



Source Apportionment of PM_{2.5} in a Subarctic Airshed - Fairbanks, Alaska

Tony Ward^{1*}, Barbara Trost², Jim Conner³, James Flanagan⁴, R.K.M. Jayanty⁴

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/m³. 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/m³ and 26.5 ± 18.9 µg/m³, 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

* Corresponding author. Tel.: (406) 243-4092;
Fax: (406) 243-2807
E-mail address: tony.ward@umontana.edu

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 m³ 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, pure 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/m³ (RAMS) and 26.5 ± 18.9 µg/m³ (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/m³) was measured on December 30, 2009 at the North Pole site. Note that this sample day had elevated levels of OC (68.4 µg/m³) 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/m³).

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/m³) 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/m³). 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/m³, with EC concentrations between 1.4 and 2.3 µg/m³. 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 R², Chi², 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 \pm standard errors ($\mu\text{g}/\text{m}^3$). Percent contributions to overall $\text{PM}_{2.5}$ mass are also presented per source.

	Sulfate	Ammonium Nitrate	Diesel	Autos	Wood smoke	Unexplained	$\text{PM}_{2.5}$ Mass	n	Sampling Dates
2008/2009									
State Building	5.1 ± 0.6 (20.0 %)	2.1 ± 0.7 (8.1 %)	0.3 ± 0.1 (1.1 %)	1.7 ± 0.7 (6.8 %)	16.0 ± 2.3 (63.1 %)	0.2 (0.8 %)	25.3	47	11/8/08– 4/7/09
North Pole	1.9 ± 0.2 (9.8 %)	1.0 ± 0.2 (5.1 %)	0.2 ± 0.1 (0.8 %)	0.7 ± 0.3 (3.7 %)	15.0 ± 2.0 (79.8 %)	0.2 (0.8 %)	18.9	21	1/25/09– 4/7/09
Peger Road	2.8 ± 0.3 (16.7 %)	1.5 ± 0.4 (8.9 %)	1.2 ± 0.5 (7.3 %)	0.7 ± 0.2 (3.9 %)	10.6 ± 1.6 (62.7 %)	0.1 (0.5 %)	16.8	26	1/25/09– 4/7/09
RAMS	1.1 ± 0.1 (13.0 %)	0.9 ± 0.1 (10.5 %)	ND	ND	6.3 ± 0.8 (76.0 %)	0.04 (0.5 %)	8.2	23	1/25/09– 4/7/09
2009/2010									
State Building	5.2 ± 0.6 (18.1 %)	2.5 ± 0.7 (8.9 %)	0.6 ± 0.3 (2.2 %)	0.7 ± 0.3 (2.5 %)	19.5 ± 1.9 (67.8 %)	0.2 (0.6 %)	28.8	40	11/3/09– 3/15/10
North Pole	2.6 ± 0.3 (7.8 %)	1.2 ± 0.3 (3.6 %)	0.8 ± 0.2 (2.5 %)	1.3 ± 0.4 (3.8 %)	27.1 ± 3.7 (81.2 %)	0.3 (1.0 %)	33.7	35	11/3/09– 3/15/10
Peger Road	4.8 ± 0.5 (16.5 %)	2.1 ± 0.6 (7.4 %)	2.8 ± 0.7 (9.6 %)	0.4 ± 0.1 (1.3 %)	18.6 ± 3.0 (64.4 %)	0.3 (0.9 %)	29.0	38	11/3/09– 3/15/10
RAMS	4.0 ± 0.5 (10.9 %)	0.9 ± 0.2 (2.5 %)	2.5 ± 0.6 (6.8 %)	2.3 ± 0.7 (6.2 %)	26.9 ± 4.1 (73.5 %)	0.04 (0.1 %)	36.7	29	11/15/09– 3/15/10
2010/2011									
State Building	3.5 ± 0.4 (17.3 %)	1.7 ± 0.5 (8.4 %)	ND	0.4 ± 0.1 (1.9 %)	14.6 ± 1.1 (72.4 %)	0.004 (0.02 %)	20.2	15	11/1/10– 2/8/11
North Pole	2.1 ± 0.3 (8.0 %)	0.9 ± 0.2 (3.5 %)	0.9 ± 0.3 (3.4 %)	1.4 ± 0.5 (5.1 %)	21.3 ± 3.2 (79.4 %)	0.2 (0.6 %)	26.8	10	1/9/11– 2/5/11
Peger Road	4.8 ± 0.5 (16.6 %)	2.0 ± 0.5 (7.1 %)	0.8 ± 0.2 (2.9 %)	0.7 ± 0.3 (2.5 %)	20.2 ± 3.9 (70.6 %)	0.1 (0.3 %)	28.6	10	1/9/11– 2/5/11

Note: NH_4NO_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
R^2	0.96	0.97	0.97	0.98	0.8–1.00
Chi^2	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 $\text{PM}_{2.5}$ (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), 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_4NO_3), also a secondary particle. It should be noted that even though ammonium sulfate was not detected by the CMB model as a $\text{PM}_{2.5}$ source (secondary) when both sulfate and ammonium nitrate were used as fitting species, it is likely a significant contributor to the measured $\text{PM}_{2.5}$ 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 (NO_x) 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 airshed 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 $\text{PM}_{2.5}$ at each of the sites throughout the winter months. Automobile exhaust (gasoline-powered) $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$, 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 $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ 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 anions are routinely analyzed; cations are limited to ammonium, sodium, and potassium.

Limitations of Study

In presenting the final $\text{PM}_{2.5}$ 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 $\text{PM}_{2.5}$ mass. If the measured $\text{PM}_{2.5}$ concentration is less than $5 \mu\text{g}/\text{m}^3$, the percent mass may be outside of the acceptable ranges because the uncertainty in the mass measurement is approximately 1 to $2 \mu\text{g}/\text{m}^3$. 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

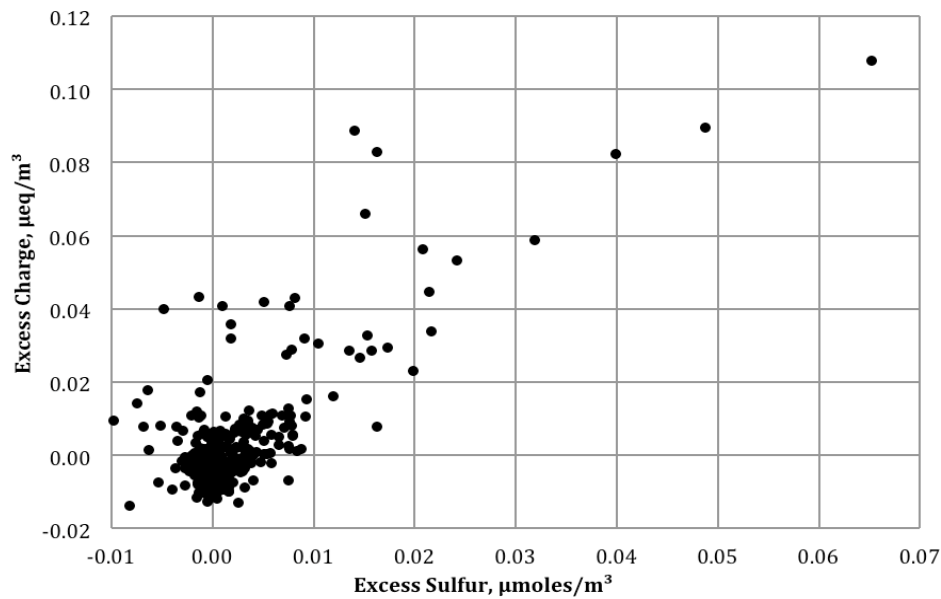


Fig. 1. Relationship between excess sulfur vs. excess charge from.

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 fits (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.

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