, Motor Vehicle (M2MVG3C, M2MVG2C, M2MVG1C, M2WVC, M2MVG5C, M2MVG6C, M2MVG7C, M2MVG8C, M2MVG9C, M2MVG10C, M2MVG11C, M2MVG12C, M2MVG13C, M2MVG14C, M2MVG15C, M2MVG16C, M2MVG17C, M2MVG18C, M2MVG19C, M2MVG20C, M2MVG21C, M2MVG22C, M2MVG23C, M2MVG24C, M2MVG25C, M2MVG26C, M2MVG27C, M2MVG28C, M2MVG29C, M2MVG30C, M2MVG31C, M2MVG32C, M2MVG33C, M2MVG34C, M2MVG35C, M2MVG36C, M2MVG37C, M2MVG38C, M2MVG39C, M2MVG40C, M2MVG41C, M2MVG42C, M2MVG43C, M2MVG44C, M2MVG45C, M2MVG46C, M2MVG47C, M2MVG48C, M2MVG49C, M2MVG50C, M2MVG51C, M2MVG52C, M2MVG53C, M2MVG54C, M2MVG55C, M2MVG56C, M2MVG57C, M2MVG58C, M2MVG59C, M2MVG60C, M2MVG61C, M2MVG62C, M2MVG63C, M2MVG64C, M2MVG65C, M2MVG66C, M2MVG67C, M2MVG68C, M2MVG69C, M2MVG70C, M2MVG71C, M2MVG72C, M2MVG73C, M2MVG74C, M2MVG75C, M2MVG76C, M2MVG77C, M2MVG78C, M2MVG79C, M2MVG80C, M2MVG81C, M2MVG82C, M2MVG83C, M2MVG84C, M2MVG85C, M2MVG86C, M2MVG87C, M2MVG88C, M2MVG89C, M2MVG90C, M2MVG91C, M2MVG92C, M2MVG93C, M2MVG94C, M2MVG95C, M2MVG96C, M2MVG97C, M2MVG98C, M2MVG99C, M2MVG100C). The table contains numerical data for each element-station combination.

to differences in coal composition, pollution control devices, sampling methods, sampling periods, and analytical techniques.

3.2. Residential wood and coal combustion

Chemical abundances differ for RWC and (RCC), although the majority of $PM_{2.5}$ from both sources is composed of carbonaceous material; carbon accounts for 63–96% of $PM_{2.5}$ mass. Average OC abundances range from $51.4 \pm 11.7\%$ in RWC to $69.5 \pm 19.2\%$ in RCC, whereas EC ranges from $12.4 \pm 4.2\%$ in RWC to $26.1 \pm 15.6\%$ in RCC. The EC abundance in RCC $PM_{2.5}$ is twice that of RWC. OC/TC ratios are similar, however, ranging from 0.73 in RCC to 0.81 in RWC.

K in RWC is completely water-soluble (K^+), exceeding an abundance of 1% in these emissions. The RWC Cl^- abundance is 55% higher than that of RCC. On average, the abundances of SO_4^{2-} , NO_3^- , and Si in RCC are four times those of RWC. The NH_4^+ abundance is highly variable, with an average of $1.4 \pm 1.3\%$ for RCC and $0.13 \pm 0.02\%$ for RWC. The SO_4^{2-} abundance for RCC ($3.3 \pm 2.8\%$) is three times that of RWC ($0.91 \pm 0.38\%$).

SO_2 was not detected in any of the RWC samples, and only 50% of the RCC samples reported non-negligible $SO_2/PM_{2.5}$ ratios. These abundances are highly variable, ranging from $112 \pm 3\%$ to $532 \pm 27\%$ in the individual samples of the MZRCC composite, even though the coal was from the same mine. Combustion conditions in different stoves may have caused these differences. The Se abundance is only $0.004 \pm 0.004\%$ in the MZRCC profile, and it was detectable in only two of the four samples in the composite.

Denver, CO, RWC profiles were generated in 1987 from a mixture of lodgepole pine, ponderosa, pine, spruce, pinion, aspen, oak, Douglas fir, and cedar in five different types of fireplaces and woodstoves (Watson et al., 1988). The Denver RWC profiles are similar to the Table 2 RWC profiles. The Denver profiles contained 54–74% OC and 9–29% EC, as compared to 40–64% OC and 8–16% EC in this study. Among the inorganic species, both studies reported sulfur (S), Cl, and K with $\sim 0.1\%$ abundances.

Las Vegas, NV, RWC profiles were taken in 1995 from fireplaces and wood stoves burning mesquite, ponderosa pine, lumber, and DuraLogs® (Chow and Watson, 1997). OC abundances were $5.5 \pm 2.4\%$ to $57 \pm 13\%$, and EC abundances were $4.4 \pm 1.3\%$ to $26 \pm 8\%$; these abundances are similar in magnitude to those found in the Denver and Yampa Valley profiles. Cl abundances ranged from $0.39 \pm 0.4\%$ to $6.9 \pm 3.1\%$, and K^+ abundances ranged from $0.57 \pm 0.37\%$ to $4.6 \pm 1.5\%$, much higher than the $\sim 0.1\%$ abundances found in Denver and Yampa Valley profiles.

3.3. Forest fires

TC accounted for 50% of $PM_{2.5}$ mass in the forest fire profile (MZFIREC). OC abundances in the individual samples that formed the composite profile were variable, ranging from $30.7 \pm 1.5\%$ to $66.1 \pm 3.3\%$, with an average OC/TC ratio of 0.94. This is the highest OC/TC ratio observed among all measured source types in this study. The abundance of SO_2 ($0.30 \pm 0.14\%$) in MZFFIREC is similar in magnitude to that of motor vehicle exhaust. Other inorganic species such as SO_4^{2-} , S, Cl^- , Cl, K^+ , and K are present at $\sim 0.1\%$ abundances, whereas Na, Mg, Al, Si, and Fe are present at $\sim 0.01\%$ abundances.

Chow and Watson (2000) measured profiles for asparagus field burning in California's Imperial Valley with OC/TC ratios of 0.93, similar to the 0.94 ratio found in the forest fire emissions. OC was the most abundant species in the profile, accounting for $55.6 \pm 15\%$ of $PM_{2.5}$ mass. A similar observation was made for charbroil cooking emissions in Mexicali, Mexico, with 60–70% OC abundances and high (>0.95) OC/TC ratios.

Most of the K in the MZRWC and MZFIREC profiles is soluble, as indicated by the high K^+/K ratios (Calloway et al., 1989). This is consistent with the Denver, Las Vegas, Imperial Valley, and Mexicali profiles.

3.4. Geothermal hot springs

To maintain consistency with other profiles, the abundance of H_2S in Table 2 was converted to SO_2 , assuming complete oxidation in the atmosphere after release. Since the mass collected on the samples was low and imprecise, chemical abundances were normalized to the sum of species rather than to the measured mass. The oxidized H_2S (i.e., SO_2) is the most abundant species, but its abundance is variable, ranging from $655 \pm 506\%$ to $3378 \pm 2603\%$. The two composite profiles are grouped based on the detectability of the distinctive H_2S odor during sampling. The average abundance of SO_2 (oxidized H_2S) is 40% higher for MZGS2C (with odor) than for MZGSC (without odor). The largest variation is found in the TC abundance with measurement uncertainty exceeding the concentration by 10-fold. SO_4^{2-} , NO_3^- , Cl^- , and NH_4^+ are present at 15–20% abundances, while Al, Si, K, Ca, and Fe are present at 2–10% abundances. The S abundance is 30% of SO_4^{2-} abundance. The remaining chemical abundances are not detectable.

3.5. Motor vehicle exhaust

Though dominated by motor vehicle emissions, roadside samples also contain suspended road dust and

particles from other sources in the background air. The geological contribution was removed from each sample by applying the CMB model with Al, Si, K, and Ca as fitting species for the MZGEOLC profile, then subtracting the calculated geological contribution from each chemical species and the measured mass. NH_4^+ and NO_3^- were also used as CMB fitting species with secondary ammonium nitrate and sulfate as sources to remove background concentrations of secondary aerosol from these samples.

MZMVCGC and MZMVSBC in Table 2 represent composite motor vehicle emissions at Craig and Steamboat Springs, respectively, and the MZMVC abundances are the averages and standard deviations for 12 of the individual motor vehicle profiles.

OC and EC are the most abundant species in motor vehicle exhaust, accounting for over 95% of the total mass. OC abundances range from $38.8 \pm 2.4\%$ (MZMVSBC) to $69.5 \pm 17.2\%$ (MZMVCG3C). OC/TC ratios range from 0.40 for the Steamboat Springs profile (MZMVSBC) to 0.71 for the Craig profile (MZMVCG3C), with an average ratio of 0.58 (MZMVC). Watson et al. (1994a) reported OC/TC ratios of 0.69 for gasoline-fueled vehicle exhaust (PHAUTO), 0.55 for diesel-fueled vehicle exhaust (PHDIES), and 0.52 for a mixture of vehicle types in roadside tests (PHRD) from Phoenix, AZ, in 1988. Roadside sampling in Las Vegas, NV, during 1995 resulted in similar OC and EC abundances and OC/TC ratios of 0.48–0.67 with an average of 0.59 (Chow and Watson, 1997).

In 1987, Federal Test Procedure (FTP) dynamometer tests of four closed-loop and four oxidation-catalyst vehicles in Denver, CO (Watson et al., 1990b) reported an OC/TC ratio of 0.39 for the cold transient cycle and 0.81 for the cold stabilized cycle. Samples from an underground Denver bus transfer station reported an OC/TC ratio of 0.76 for diesel buses, while in situ samples taken from a parking garage during cold winter time (for comparison with the cold transient portion of the FTP cycle) yielded an OC/TC ratio of 0.48 (Watson et al., 1990b). These ratios are within one standard deviation of the MZMVC profile (OC/TC = 0.58 ± 0.15) derived from all vehicle samples.

The lead (Pb) abundance is negligible and highly variable ($0.024 \pm 0.067\%$) in the MZMVC and other profiles. The abundance of bromine (Br) is also low, in the range of 0.01–0.05%. These contrast with higher Pb and Br abundances from earlier profiles taken when leaded fuel was still used in the US. Watson and Chow (2000) found 0.1–0.3% lead in 1995 vehicle exhaust profiles near the California/Mexico border consistent with leaded gasoline use in Mexico at that time. Zinc (Zn) is present in most of these profiles, usually at levels of 0.05% or less. The Cl^- abundance is 1.4–3.3%.

The SO_4^{2-} abundance is low, ranging from $0.6 \pm 1.8\%$ in the Craig profile (MZMVCGC) to $1.8 \pm 1.0\%$ in the Steamboat Springs profile (MZMVSBC). The SO_2 abundance ranges from $0.13 \pm 0.02\%$ in the Steamboat Springs profile (MZMVSBC) profile to $0.73 \pm 0.06\%$ in the Craig profile (MZMVCGC), consistent with low sulfur content in Colorado gasoline and diesel fuels.

3.6. Fugitive dust

In each of the geological profiles, Al, Si, K, Ca, and Fe have large abundances with low variabilities. The abundance of total potassium (K) is 15–30 times the abundance of soluble potassium (K^+). The abundances of Al, K, Ca, and Fe are similar among the profiles, but Si abundances range from $14.4 \pm 2.5\%$ in unpaved road dust (MZUPRDC) to $20.1 \pm 2.5\%$ in paved road dust (MZPVRDC).

Pb is most abundant ($0.018 \pm 0.009\%$) in paved road dust, and is as low as 0.004% in the other profiles. TC abundances range from 5% to 10%. EC abundances are from 0.4% to 1.1% in individual profiles, and are small ($0.78 \pm 0.84\%$) in the composite geological profile (MZGEOLC). OC abundances differ among the composite paved ($7.4 \pm 2.2\%$) and unpaved ($4.6 \pm 2.2\%$) road dust samples, with similar abundances in the MZSOILC ($6.1 \pm 2.6\%$) and MZGEOLC ($6.5 \pm 2.5\%$) profiles. OC/TC ratios are similar with an average ratio of 0.90. The effect of motor vehicle contributions to paved road dust (e.g., brake and tire wear, oil drips, deposited exhaust) is evident in larger abundances of Pb, EC, and OC. SO_4^{2-} , NO_3^- , and NH_4^+ are generally low, in the range of 0–0.1%, consistent with the subtraction of secondary ammonium sulfate and ammonium nitrate contamination of the roadside sampling. Na and Cl^- abundances are also low, at <0.5% abundances. The effect of road sanding and salting on composition is not evident.

These profiles are similar to paved road dust profiles from 1987 Denver, CO (Watson et al., 1988, 1990b). Previous source apportionment studies (Chow et al., 1992a,b; Watson et al., 1994b) show that the chemical abundances and variabilities in Table 2 are sufficient to separate geological contributions from other source types, but they are insufficient to distinguish paved road, unpaved road, and native soil compositions from each other.

4. Conclusions

Coal-fired power station profiles differed substantially between different units using similar coals. The major difference was the lack of selenium in emissions from Craig Unit 3 that was equipped with a dry limestone SO_2 scrubber. It is probable selenium was in the

vapor phase as the hot exhaust passed through the scrubber, and that this vapor was removed by the limestone scrubber along with the SO₂.

SO₂ abundances in power plant emissions were seven to nine times higher than H₂S abundances from geothermal springs, and one to two orders of magnitude higher than SO₂ in RCC emissions. SO₂ abundances were less than 2% for vehicle exhaust and vegetative burning emissions. The ratio of sulfur dioxide to PM_{2.5} mass is therefore an important marker for primary particle contributions of non-aged power station contributions. This is true only for near-source contributions because SO₂-to-PM_{2.5} ratios will decrease with time as particles and gases deposit and sulfur dioxide converts to PM_{2.5} sulfate. Ammonia abundances in power plant emissions were one to two orders of magnitude higher for ammonia injection.

Organic and elemental carbon were found in all emission profiles except for geothermal hot springs. The sum of organic and elemental carbon ranged from 1% to 10% in coal-fired power plant PM_{2.5} emissions, from 5% to 10% in geological material, >50% of forest fire emissions, >60% of RWC emissions, and >95% of RCC and vehicle exhaust emissions.

Primary particulate sulfate was a minor component of forest fire (0.1%) and RWC (1%) emissions. Sulfate abundances were higher in RCC (3%), coal-fired power plant (3–23%), and geothermal springs (24–32%) PM_{2.5} emissions. Certain elements were most abundant in geological profiles, although detectable levels also occurred in coal-fired power plant profiles. Water-soluble potassium was most abundant in vegetative burning profiles. K⁺/K ratios ranged from 0.1 in geological material profiles to 0.9 in vegetative burning emissions, confirming previous observations that soluble potassium is a good marker for wood combustion.

References

- Calloway, C.P., Li, S.M., Buchanan, J.W., Stevens, R.K., 1989. A refinement of the potassium tracer method for residential wood smoke. *Atmos. Environ.* 23, 67–69.
- Cass, G.R., McRae, G.J., 1983. Source–receptor reconciliation of routine air monitoring data for trace metals: an emission inventory assisted approach. *Environ. Sci. Technol.* 17, 129–139.
- Chow, J.C., Ono, D.M., 1992. PM₁₀ standards and nontraditional particulate source controls: overview of the technical program. In: Chow, J.C., Ono, D.M. (Eds.), *Transactions, PM₁₀ Standards and Nontraditional Particulate Source Controls*. Air and Waste Management Association, Pittsburgh, PA, pp. xxvii–xxxv.
- Chow, J.C., Watson, J.G., 1994. Contemporary source profiles for geological material and motor vehicle emissions. Report no. DRI 2625.2F. Prepared for US EPA, Office of Air Quality Planning and Standards, Research Triangle Park, NC, by Desert Research Institute, Reno, NV.
- Chow, J.C., Watson, J.G., 1997. Fugitive dust and other source contributions to PM₁₀ in Nevada's Las Vegas Valley – Final Report. Prepared for the Clark County Department of Comprehensive Planning, Las Vegas, NV, by the Desert Research Institute, Reno, NV. 18 April 1997.
- Chow, J.C., Watson, J.G., 1999. Ion chromatography. In: Landsberger, S., Creatchman, M. (Eds.), *Elemental Analysis of Airborne Particles*. Gordon and Breach, New York, NJ, pp. 97–137.
- Chow, J.C., Watson, J.G., Crow, D., Lowenthal, D.H., Merrifield, T., 2000. Comparison of IMPROVE and NIOSH carbon measurements. *Aerosol Sci. Technol.*, accepted.
- Chow, J.C., Liu, C.S., Cassmassi, J.C., Watson, J.G., Lu, Z., Pritchett, L.C., 1992b. A neighborhood-scale study of PM₁₀ source contributions in Rubidoux, California. *Atmos. Environ.* 26, 693–706.
- Chow, J.C., Watson, J.G., Pritchett, L.C., Pierson, W.R., Frazier, C.A., Purcell, R.G., 1993. The DRI thermal/optical reflectance carbon analysis system: description, evaluation and applications in US air quality studies. *Atmos. Environ.* 27, 1185–1201.
- Chow, J.C., Watson, J.G., Houck, J.E., Pritchett, L.C., Rogers, C.F., Frazier, C.A., Egami, R.T., Ball, B.M., 1994. A laboratory resuspension chamber to measure fugitive dust size distributions and chemical compositions. *Atmos. Environ.* 28, 3463–3481.
- Chow, J.C., Watson, J.G., Lowenthal, D.H., Solomon, P.A., Magliano, K.L., Ziman, S.D., Richards, L.W., 1992a. PM₁₀ source apportionment in California's San Joaquin Valley. *Atmos. Environ.* 26, 3335–3354.
- Cooper, J.A., Redline, D.C., Sherman, J.R., Valdovinos, L.M., Pollard, W.L., Scavone, L.C., West, C.R., 1987. PM₁₀ source composition library for the South Coast Air Basin. Volume I: Source profile development documentation, Final report. Prepared by South Coast Air Quality Management District, El Monte, CA.
- Core, J.E., Houck, J.E., 1987. Pacific northwest source profile library sampling and analytical protocols. Prepared by Oregon Department of Environmental Quality, Portland, OR.
- Han, M., 1992. Coal- and oil-fired power plant contributions to the atmosphere of Maryland. Ph.D. Dissertation. University of Maryland, College Park, MD.
- Houck, J.E., Chow, J.C., Ahuja, M.S., 1989a. The chemical and size characterization of particulate material originating from geological sources in California. In: Watson, J.G. (Ed.), *Transactions, Receptor Models in Air Resources Management*. Air and Waste Management Association, Pittsburgh, PA, pp. 322–333.
- Houck, J.E., Goulet, J.M., Chow, J.C., Watson, J.G., Pritchett, L.C., 1990. Chemical characterization of emission sources contributing to light extinction. In: Mathai, C.V. (Ed.), *Transactions, Visibility and Fine Particles*. Air and Waste Management Association, Pittsburgh, PA, pp. 437–446.
- Houck, J.E., Chow, J.C., Watson, J.G., Simons, C.A., Pritchett, L.C., Goulet, J.M., Frazier, C.A., 1989b. Determination of particle size distribution and chemical composition of particulate matter from selected sources in California. Prepared for California Air Resources Board, Sacramento, CA, by OMNI Environmental Services, Inc. and Desert Research Institute, Beaverton, OR and Reno, NV.

- Kuykendal, W.B., Brooks, G., Waddell, J.T., Butler, W.A., 1990. Data base for characterizing the chemical composition of source emissions for particulate matter and volatile organic compounds. In: Mathai, C.V. (Ed.), *Transactions, Visibility and Fine Particles*. Air and Waste Management Association, Pittsburgh, PA, pp. 447–455.
- Shareef, G.S., Butler, W.A., Bravo, L.A., Stockton, M.B., 1988a. Air Emissions Species Manual: Volatile organic compound species profiles. Report no. EPA-450/2-88-003a. Prepared by US Environmental Protection Agency, Research Triangle Park, NC.
- Shareef, G.S., Butler, W.A., Bravo, L.A., Stockton, M.B., 1988b. Air Emissions Species Manual, Volume 2: Total suspended particulate species profile. Report no. EPA-450/2-88-003B. Prepared by US Environmental Protection Agency, Research Triangle Park, NC.
- Sheffield, A.E., Gordon, G.E., 1986. Variability of particle composition from ubiquitous sources: results from a new source-composition library. In: Pace, T.G. (Ed.), *Transactions, Receptor Methods for Source Apportionment: Real World Issues and Applications*. Air Pollution Control Association, Pittsburgh, PA, pp. 9–22.
- US EPA, 1999. Compilation of air pollutant emission factors, fifth edition. Report no. AP-42 U.S. Environmental Protection Agency, Research Triangle Park, NC.
- Watson, J.G., Chow, J.C., 2000. Source characterization of major emission sources in the imperial and Mexicali Valleys along the US/Mexico Border. *Sci. Total Environ.*, accepted.
- 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*. Gordon and Breach, New York, NJ, pp. 67–96.
- Watson, J.G., Cooper, J.A., Huntzicker, J.J., 1984. The effective variance weighting for least squares calculations applied to the mass balance receptor model. *Atmos. Environ.* 18, 1347–1355.
- Watson, J.G., Chow, J.C., Mathai, C.V., 1989a. Receptor models in air resources management: a summary of the APCA international specialty conference. *JAPCA* 39, 419–426.
- Watson, J.G., Chow, J.C., Pace, T.G., 1991. Chemical mass balance. In: Hopke, P.K. (Ed.), *Receptor Modeling for Air Quality Management*. Elsevier, New York, NY, pp. 83–116.
- Watson, J.G., Turpin, B.J., Chow, J.C., 2000. The measurement process: precision, accuracy, and validity. In: *Air Sampling Instruments for Evaluation of Atmospheric Contaminants*, ninth ed. American Conference of Governmental Industrial Hygienists, Cincinnati, OH, in press.
- Watson, J.G., Chow, J.C., Lu, Z., Fujita, E.M., Lowenthal, D.H., Lawson, D.R., 1994b. Chemical mass balance source apportionment of PM₁₀ during the Southern California Air Quality Study. *Aerosol Sci. Technol.* 21, 1–36.
- Watson, J.G., Chow, J.C., Pritchett, L.C., Houck, J.E., Burns, S., Ragazzi, R.A., 1990b. Composite source profiles for particulate motor vehicle exhaust source apportionment in Denver, CO. In: Mathai, C.V. (Ed.), *Transactions, Visibility and Fine Particles*. Air and Waste Management Association, Pittsburgh, PA, pp. 422–436.
- Watson, J.G., Chow, J.C., Richards, L.W., Andersen, S.R., Houck, J.E., Dietrich, D.L., 1988. The 1987–88 Metro Denver Brown Cloud Air Pollution Study, Volume II: Measurements. Report no. 8810.1F2. Prepared for 1987–88 Metro Denver Brown Cloud Study, Inc., Greater Denver Chamber of Commerce, Denver, CO, by Desert Research Institute, Reno, NV.
- Watson, J.G., Chow, J.C., Lowenthal, D.H., Pritchett, L.C., Frazier, C.A., Neuroth, G.R., Robbins, R., 1994a. Differences in the carbon composition of source profiles for diesel- and gasoline-powered vehicles. *Atmos. Environ.* 28, 2493–2505.
- Watson, J.G., Robinson, N.F., Chow, J.C., Henry, R.C., Kim, B.M., Pace, T.G., Meyer, E.L., Nguyen, Q., 1990a. The USEPA/DRI chemical mass balance receptor model, CMB 7.0. *Environ. Software* 5, 38–49.
- Watson, J.G., Blumenthal, D.L., Chow, J.C., Cahill, C.F., Richards, L.W., Dietrich, D., Morris, R., Houck, J.E., Dickson, R.J., Andersen, S.R., 1996. Mt. Zirkel Wilderness Area reasonable attribution study of visibility impairment – Volume II: Results of data analysis and modeling. Prepared for Colorado Department of Public Health and Environment, Denver, CO, by Desert Research Institute, Reno, NV.