Source Apportionment of PM$_{2.5}$ in a Subarctic Airshed - Fairbanks, Alaska

Tony Ward$^{1,*}$, Barbara Trost$^2$, Jim Conner$^3$, James Flanagan$^4$, R.K.M. Jayanty$^4$

$^1$ Center for Environmental Health Sciences, The University of Montana, Missoula, Montana, USA
$^2$ Alaska Department of Environmental Conservation, Anchorage, Alaska, USA
$^3$ Fairbanks North Star Borough, Fairbanks, Alaska, USA
$^4$ RTI International, Research Triangle Park, North Carolina, USA

ABSTRACT

Fairbanks, Alaska has some of the highest measured ambient PM$_{2.5}$ concentrations in the United States, with wintertime levels often exceeding the 24-hour PM$_{2.5}$ National Ambient Air Quality Standard (NAAQS) of 35 µg/m$^3$. In an effort to understand the sources of PM$_{2.5}$ in the Fairbanks airshed, source apportionment using Chemical Mass Balance (CMB) modeling was conducted at four locations in Fairbanks over a three-winter period (2008/2009, 2009/2010, and 2010/2011). At each of the four sites, PM$_{2.5}$ concentrations averaged between 22.5 ± 12.0 µg/m$^3$ and 26.5 ± 18.9 µg/m$^3$, with frequent exceedances of the 24-hour NAAQS on the scheduled sample days. The results of the CMB modeling revealed that wood smoke (likely residential wood combustion) was the major source of PM$_{2.5}$ throughout the winter months in Fairbanks, contributing between 60% and nearly 80% of the measured PM$_{2.5}$ at the four sites. The other sources of PM$_{2.5}$ identified by the CMB model were secondary sulfate (8–20%), ammonium nitrate (3–11%), diesel exhaust (not detected-10%), and automobiles (not detected-7%). Approximately 1% of the PM$_{2.5}$ was unexplained by the CMB model. Additional research is needed to confirm the woodsmoke results of the CMB model, as well as determine which sources (fuel oil residential heating, coal combustion, etc.) contribute to the measured secondary sulfate.

Keywords: Chemical Mass Balance; Woodstoves; Source apportionment; Biomass smoke, PM$_{2.5}$.

INTRODUCTION

Numerous studies have shown an association between PM$_{2.5}$ exposure and adverse health effects. For airsheds with elevated concentrations of PM$_{2.5}$, an important step towards implementing emission reduction strategies is to first determine the sources and their respective PM$_{2.5}$ contributions (i.e., source apportionment) to the airshed. The Environmental Protection Agency’s (EPA) Chemical Mass Balance (CMB) model is a receptor model commonly used for PM$_{2.5}$ source apportionment, with CMB studies conducted not only in the U.S., but also around the world (Subramanian et al., 2007; Stone et al., 2008; Kleeman et al., 2009; Gibson et al., 2009; Vega et al., 2009; Andriani et al., 2010; Yin et al., 2010; Roy et al., 2011; Rutter et al., 2011; Zheng et al., 2011). The CMB model can also be used in PM$_{2.5}$ nonattainment areas as a regulatory planning tool for local and state environmental agencies (Ward et al., 2006, 2010; USEPA, 2011).

As the seat of the North Star Borough, Fairbanks, Alaska is the northernmost Metropolitan Statistical Area in the United States. With a population of 31,535, it is also the largest city in the interior of Alaska. Classified as a subarctic climate, winters in Fairbanks begin in late September/early October and last through early May. Average temperatures throughout the long winter months range from –19°F (–28°C) to 31.4°F (–0.3°C), with extreme low temperatures getting down to –60°F (–51°C).

In addition to the cold winter temperatures, the topography of Fairbanks contributes to temperature inversions that frequently occur throughout the winter months. Surrounded by hills on three sides, inversions trap air pollution in the valley for days (and sometimes weeks) at a time, often leading to ice fog events. These factors have historically contributed to problems with carbon monoxide within the city, with the EPA designating Fairbanks nonattainment in 1991 (Alaska DEC, 2011). After several mitigation strategies were employed throughout the city, the Borough became a Carbon Monoxide Maintenance Area on September 27, 2004. Today, there are issues with ambient PM$_{2.5}$ throughout the winter months, with the EPA designating the Fairbanks North Star Borough as nonattainment in December 2009 for exceeding the 24-hour NAAQS. Compared with PM$_{2.5}$ concentrations in the lower 48, Fairbanks has some of the
highest wintertime ambient PM$_{2.5}$ concentrations measured throughout the United States.

Using a CMB source apportionment model, the goal of this program was to identify the major sources of PM$_{2.5}$ within Fairbanks during the winter months over a three-winter period. This manuscript describes the sampling, analytical, and computer modeling efforts that composed this program, as well as the results of the PM$_{2.5}$ air sampling and CMB modeling.

MATERIALS AND METHODS

Sampling Program

Within Fairbanks, 24-hour PM$_{2.5}$ sampling was conducted using a MetOne (Grants Pass, OR) Spiral Ambient Speciation Sampler (SASS) at four sites. Sampling was conducted every three days following the EPA’s fixed monitoring schedule at the State Building, North Pole, and Peger Road (also known as the Transit Yard) sites during the winters of 2008/2009, 2009/2010, and 2010/2011, respectively. Samples were collected only during the winters of 2008/2009 and 2009/2010 for the Relocatable Air Monitoring System (RAMS) site. The State Building site is both a State and Local Air Monitoring Site (SLAMS) for PM$_{2.5}$ as well as a Speciation Trend Network (STN) site, while the other sites are Special Purpose Monitoring (SPM) sites.

During each 24-hour sampling event, the SASS collected ~9.7 m$^3$ of air through Teflon, nylon, and quartz filter media, respectively. A stringent Quality Assurance/Quality Control (QA/QC) program was employed throughout the program. During shipment of both clean and exposed filter sample media, all PM$_{2.5}$ filters remained in their protective containers and were FedEx overnighted in a cooler containing cold packs during transport. PM$_{2.5}$ filter field and trip blanks were collected periodically throughout the program in an effort to determine any artifact contamination.

Analytical Program

$PM_{2.5}$ Speciation Data

Exposed SASS filter samples were analyzed by Research Triangle Institute (RTI, Research Triangle Park, NC). From the Teflon filter, a gravimetric analysis (RTI, 2008) was initially performed followed by an elemental analysis (RTI, 2009a) using energy-dispersive X-ray fluorescence (EDXRF) where 33 elements were quantified. From the nylon filter, ions (including ammonium, potassium, sodium, nitrate, and sulfate) were measured by ion chromatography (IC) (RTI, 2009b; RTI, 2009c). From the quartz filter, elemental carbon and organic carbon (EC/OC) concentrations were quantified by Thermal Optical Transmittance (RTI, 2009d).

Computer Modeling Program

A Chemical Mass Balance (CMB) computer model (version 8.2) was utilized to apportion the sources of PM$_{2.5}$ in Fairbanks. The CMB receptor model (Friedlander, 1973; Cooper and Watson, 1980; Gordon, 1980, 1988; Watson, 1984; Watson et al., 1984; 1990; Hidy and Venkataraman, 1996) is based on an effective-variance least squares method, and consists of a solution to linear equations that expresses each receptor chemical concentration as a linear sum of products of source fingerprint abundances and contributions.

For each sample day (from the four sites), the CMB modeling process began by selecting from a combination of 91 sources and 50 chemical species (38 elements, 9 ions, TC/OC/EC) in an effort to reconstruct the measured Fairbanks ambient PM$_{2.5}$ mass and chemical composition. As part of the CMB modeling procedure, multiple combinations would be tried for each sample run in an effort to select the best combination of sources and species, with an evaluation of the diagnostic performance measures conducted each time until an optimal fit could be obtained. The resulting output file contained the source contribution estimate (SCE) of each identified source, along with the associated standard errors (STD ERR). Unexplained concentrations were also calculated by taking the difference between the actual measured mass and the CMB predicted mass for each sample run.

CMB Model Source Profiles

Discussions were held with Fairbanks Borough and Alaska Department of Environmental Conservation (ADEC) personnel in an effort to identify all of the potential sources of PM$_{2.5}$ in Fairbanks prior to setting up the CMB model. Following these discussions, a comprehensive list of sources that could potentially contribute PM$_{2.5}$ to the Fairbanks airshed was developed. For each identified source, an attempt was made to locate a source profile. Source profiles are the fractional mass abundances of measured chemical species relative to primary PM$_{2.5}$ mass in source emissions, and are part of the input data loaded into the CMB model.

The source profiles used in this three-winter study represented sources such as street sand, road dust, primary secondary source emissions (sulfate, ammonium nitrate, ammonium sulfate), gasoline and diesel exhaust emissions, meat cooking, residential wood combustion, and other local sources/industry in Fairbanks. Source profiles were either taken directly from the most recent version of SPECIATE 4.0 (USEPA, 2006) or from previous CMB applications (Carlson, 1990; Schmidt, 1996; Ward and Smith, 2005).

RESULTS

$PM_{2.5}$ Mass

Table 1 presents a three-winter average of 24-hr PM$_{2.5}$ mass concentrations (note that a two-winter average is presented for the RAMS site). At each of the four sites, PM$_{2.5}$ concentrations averaged between 22.5 ± 12.0 µg/m$^3$ (RAMS) and 26.5 ± 18.9 µg/m$^3$ (North Pole). Throughout the multi-winter sampling program at the State Building site, there were 25 sample days (out of 102) that exceeded the 24-hour NAAQS. At the North Pole site, 18 days exceeded the 24-hour standard (n = 66). At the RAMS (n = 52) and Peger Road (n = 74) sites, there were 14 and 16 exceedances, respectively. The highest 24-hour concentration (115.4 µg/m$^3$) was measured on December 30, 2009 at the North Pole site. Note that this sample day had elevated levels of OC (68.4 µg/m$^3$) measured from the quartz filter, and was determined by CMB modeling to be heavily influenced by wood burning.
Table 1. Three-winter average of speciated PM$_2.5$ concentrations ± standard deviations (µg/m$^3$).

| Analyte          | State Building n = 102 | North Pole n = 66 | *RAMS n = 52 | Peger Road n = 74 | MDL  
|------------------|------------------------|-------------------|--------------|-------------------|------
| Mass             | 24.7 ± 14.4            | 26.5 ± 18.9       | 22.5 ± 12.0  | 24.8 ± 13.1       | 0.740
| Magnesium        | 0.007 ± 0.012          | 0.005 ± 0.009     | 0.009 ± 0.016| 0.008 ± 0.012     | 0.013
| Aluminum         | 0.016 ± 0.020          | 0.008 ± 0.012     | 0.010 ± 0.016| 0.019 ± 0.015     | 0.014
| Silicon          | 0.043 ± 0.032          | 0.022 ± 0.019     | 0.044 ± 0.045| 0.056 ± 0.047     | 0.011
| Sulfur           | 1.6 ± 1.2              | 0.770 ± 0.508     | 0.877 ± 0.497| 1.4 ± 0.939       | 0.008
| Chlorine         | 0.121 ± 0.117          | 0.122 ± 0.129     | 0.127 ± 0.120| 0.240 ± 0.178     | 0.007
| Potassium        | 0.118 ± 0.101          | 0.166 ± 0.116     | 0.113 ± 0.071| 0.114 ± 0.061     | 0.006
| Calcium          | 0.039 ± 0.021          | 0.015 ± 0.011     | 0.021 ± 0.022| 0.050 ± 0.025     | 0.006
| Iron             | 0.053 ± 0.035          | 0.023 ± 0.022     | 0.048 ± 0.095| 0.080 ± 0.055     | 0.002
| Copper           | 0.004 ± 0.004          | 0.003 ± 0.009     | 0.002 ± 0.003| 0.006 ± 0.005     | 0.002
| Zinc             | 0.062 ± 0.042          | 0.025 ± 0.023     | 0.026 ± 0.017| 0.095 ± 0.056     | 0.003
| Bromine          | 0.004 ± 0.003          | 0.003 ± 0.002     | 0.008 ± 0.009| 0.009 ± 0.008     | 0.002
| Strontium        | 0.003 ± 0.005          | 0.001 ± 0.002     | 0.001 ± 0.003| 0.003 ± 0.008     | 0.002
| Sodium           | 0.080 ± 0.063          | 0.062 ± 0.068     | 0.097 ± 0.093| 0.114 ± 0.075     | 0.037
| Organic carbon   | 10.6 ± 6.4             | 15.4 ± 11.3       | 13.1 ± 7.7   | 11.6 ± 5.9        | 0.240
| Elemental carbon | 1.4 ± 1.0              | 1.8 ± 1.4         | 1.5 ± 0.9    | 2.3 ± 1.1         | 0.240
| Sulfate          | 4.2 ± 3.0              | 2.2 ± 1.3         | 2.5 ± 1.3    | 3.9 ± 2.4         | 0.010
| Nitrate          | 1.3 ± 0.7              | 0.784 ± 0.394     | 0.822 ± 0.479| 1.5 ± 0.91        | 0.007
| Ammonium         | 2.1 ± 1.8              | 0.933 ± 0.625     | 1.1 ± 0.599  | 2.0 ± 1.3         | 0.018
| Potassium ion    | 0.121 ± 0.096          | 0.161 ± 0.107     | 0.114 ± 0.083| 0.122 ± 0.055     | 0.015
| Sodium ion       | 0.079 ± 0.067          | 0.111 ± 0.081     | 0.142 ± 0.099| 0.126 ± 0.075     | 0.027

Note: Only those analytes measured above their respective minimum detection limits (MDL) are presented in Table 1.

*Samples only collected during winters of 2008/2009 and 2009/2010.

PM$_2.5$ Speciation

Table 1 also presents the average concentrations (in µg/m$^3$) of the most prevalent chemical species composing the ambient PM$_2.5$ (including elements, ions, and OC/EC) for each of the sites measured throughout the sampling program. Only those analytes whose averages were above their respective minimum detection limits (MDL) at one or more of the four sites are presented in Table 1.

Out of the 33 elements quantified, only 13 were consistently measured at or above their reported MDLs. Sulfur had the highest concentration of the measured elements, with the highest overall program levels measured at the State Building site (1.6 ± 1.2 µg/m$^3$). The next highest concentrations of elements measured included chlorine and potassium. Regarding the ions measured, sulfate had the highest concentration at each of the sites, followed by ammonium and nitrate. OC concentrations averaged between 10.6 and 15.4 µg/m$^3$, with EC concentrations between 1.4 and 2.3 µg/m$^3$. PM$_2.5$ mass was composed of 43–58% OC and 6–9% EC, respectively, at each of the sites. Results from the field and trip blanks for the species listed in Table 1 were minimal throughout the sampling/analytical program, therefore data were not corrected prior to using in the CMB model.

Chemical Mass Balance Modeling

Table 2 presents the PM$_2.5$ sources identified by the CMB models for each of the four sites. Also presented are the source contribution estimates (± standard errors) and percent of total PM$_2.5$. In total, five source profile types were identified by the CMB model as contributors to the ambient PM$_2.5$ throughout the winter months. Wood smoke (likely residential wood combustion) was the major source of PM$_2.5$ identified, contributing between 63% and ~80% of the measured PM$_2.5$ at the four sites. The other sources of PM$_2.5$ identified by the CMB model were secondary sulfate (8–20%), ammonium nitrate (3–11%), diesel exhaust (not detected-10%), and automobiles (not detected-7%). Approximately 1% of the PM$_2.5$ was unexplained by the CMB model.

CMB QA/QC Results

EPA’s validation protocol (Watson et al., 2004) was followed throughout this CMB modeling program to ensure accurate results. The source contribution estimates, sample run statistics, and diagnostic information were reviewed for each model run to determine the validity of the initial model results. The majority of the CMB fitting parameters used to evaluate the validity of source contribution estimates were well within EPA target ranges. Table 3 presents the program average key ‘goodness-of-fit’ statistics commonly evaluated for CMB models, the average results for each of the CMB programs, respectively, and the EPA target ranges for each parameter. The values for $R^2$, Chi$^2$, Degrees of Freedom, and percent mass explained for each CMB model run were generally well within the EPA target ranges. Colinearity was an issue when loading source profiles with similar chemical makeups into the model (such as diesel exhaust and gasoline exhaust profiles), however, this issue was resolved when selecting the profile combinations per modeling run that provided the best statistical fits.
Table 2. Source contribution estimates ± standard errors (µg/m³). Percent contributions to overall PM_{2.5} mass are also presented per source.

|                     | Sulfate | Ammonium Nitrate | Diesel | Autos | Wood smoke | Unexplained | PM_{2.5} Mass | n       | Sampling Dates |
|---------------------|---------|------------------|--------|-------|------------|-------------|--------------|--------|----------------|
| **2008/2009**       |         |                  |        |       |             |             |              |        |                |
| State Building      | 5.1 ± 0.6 | 2.1 ± 0.7     | 0.3 ± 0.1 | 1.7 ± 0.7 | 16.0 ± 2.3 | 0.2         | 25.3         | 47     | 11/8/08–4/7/09 |
| North Pole          | 1.9 ± 0.2 | 1.0 ± 0.2     | 0.2 ± 0.1 | 0.7 ± 0.3 | 15.0 ± 2.0 | 0.2         | 18.9         | 21     | 1/25/09–4/7/09 |
| Peger Road          | 2.8 ± 0.3 | 1.5 ± 0.4     | 1.2 ± 0.5 | 0.7 ± 0.2 | 10.6 ± 1.6 | 0.1         | 16.8         | 26     | 1/25/09–4/7/09 |
| RAMS                | 1.1 ± 0.1 | 0.9 ± 0.1     | ND     | ND    | 6.3 ± 0.8  | 0.04        | 8.2          | 23     | 1/25/09–4/7/09 |
| **2009/2010**       |         |                  |        |       |             |             |              |        |                |
| State Building      | 5.2 ± 0.6 | 2.5 ± 0.7     | 0.6 ± 0.3 | 0.7 ± 0.3 | 19.5 ± 1.9 | 0.2         | 28.8         | 40     | 11/3/09–3/15/10 |
| North Pole          | 2.6 ± 0.3 | 1.2 ± 0.3     | 0.8 ± 0.2 | 1.3 ± 0.4 | 27.1 ± 3.7 | 0.3         | 33.7         | 35     | 11/3/09–3/15/10 |
| Peger Road          | 4.8 ± 0.5 | 2.1 ± 0.6     | 2.8 ± 0.7 | 0.4 ± 0.1 | 18.6 ± 3.0 | 0.3         | 29.0         | 38     | 11/3/09–3/15/10 |
| RAMS                | 4.0 ± 0.5 | 0.9 ± 0.2     | 2.5 ± 0.6 | 2.3 ± 0.7 | 26.9 ± 4.1 | 0.04        | 36.7         | 29     | 11/15/09–3/15/10 |
| **2010/2011**       |         |                  |        |       |             |             |              |        |                |
| State Building      | 3.5 ± 0.4 | 1.7 ± 0.5     | ND     | 0.4 ± 0.1 | 14.6 ± 1.1 | 0.004       | 20.2         | 15     | 11/1/10–2/8/11  |
| North Pole          | 2.1 ± 0.3 | 0.9 ± 0.2     | 0.9 ± 0.3 | 1.4 ± 0.5 | 21.3 ± 3.2 | 0.2         | 26.8         | 10     | 1/9/11–2/5/11  |
| Peger Road          | 4.8 ± 0.5 | 2.0 ± 0.5     | 0.8 ± 0.2 | 0.7 ± 0.3 | 20.2 ± 3.9 | 0.1         | 28.6         | 10     | 1/9/11–2/5/11  |

Note: NH_{4}NO_{3}: ammonium nitrate; RWC: residential wood combustion; ND: not detected by the CMB model. Sampling was not conducted at the RAMS site during the winter of 2010/2011.

Table 3. Average goodness-of-fit parameters.

| Goodness-of-Fit Parameter | State Building | North Pole | RAMS | Peger Road | EPA Target |
|---------------------------|----------------|------------|------|------------|------------|
| R²                        | 0.96           | 0.97       | 0.97 | 0.98       | 0.8–1.00   |
| Chi²                      | 0.26           | 0.14       | 0.13 | 0.11       | 0.00–4.0   |
| Degrees of Freedom        | 34             | 36         | 37   | 36         | > 5        |
| % Mass Explained          | 99.6%          | 99.2%      | 100.2% | 99.5%     | 80–120%    |
| TSTAT                     | > 2            | > 2        | > 2  | > 2        | > 2        |

Note: values presented are averages of winters per site.

DISCUSSION

The wood smoke source identified by the CMB model should be viewed as a general source predominantly composed of wood stove emissions. In addition to residential wood stoves, other biomass combustion emission sources could have contributed to the wood smoke results in Fairbanks, including smoke from outdoor boilers, residential open burning of biomass waste, and small industrial sources. A source profile developed in Missoula, Montana in the late 1980s served as the best statistically fitting wood smoke profile for each of the four sites when conducting the Fairbanks CMB analyses. It should also be noted that many other residential wood combustion source profiles from the EPA SPECIATE database gave good statistical fits throughout the computer modeling process for each of the four sites. When compared to profiles of other sources, these wood smoke profiles typically had higher levels of elemental potassium, potassium ion, and OC. Generally, both elemental potassium and the potassium ion gave good fits when modeling, with the elemental form usually providing the better statistical fit. The CMB results identifying wood smoke in the Fairbanks airshed are consistent with findings from other recent source apportionment studies demonstrating the significant impact that biomass smoke can have on ambient PM_{2.5} (Ward et al., 2006; Gelencser et al., 2007; Puxbaum et al., 2007; Sheesley et al., 2007; Szidat et al., 2007; Caseiro et al., 2009; Ward et al., 2010).

Secondary Pollutants

“Pure secondary” aerosols such as ammonium nitrate and sulfate are represented by their chemical form in the model.
Following wood smoke, the second largest source contributor was sulfate (SO$_4^{2-}$), a compound that includes particles directly emitted during combustion and secondary particles formed in the atmosphere. The third largest source identified was ammonium nitrate (NH$_4$NO$_3$), also a secondary particle. It should be noted that even though ammonium sulfate was not detected by the CMB model as a PM$_{2.5}$ source (secondary) when both sulfate and ammonium nitrate were used as fitting species, it is likely a significant contributor to the measured PM$_{2.5}$ levels. When using the secondary sulfate source profile in the model, sulfur was used as the fitting species in each model run to apportion sulfate contributions.

Ammonia (NH$_3$) and oxides of nitrogen (NOx) are the precursors for ammonium nitrate particles, with just under half all NO$_x$ emissions in the United States estimated to come from the transportation sector (Dreher and Harley, 1998; Seinfeld and Pandis, 1998). Other sources of NO$_x$ in Fairbanks might include industry, natural gas furnaces, and residential wood combustion (Schmidt, 1996). In other parts of the lower 48, ammonia emissions to the atmosphere can arise from many sources including the decay of livestock waste, use of chemical fertilizers, emissions from sewage waste treatment plants, and biological processes in soils (Fraser and Cass, 1998). In Fairbanks, combustion processes such as motor vehicles likely are a significant source of ammonia. Sulfate is a function of the sulfur content of the fuels burned in the Fairbanks community. Recent regulations have all but eliminated sulfur from gasoline and diesel fuel in Alaska. Therefore, the fuels contributing sulfur (and sulfate) to the Fairbanks airedhul include distillate fuel oil used in space heating and coal combustion.

**Mobile Sources**

Profiles for the mobile source group typically had higher levels of EC when compared to the wood smoke profiles. The CMB model determined that vehicles were a measurable source of PM$_{2.5}$ at each of the sites throughout the winter months. Automobile exhaust (gasoline-powered) PM$_{2.5}$ was detected at the State Building more frequently when compared to the other sites (18% of all modeling runs). Diesel exhaust was also measured more frequently at the Peger Road site when compared to the other sites, measured in 50% of all modeling runs. Neither automobile nor diesel exhaust was detected by the CMB model at the RAMS sites throughout the 2008/2009 program, and diesel exhaust was not detected at the State Building site during the winter of 2010/2011.

**Other Sources**

It should be mentioned that there were other sources identified by the CMB model as contributors to the ambient PM$_{2.5}$, yet were not identified as statistically significant contributors (i.e., evaluated based on statistical criteria). These include the following: street sand, distillate oil combustion, natural gas combustion, residual oil combustion, and sub-bituminous coal combustion.

The CMB model was run with both the distillate oil and coal profile in the model, and in the absence of the secondary sulfate profile (using both the sulfur and sulfate fitting species). In both instances, the model provided very poor statistical fits. Using the secondary sulfate profile (as a potential surrogate for these sources) provided excellent statistical fits on nearly each sample run. Either these sources are not contributors to the overall PM$_{2.5}$ throughout the winter months, or the emissions from these sources are represented by the secondary sulfate source profile in the CMB model.

**Sulfur and Sulfate Concentrations**

The Fairbanks State Building site has the highest winter-to-summer sulfate ratio among all of the EPA’s PM$_{2.5}$ Chemical Speciation Network (CSN) sites in the U.S. This is a consequence of high sulfate concentrations during the winter combined with very low concentrations during the summer. Correlations between sulfate and ammonium ion were very high (R = 0.979) for the Fairbanks CSN dataset, strongly implying that most of the sulfate charge was balanced by ammonium ion. This high ammonium-sulfate correlation held even after the total mass loadings were normalized out (R = 0.871). Correlation coefficients between ammonium and nitrate ions were found to be significantly lower for both the mass and normalized data, R = 0.754 and 0.544, respectively.

The average ratio of sulfur by EDXRF to sulfate ion by ion chromatography (IC) was found to be close to the theoretical value of 0.33 based on molecular weights. For the Fairbanks State Building dataset, the average sulfur/sulfate ratio was 0.348 with a standard deviation of 0.056. This implies that on an annual basis, sulfate accounts for a large majority of the total sulfur. However, it has been found that for the Fairbanks State Building CSN site, there are winter events that have a clear excess of total sulfur (measured by EDXRF) relative to the amount that can be attributed to sulfate (measured by IC). Fig. 1 shows the relationship between excess sulfur vs. excess charge, with the excess of total sulfur correlating well with the excess of cation charge relative to the anion charge (r$^2$ of ~0.6 and a slope of 1.86). The slope of charge vs. missing sulfur suggests that the unmeasured sulfur compound(s) might have a charge less than –1. The apparent excess of cations is most likely caused by the presence of anions that are not included among those that are routinely measured for the CSN program. For the CSN program, only sulfate and nitrate ions are routinely analyzed; cations are limited to ammonium, sodium, and potassium.

**Limitations of Study**

In presenting the final PM$_{2.5}$ results, there were several sample days throughout the program that were excluded from the overall average calculations due to sampler malfunctions or collection errors. CMB source apportionment was not conducted on additional sample days due to low PM$_{2.5}$ mass. If the measured PM$_{2.5}$ concentration is less than 5 μg/m$^3$, the percent mass may be outside of the acceptable ranges because the uncertainty in the mass measurement is approximately 1 to 2 μg/m$^3$. As noted earlier, the majority of the source profiles used in this model were taken from the EPA SPECIATE database. It would be beneficial to have Fairbanks-specific profiles for these combustion sources.
Ward et al., Aerosol and Air Quality Research, 12: 536–543, 2012

Fig. 1. Relationship between excess sulfur vs. excess charge from.

loaded into the model in an effort to further address the contributions from these sources. In particular, it would be valuable to have a wood smoke source profile developed using the biomass fuel types specific to the Fairbanks region, and generated under similar burn and meteorological conditions experienced in Fairbanks throughout the winter months. It would also be beneficial to have Fairbanks-specific source profiles for coal burning and distillate home heating emissions developed for use in future Fairbanks CMB modeling applications.

CONCLUSIONS

Understanding sources in an airshed is a vital step to establish policies that might reduce pollution from these sources. The results of the CMB modeling revealed that wood smoke (likely residential wood combustion) was the major source of PM$_{2.5}$ throughout the winter months in Fairbanks, contributing between 63% and ~80% of the measured PM$_{2.5}$ at the four sites. The other sources of PM$_{2.5}$ identified by the CMB model using EPA SPECIATE source profiles were ammonium nitrate, secondary sulfate, diesel exhaust, and automobiles. Approximately 1% of the PM$_{2.5}$ was unexplained by the CMB model.

Regarding the combustion sources such as distillate oil, waste oil, residual oil, and sub-bituminous coal, primary PM$_{2.5}$ emissions were identified by the CMB model (using EPA SPECIATE profiles) but not identified as being statistically significant. When conducting the CMB modeling, the secondary sulfate profile (as a potential surrogate for these sources) provided excellent statistical fits on nearly each sample run. In addition, we expected to see ammonium sulfate identified by the CMB model in greater amounts. However, using secondary sulfate and ammonium nitrate as source inputs provided better statistical results (i.e., better results) in the absence of ammonium sulfate. It is likely that ammonium sulfate is a large contributor to the overall wintertime PM$_{2.5}$ in Fairbanks, yet the exact contributions could not be determined in this modeling application. It is still undetermined as to which specific sources (and in what amounts) are contributing to the elevated sulfur and sulfate concentrations (as well as ammonium sulfate) in the Fairbanks airshed throughout the winter months.

Finally, there are ways that results from this study can be improved. It is recommended that additional modeling (not only CMB, but also other receptor and/or dispersion models) be conducted to further investigate the sulfate and secondary aerosol contributions (sulfate vs. ammonium and sulfate vs. ammonium nitrate) to the ambient PM$_{2.5}$. In addition, the use of molecular markers (individual organic compounds specific to individual sources) could be utilized for this application. For example, levoglucosan is a chemical marker of wood smoke (Simoneit et al., 1998) that could help to further apportion the wood stove contributions. Sulfur-containing compounds such as dibenzothiophene and benzo naphtho thiophene (known markers of diesel vehicles and residential oil burners) as well as picene (marker for coal combustion) could be measured to investigate the elevated concentrations of sulfur and sulfate in the airshed. These additional analyses could help confirm the CMB modeling results that wood smoke is the largest contributor to the Fairbanks airshed throughout the winter months, and accurately determine which sources contribute to the elevated levels of sulfur and sulfate.

ACKNOWLEDGEMENTS

Funding for this project was provided by the Alaska Department of Environmental Conservation, with additional funding by NIH COBRE grant P20-RR017670. The authors would like to thank the personnel from the Fairbanks North Star Borough that conducted the air sampling, as well as Mohamed Elashheb who assisted with the CMB modeling effort.
REFERENCES

Alaska Department of Environmental Conservation (ADEC). (2011). http://www.dec.state.ak.us/air/anpms/comm/fbs1co.htm, accessed September 20, 2011.

Andriani, E., Caselli, M., Ielpo, P., de Gennaro, G., Daresta, B.E., Fermo, P., Piazzalunga, A. and Placentino, M.C. (2010). Application of CMB Model to PM$_{10}$ Data Collected in a Site of South Italy: Results and Comparison with APCS Model. Curr. Anal. Chem. 6: 19–25.

Carlson, J. (1990). PM$_{10}$ Chemical Mass Balance Study for Missoula, Montana, Missoula City-County Health Department (MCCHD).

Caseiro, A., Bauer, H., Schmidl, C., Pio, C.A. and Puxbaum, H. (2009). Wood Burning Impact on PM$_{10}$ in Three Austrian Regions. Atmos. Environ. 43: 2186–2195.

Cooper, J.A. and Watson, J.G. (1980). Receptor Oriented Methods of Air Particulate Source Apportionment. J. Air Pollut. Contr. Assoc. 30: 1116–1125.

Dreher D.B. and Harley, R.A. (1998). A Fuel-Based Inventory for Heavy-Duty Diesel Truck Emissions. J. Air Waste Manage. Assoc. 48: 352–358.

Fraser, M.P. and Cass, G.R. (1998). Detection of Excess Ammonia Emissions from In-Use Vehicles and the Implications for Fine Particle Control. Environ. Sci. Technol. 32: 1053–1057.

Friedlander, S.K. (1973). Chemical Element Balances and Identification of Air Pollution Sources. Environ. Sci. Technol. 7: 235–240.

Gelencser, A., May, B., Simpson, D., Sanchez-Ochoa, A., Kasper-Giebl, A., Puxbaum, H., Caseiro, A., Pio, C. and Legrand, M. (2007). Source Apportionment of PM$_{2.5}$ Organic Aerosol over Europe: Primary/Secondary, Natural/Anthropogenic, and Fossil/Biogenic Origin. J. Geophys. Res. 112: D23S04/1–D23S04/12.

Gibson, M.D., Heal, M.R., Bache, D.H., Hursthorne, A.S., Beverland, I.J., Craig, S.E., Clark, C.F., Jackson, M.H., Guersey, J.R. and Jones, C. (2009). Using Mass Reconstruction Along a Four-Site Transect as a Method to Interpret PM$_{10}$ in West-Central Scotland, United Kingdom. J. Air Waste Manage. Assoc. 59: 1429–1436.

Gordon, G.E. (1980). Receptor Models. Environ. Sci. Technol. 14: 792–800.

Gordon, G.E. (1988). Receptor Models. Environ. Sci. Technol. 22: 1132–1142.

Hidy, G.M. and Venkataraman, C. (1996). The Chemical Mass Balance Method for Estimating Atmospheric Particle Sources in Southern California. Chem. Eng. Commun. 151: 187–209.

Kleeman, M.J., Riddle, S.G., Robert, M.A., Jakober, C.A., Fine, P.M., Hays, M.D., Schauer, J.J. and Hannigan, M.P. (2009). Source Apportionment of Fine (PM$_{2.5}$) and Ultrafine (PM$_{0.1}$) Airborne Particulate Matter During a Severe Winter Pollution Episode. Environ. Sci. Technol. 43: 272–279.

Puxbaum, H., Caseiro, A., Sanchez-Ochoa, A., Kasper-Giebl, A., Claeyts, M., Gelencser, A., Legrand, M., Preunkert, S. and Pio, C. (2007). Levoglucosan Levels at Background Sites in Europe for Assessing the Impact of Biomass Combustion on the European Aerosol Background. J. Geophys. Res. 112: D23S05, doi: 10.1029/2006JD008114.

Roy, A.A., Wagstrom, K.M., Adams, P.J., Pandis, S.N. and Robinson, A.L. (2011). Quantification of the Effects of Molecular Marker Oxidation on Source Apportionment Estimates for Motor Vehicles. Atmos. Environ. 45: 3132–3140.

RTI International (2008). SOP for Particulate Matter (PM) Gravimetric Analysis, July 8, 2008, http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/RTIGravMassOPFinanl.pdf (accessed 10/7/2011).

RTI International (2009a). SOP for the X-Ray Fluorescence Analysis of Particulate Matter Deposits on Teflon Filters, August 19, 2009, http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/pmxrsfop.pdf (accessed 10/7/2011).

RTI International (2009b). SOP for PM$_{2.5}$ Cation Analysis, August 25, 2009, http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/pm25cationsop.pdf (accessed 10/7/2011).

RTI International (2009c). SOP for PM$_{2.5}$ Anion Analysis, August 26, 2009, http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/pm25anionsop.pdf (accessed 10/7/2011).

RTI International (2009d). SOP for the Determination of Organic, Elemental, and Total Carbon in Particulate Matter Using a Thermal/Optical-Transmittance Carbon Analyzer, February 16, 2009, http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/RTIOCECSOP.pdf (accessed 10/7/2011).

Rutter, A.P., Snyder, D.C., Schauer, J.J., Sheesley, R.J., Olson, M.R. and DeMinter, J. (2011). Contributions of Resuspended Soil and Road Dust to Organic Carbon in Fine Particulate Matter in the Midwestern US. Atmos. Environ. 45: 514–518.

Schmidt, B. (1996). Chemical Mass Balance Source Apportionment of Missoula, Montana 1995/1996 Winter Suspended Particulate Matter, Missoula City-County Health Department (MCCHD).

Seinfeld, J.H. and Pandis, S.N. (1998). Atmospheric Chemistry and Physics. From Air Pollution to Climate Change, New York, John Wiley & Sons.

Sheesley, R.J., Schauer, J.J., Zheng, M. and Wang, B. (2007). Sensitivity of Molecular Marker-Based CMB Models to Biomass Burning Source Profiles. Atmos. Environ. 41: 9050–9063.

Simoneit, B.R.T., Schauer, J.J., Nolte, C.G., Oros, D.R., Elias, V.O., Fraser, M.P., Rogge, W.F. and Cass, G.R. (1998). Levoglucosan, a Tracer for Cellulose in Biomass Burning and Atmospheric Particles. Atmos. Environ. 33: 173–182.

Stone, E.A., Snyder, D.C., Sheesley, R.J., Sullivan, A.P., Weber, R.J. and Schauer, J.J. (2008). Source Apportionment of Fine Organic Aerosol in Mexico City during the MILAGRO Experiment 2006. Atmos. Chem. Phys. 8: 1249–1259.

Subramanian, R., Donohue, N.M., Bernardo-Bricker, A., Rogge, W.F. and Robinson, A.L. (2007). Insights into the Primary, Secondary and Regional-Local Contributions to Organic Aerosol and PM$_{2.5}$ Mass in Pittsburgh, Pennsylvania. Atmos. Environ. 41: 7414–7433.

Szidat, S., Prévôt, A.S.H., Sandradewi, J., Alfarra, M.R., Ward et al., Aerosol and Air Quality Research, 12: 536–543, 2012
Synal, H.A., Wacker, L., and Baltensperger, U. (2007). Dominant Impact of Residential Wood Burning on Particulate Matter in Alpine Valleys during Winter. Geophys. Res. Lett. 34: L05820.

United States Environmental Protection Agency (USEPA) (2006). SPECIATE 4.0: EPA’s Repository of Total Organic Compound (TOC) and Particulate Matter (PM) Speciated Profiles for a Variety of Sources for Use in Source Apportionment Studies, U.S. Environmental Protection Agency OAQPS, Research Triangle Park, NC. http://www.epa.gov/ttn/chief/software/speciate/index.

United States Environmental Protection Agency (USEPA) (2011). Technology Transfer Network, Support Center for Regulatory Atmospheric Modeling http://www.epa.gov/scram001/receptor cmb.htm, accessed September 28, 2011.

Vega, E., Lowenthal, D., Ruiz, H., Reyes, E., Watson, J.G., Chow, J.C., Viana, M., Querol, X., and Alastuey, A. (2009). Fine Particle Receptor Modeling in the Atmosphere of Mexico City. J. Air Waste Manage. Assoc. 59: 1417–1428.

Ward, T.J. and Smith, G.C. (2005). The 2000/2001 Missoula Valley PM$_{2.5}$ Chemical Mass Balance Study, Including the 2000 Wildfire Season – Seasonal Source Apportionment. Atmos. Environ. 39: 709–717.

Ward, T.J., Rinehart, L.R. and Lange, T. (2006). The 2003/2004 Libby, Montana PM$_{2.5}$ Source Apportionment Research Study. Aerosol Sci. Technol. 40: 166–177.

Ward, T.J., Palmer, C.P. and Noonan, C. W. (2010). PM$_{2.5}$ Source Apportionment Following a Large Woodstove Changeout Program in Libby, Montana. J. Air Waste Manage. Assoc. 60: 688–693.

Watson, J.G. (1984). Overview of Receptor Model Principles. J. Air Pollut. Contr. Assoc. 34: 619–623.

Watson, J.G., Cooper, J.A. and 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., Robinson, N.F., Chow, J.C., Henry, R.C., Kim, B.M., Pace, T.G., Meyer, E.L., and Nguyen, Q. (1990). The USEPA/DRI Chemical Mass Balance Receptor Model, CMB 7.0. Environ. Software 5: 38–49.

Watson, J.G., et al. (2004). Protocol for Applying and Validating the CMB Model for PM$_{2.5}$ and VOC. Report No. EPA-451/R-04-001, USEPA QAQPS.

Yin, J., Harrison, R.M., Chen, Q., Rutter, A. and Schauer, J.J. (2010). Source Apportionment of Fine Particles at Urban Background and Rural Sites in the UK Atmosphere. Atmos. Environ. 44: 841–851.

Zheng, M., Wang, F., Hagler, G.S.W., Hou, X., Bergin, M., Cheng, Y., Salmon, L.G., Schauer, J.J., Louie, P.K.K., Zeng, L. and Zhang, Y. (2011). Sources of Excess Urban Carbonaceous Aerosol in the Pearl River Delta Region, China. Atmos. Environ. 45: 1175–1182.

Received for review, November 18, 2011
Accepted, February 28, 2012