Sonoma Technology, Inc.

1360 Redwood Way, Suite C
Petaluma, CA 94954-1169
707/665-9900
FAX 707/665-9800
www.sonomatech.com

SOURCE APPORTIONMENT OF $PM_{2.5}$ IN PRINCE GEORGE, BRITISH COLUMBIA

FINAL REPORT
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By:
Juli I. Rubin
Steven G. Brown
Hilary R. Hafner
Paul T. Roberts
Sonoma Technology, Inc.
1360 Redwood Way, Suite C
Petaluma, CA 94954-1169

Prepared for:
Mark Graham
Ministry of the Environment
P.O. Box 9341, Stn Prov Govt
Victoria, British Columbia V8W9M1

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1. INTRODUCTION

1.1 OVERVIEW

Canada-wide standards (CWS) were developed as achievable goals for improving air quality in Canada, therefore reducing health impacts and environmental risks associated with air pollution. Fine particulate matter ($PM_{2.5}$), which has been shown to increase mortality through effects on the cardiovascular system (Dockery and Pope, 1994; Dockery and Stone, 2007), was identified as a priority substance to target with the CWS, with a level of 30 $\mu g/m^3$ to be attained by 2010. To reach this goal, sources of $PM_{2.5}$ in areas exceeding the CWS need to be understood. Prince George, an industrial city located in northern British Columbia, is one of these areas. Frequent temperature inversions and low-to-calm wind speeds provide poor mixing conditions in the Prince George area that are further aggravated by its valley setting, resulting in stagnant air and emissions trapping. Currently, Prince George has the highest ambient levels of $PM_{2.5}$ in the British Columbia province with average 98^{th} percentile values exceeding the CWS over the most recent three-year period (Graham and Sutherland, 2004). The goal of this study is to understand the sources contributing to $PM_{2.5}$ levels in and around the Prince George area to facilitate $PM_{2.5}$ reductions.

Many large industrial facilities are located in Prince George including several pulp and saw mills. Wood-burning is an important source of home heating in the area. Approximately 20% of households use wood-burning appliances based on results of a recent survey in Prince George (Residential Wood Burning in British Columbia, 2006). These sources, as well as several others, are likely contributors to high $PM_{2.5}$ levels in the area and need to be investigated (**Table 1-1**).

Table 1-1. Sources in the Prince George area that are potential contributors to $PM_{2.5}$, their seasonality, and key components.

Source	Seasonality	Key Component
Pulp mill	None	Sulfur
Saw mill	None	Potassium
Mobile	None	Carbon (organic, elemental)
Road salt	Expected high in winter	Chloride
Dust	None	Silicon
Wood-burning	Expected high in winter	Carbon (organic, elemental), levoglucosan

Source apportionment, also known as receptor modeling, is a useful tool for understanding the impact of sources on ambient pollution. Receptor models are often compared to the more typically used dispersion models that disperse pollutants using chemical,

meteorological, and emissions information to determine ambient levels of various chemical species at a receptor site. Receptor models do not require these inputs and instead use ambient measurements at the monitoring site to determine the contributions of the various sources to levels measured at the receptor. Chemical mass balance (CMB) and positive matrix factorization (PMF) are two methods that have been successfully used in source apportionment of $PM_{2.5}$ (Brown et al., 2007; Hwang and Hopke, 2006; Kim et al., 2003a; Kim and Hopke, 2004a; Kim et al., 2004a; Lee et al., 2002; Pekney et al., 2006; Poirot et al., 2001; Polissar et al., 2001; Ramadan et al., 2000; Song et al., 2001; Yakovleva et al., 1999; Zhou et al., 2004; Zhao et al., 2004; Watson et al., 2001). The two models require different inputs, make different assumptions, and have different limitations as shown in **Table 1-2**. The limitations of each of these methods can be overcome by applying both methods to a given data set, with overlapping results providing additional confidence. $PM_{2.5}$ source contributions in the Prince George area will be quantified with both CMB and PMF and results will be compared.

Table 1-2. Comparison of CMB and PMF source apportionment methods.

	CMB	PMF
Input	Source profiles[a], ambient data[b]	Ambient data[b]
Assumptions	Source emissions are constant	Source emissions are constant
	Chemical species do not react	Chemical species do not react
	All sources are identified	
	No collinearity in profiles	No collinearity in profiles
Limitations	Sources must be identified prior to applying model	Factors are difficult to interpret
	Source emissions are not constant	Factors do not always represent a single source
	Species react	Emissions are not constant and species react

[a] Source profiles are the fractional contributions by species to total emissions from a given source.
[b] The required ambient data set is a matrix of concentrations with columns representing the chemical species and the row representing the time.

1.2 CMB SOURCE APPORTIONMENT DESCRIPTION

CMB is a source apportionment method that solves a series of linear equations with a least squares solution in which each equation represents the concentration of a chemical species measured at the receptor as the sum of the products of source contributions and source profiles (Watson, 1979). The required inputs for running CMB are an ambient data set and source profiles. The ambient data set includes concentrations measured at the monitoring site for each chemical species over time. Source profiles include the fractional contributions for each chemical species emitted by a source to the total mass emitted by that source. Because source profiles are required input, sources must be identified and their emissions characterized prior to

running the CMB model. It is important to use source profiles that are representative of local sources and to model chemical species that have minimal reactivity. Alternatively, if sources are close to the monitoring site, reaction times are minimized. The desired result in running CMB is to determine the source contribution for each source input into the model. Determined source contributions represent the ambient concentration that can be attributed to the associated source. More detailed descriptions of the method can be found in Section 4.

1.3 PMF SOURCE APPORTIONMENT DESCRIPTION

PMF is an advanced multivariate receptor modeling technique that calculates site-specific source profiles with time variations of these sources based on correlations imbedded in ambient data. Simply, PMF decomposes a matrix of ambient data into two matrices that must be interpreted by an analyst to determine which source types are represented. The method is described in detail elsewhere (Paatero and Tapper, 1994; Paatero, 1997). The only required input for PMF is an ambient data set with concentrations measured at the monitoring site for each chemical species over time. Unlike CMB, source profiles are an output of PMF in addition to source contributions. Ideally, each factor identified with PMF is representative of a single source. Factors are not always associated with a single source and are often difficult to interpret because the sources associated with each factor must be identified by the user based on the composition of the source profiles. More detailed descriptions of the method can be found in Section 5.

2. DATA METHODS

Speciated $PM_{2.5}$ data are needed to quantify source contributions to ambient $PM_{2.5}$ levels. The following sections describe the methods used for collecting and preparing the ambient $PM_{2.5}$ data for use in source apportionment analysis.

2.1 DATA COLLECTION

Integrated 24-hr $PM_{2.5}$ samples were collected between December 2004 and March 2006 with a 1-in-3-day measurement frequency in Prince George, British Columbia. Measurements were taken at the core monitoring site in Prince George, Plaza 400, with a total of 138 samples. Speciated $PM_{2.5}$ data were collected with an R&P 2300 four-channel speciation monitor and a $PM_{2.5}$ Partisol was collocated with the speciation monitor to allow for performance of mass quality assurance (QA) on the samples. Field blanks were collected once a month over the sampling period. The location of Prince George and the Plaza 400 monitoring site are shown in **Figure 2-1**.

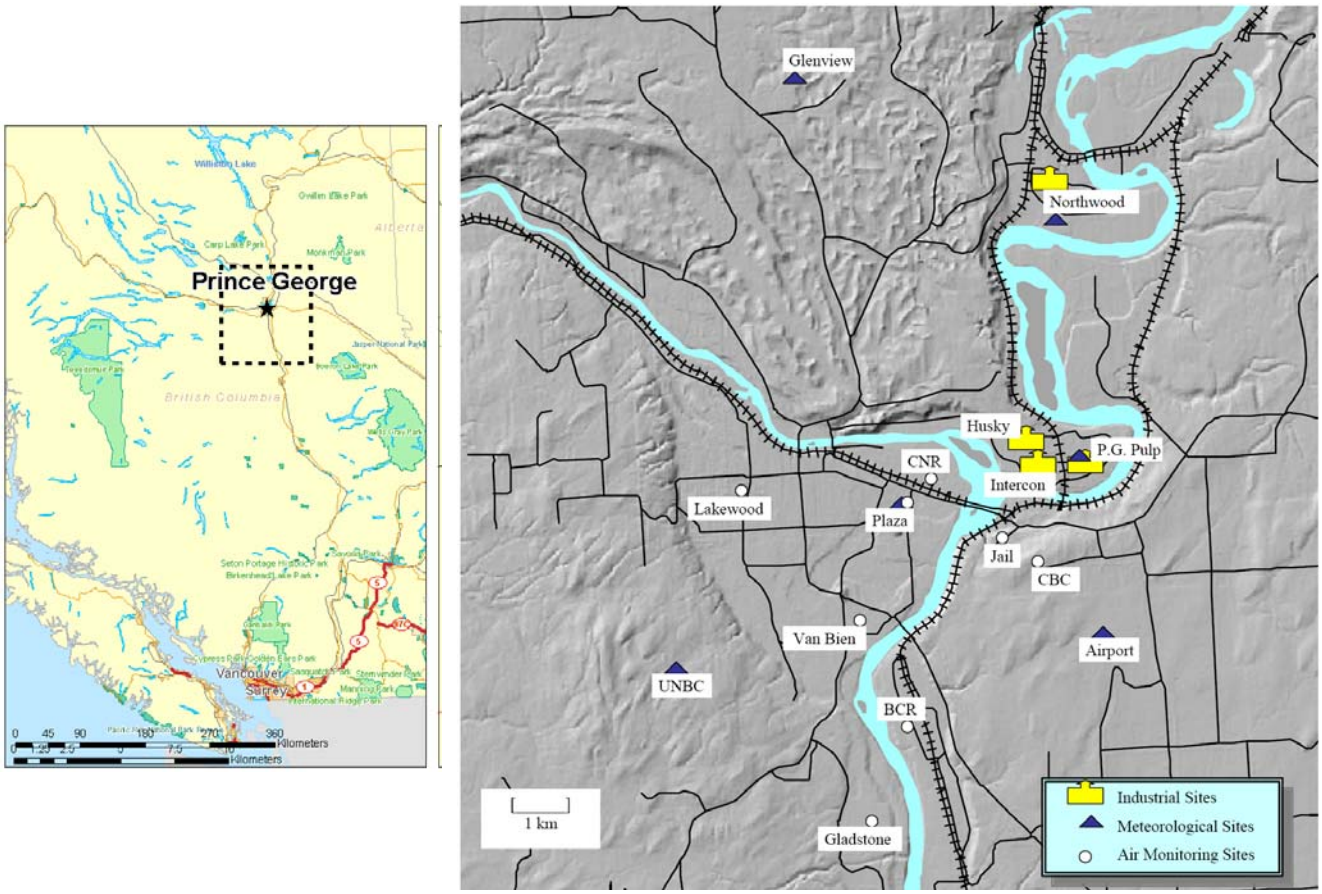


Figure 2-1. Prince George, an industrial city in the province of British Columbia, is shown in the map on the left. The detailed map shows the location of the Plaza 400 monitoring site in Prince George in addition to several large PM point sources.

A summary of the $PM_{2.5}$ data collection and analysis is shown in **Table 2-1**. Samples were collected on Teflon, Nylon, and quartz filters, which were analyzed by Research Triangle Institute (RTI). The Teflon filters with Nylon filter backups were used for ion chromatography analysis of sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), sodium (Na^+), and chloride (Cl^-). Analysis of the elements and gravimetric mass were conducted with x-ray fluorescence (XRF) on the Teflon filters with quartz filter backups. The quartz filters were analyzed via the National Institute for Occupational Safety and Health/Thermal Optical Transmittance (NIOSH/TOT) protocol as well as the Interagency Monitoring of Protected Visual Environments/Thermal Optical Reflectance (IMPROVE/TOR) protocol for organic carbon (OC) and elemental carbon (EC). The National Air Pollution Surveillance Program Environmental Technology Center (NAPS ETC) lab in Ontario, Canada, also analyzed the quartz filters for levoglucosan. Average filter blanks were applied to all species measured by XRF and carbon species.

Table 2-1. Summary of $PM_{2.5}$ mass and speciation data collected.

Sampler/Module	Filter	Lab Analysis	Compound
$PM_{2.5}$ Partisol	Teflon	Gravimetry	Mass
Speciation Channel 1	Teflon	IC[a], AA[b], GC/MS	SO_4, NO_3, Cl, Na, K, Mg, NH_4, levoglucosan
	Nylon (Backup)	IC	NO_3
Speciation Channel 2	Teflon	Gravimetry, XRF[c],	Mass, Al, Fe, Zn, Mn, Si, Ca, Ti, Cu, Ni, V, S, Se, As, Cr, Cd
	Quartz (Backup)	TOR[d], TOT[e]	OC (1-4), EC
Speciation Channel 3	Quartz	TOR, TOT	OC (1-4), EC (1-3)

[a] Ion Chromatography
[b] Atomic absorption for Na and K
[c] X-ray fluorescence
[d] Thermal-Optical Reflectance, IMPROVE method developed by Desert Research Institute
[e] Thermal-Optical Transmittance, developed by NIOSH

Levoglucosan, a sugar anhydride, was analyzed for samples collected from December 2004 through March 2006. Levoglucosan is a proven molecular marker for wood smoke from residential fireplaces and forest fires (Fine et al., 2001; Gorin et al., 2006) and was, therefore, an important chemical species to quantify. Measurements were made by solvent extraction from Teflon filters with ethyl acetate and subsequent analysis with a Varian Saturn 2000 gas chromatography/mass spectrometry (GC/MS) system. Additional information on levoglucosan measurement methods can be found in the University of British Columbia's standard operating procedure (SOP) for quantification of levoglucosan (Ma, 2005; Kharrat, 2000).

In addition to speciated $PM_{2.5}$ data, volatile organic compound (VOC), polar organics, and continuous data (NO_x, O_3, H_2S, SO_2, PM_{10}, $PM_{2.5}$, CO) were also measured at the Prince George Plaza 400 site. VOC and polar organics data were measured from August 2005 through

April 2006 with 1-in-6-day frequency. Continuous data were measured from December 2004 through March 2006 with hourly frequency.

2.2 DATA VALIDATION

Data measured at the Plaza 400 site underwent basic data validation prior to being made available for this study. Data validation included checks of sample identification and flagging of invalid or suspect samples. Approximately 15% of the samples were flagged due to OC/EC measurement problems in which no carbon data were reported or concentrations were less than or equal to the blanks. Samples with carbon measurement problems were either excluded from use in (in CMB analysis) or carbon values were substituted with a median value (in PMF analysis). Additional data checks were applied to ensure internal consistency in the datasets, including comparison of reconstructed fine mass to measured mass and comparison of XRF sulfur to ion chromatography (IC) sulfate. Approximately 10% of samples from the $PM_{2.5}$ speciated data set did not pass these checks and were excluded from use in either source apportionment analysis. Those samples for which all species were missing were also excluded from use in either analysis.

Time series were examined to identify outliers in the data. It is important to identify outliers prior to conducting source apportionment because their presence can influence analysis results. For a source apportionment analysis such as PMF, the presence of an outlier can affect the overall results by making it harder to fit the data. As a result, outliers should be removed from the data set. In CMB, the presence of an outlier will only affect the results on the date of the outlier. As long as outliers are caused by events rather than measurement error, they can be used in CMB. Outliers were identified in the levoglucosan (**Figure 2-2**), lead, and arsenic time series. The levoglucosan peak in May 2005 was caused by a nearby wildfire that was identified using satellite fire detection data (MODIS). Lead and arsenic outliers occurred on the same day (December 21, 2005), indicating a possible event.

For source apportionment, it is also important to examine data completeness as well as the amount of data that is below detection for each chemical species measured. An incomplete data set does not provide an accurate picture of ambient concentrations and their temporal trends. The same is true if a large percent of data for a given species is below detection. When data are below detection, the instrument signal cannot be distinguished from instrument noise and the actual ambient concentration is unknown. For source apportionment, species with more than 75% of data missing or below detection were excluded from use in the analysis. A summary of data completeness and percent of data below detection by species is shown in **Table 2-2**. Species highlighted in grey pass the 75% criteria and can be used for source apportionment.

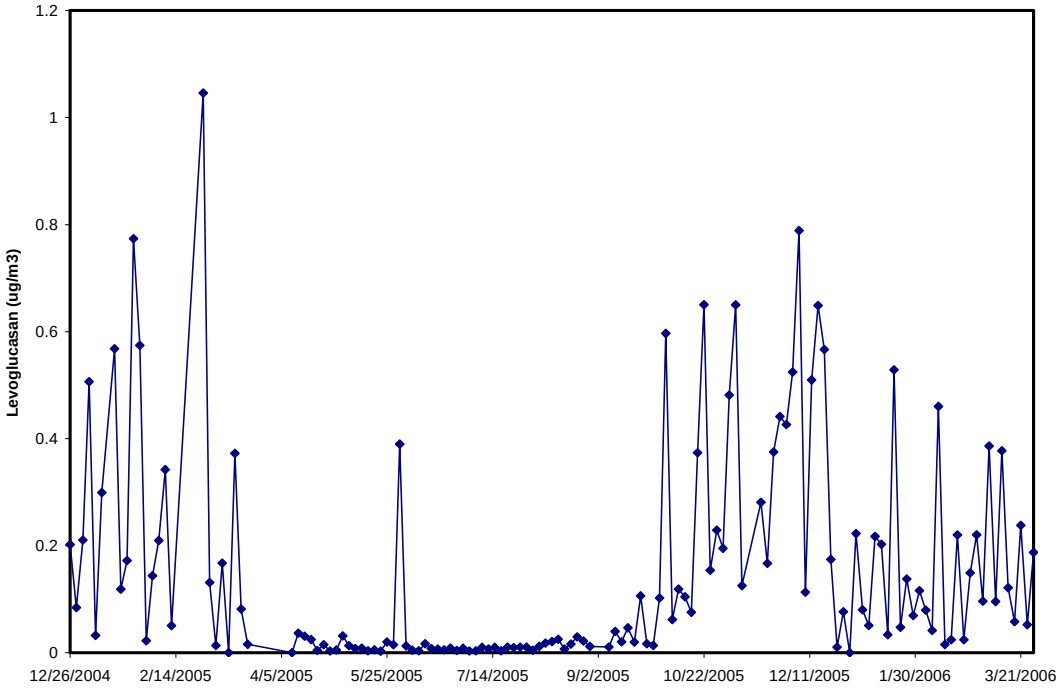


Figure 2-2. Levoglucosan time series from the Prince George Plaza 400 monitoring site (December 2004 to March 2006). A levoglucosan outlier occurs in May 2005.

Table 2-2. Percent of data missing or below detection for $PM_{2.5}$ speciated data measured at the Prince George Plaza 400 site (December 2004 to March 2006). Species highlighted in grey have less than 75% data missing/below detection and are useful for source apportionment.

Parameter	% Missing/Below Detection	Parameter	% Missing/Below Detection	Parameter	% Missing/Below Detection
Bromide	100	Se	93	Cl	21
Mo	100	Zr	91	Cu	19
Nb	100	Ir	90	OC Improve	19
Propionate	100	Rb	90	TC Improve	16
Sc	100	Cr	89	Si	12
Cs	99	W	89	Na+	7
Hf	98	Ag	88	Mn	7
Co	97	Au	88	Ca	3
Cd	96	Sr	85	Fe	3
Sn	96	Ni	82	K	3
Ba	96	Mg	80	S	3
In	96	Hg	75	Zn	3
La	96	Eu	69	Levoglucosan	2
Sb	96	V	66	NO3 Nylon	1
Ta	96	Al	62	K+	1
Y	96	As	62	Chloride	0
Ca++	94	Phosphate	57	Formate	0
Ce	94	Tb	46	NH4+	0
Mg+	94	Pb	45	NO3 Teflon	0
Ti	94	EC improve	32	Oxalate	0
P	93	Acetate	30	$PM_{2.5}$ Mass	0
Sm	93	Na	27	SO_4^-	0
Ga	93	Br	23		

2.3 DATA UNCERTAINTY

Uncertainties for the speciated $PM_{2.5}$ dataset are summarized in **Table 2-3** for the species that passed the 75% data missing or below detection criteria. For source apportionment, the chemical species associated with the most important $PM_{2.5}$ sources will have the most influence on the solution. According to Table 1-1, the sources that are expected to be most important in Prince George are pulp and saw mills, mobile sources, road salt, dust, and wood-burning. The key species associated with these sources (Table 1-1) have small percent uncertainties (≤12%) with OC and EC as the exceptions at 31% and 43%, respectively.

Table 2-3. Average percent uncertainties for chemical species measured at the Prince George Plaza 400 site (December 2004 to March 2006). Species included had less than 75% of data missing or below detection limits.

Species	Average Percent Uncertainty	Species	Average Percent Uncertainty
Acetate	11	Na+	14
Al	20	NH_4+	9
As	30	NO_3	5
Br	22	Oxalate	8
Ca	7	Pb	25
Chloride	9	Phosphate	25
Cl	12	$PM_{2.5}$ mass	5
Cu	21	S	5
Eu	28	Si	9
Fe	6	SO_4-	7
Formate	9	Tb	49
K	5	EC	43
K+	9	OC	31
Levoglucosan	12	V	26
Mn	12	Zn	7
Na	12	—	—

3. PRE-SOURCE APPORTIONMENT DATA ANALYSIS

Source apportionment analysis should be considered one part of complementary analyses that help analysts understand and quantify source contributions to ambient concentrations. Prior to running CMB or PMF, analyzing ambient data and emission inventory data to better understand the results of the source apportionment is essential. Additionally, an understanding of the meteorology of the area is important. The following subsections describe data analyses conducted on the ambient $PM_{2.5}$ data, $PM_{2.5}$ emission inventory data, and meteorological data for Prince George.

3.1 AMBIENT DATA ANALYSIS

Ambient data composition was examined on an average, seasonal, and daily basis. In addition, the correlations between various chemical species measured in the speciated $PM_{2.5}$ data set were examined. These analyses can provide information on which sources (factors) are expected to be important and can provide checks for determining whether results are sensible because source apportionment results are expected to reflect what is seen in the ambient data.

The ambient composition of data measured at the Plaza 400 monitoring site is shown in **Figure 3-1**. The composition of the $PM_{2.5}$ data is uniform across seasons with organic mass (1.8*OC) and sulfate making up a majority of the mass. The same composition is also seen on the highest $PM_{2.5}$ mass days. Mobile and wood-burning are important sources of OC (Table 1-1) and are, therefore, expected to be important $PM_{2.5}$ sources. Pulp mills are a source of sulfate in the area and are also expected to be important. $PM_{2.5}$ levels are highest during the winter with almost all the high $PM_{2.5}$ mass days occurring during these months. The ambient data composition was also examined on a daily basis and is shown for select days in **Figure 3-2**. Organic matter (OM) and sulfate make up a majority of the mass with relative contributions varying from day to day. Day-to-day differences in composition are likely due to shifts in meteorology or emission events. For example, May 31, 2005, has a larger percent of mass as OM than the other days in spring or summer. This composition difference appears to be due to a wildfire on this date.

The correlations of various species measured at the Prince George site were examined with scatter plots and time series. The scatter plots showed relationships between sodium and sulfate and potassium and manganese (**Figure 3-3**). Because some correlation is seen, it is expected that these chemical species come from similar sources and will be grouped together in the same PMF factors. Silicon and calcium are species that are commonly found in soil and a correlation was expected. The scatter shown between the silicon and calcium data (**Figure 3-4**) indicates that additional sources of these species are present in Prince George. One of the important forms of road salt in the Prince George area is calcium chloride and may be an additional source of calcium. The relationship between silicon and calcium was re-examined excluding winter months because road salt is only used during the winter. Although the correlation improved by removing winter data, scatter is still present as shown in Figure 3-4. Lime is commonly used in pulp mills and could be the other source of calcium in the area.

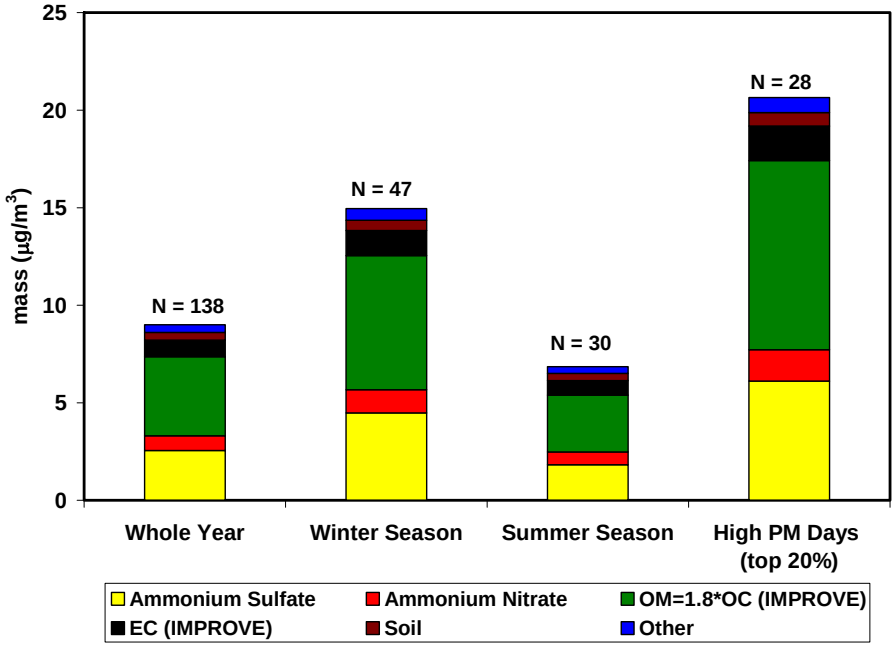


Figure 3-1. Prince George Plaza 400 ambient data composition averaged annually, seasonally (winter and summer), and for high $PM_{2.5}$ mass days (top 20%).

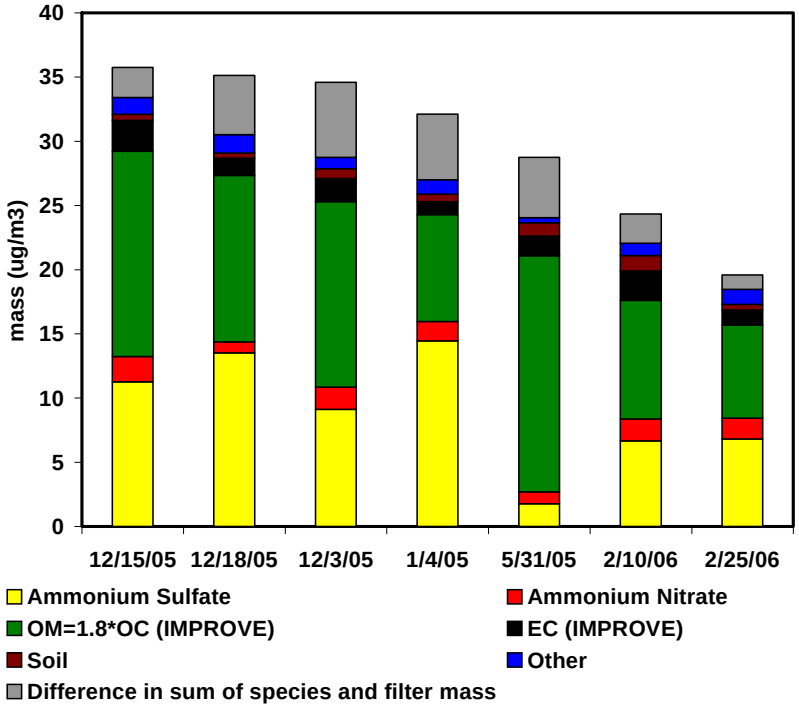


Figure 3-2. Prince George Plaza 400 $PM_{2.5}$ composition for select days.

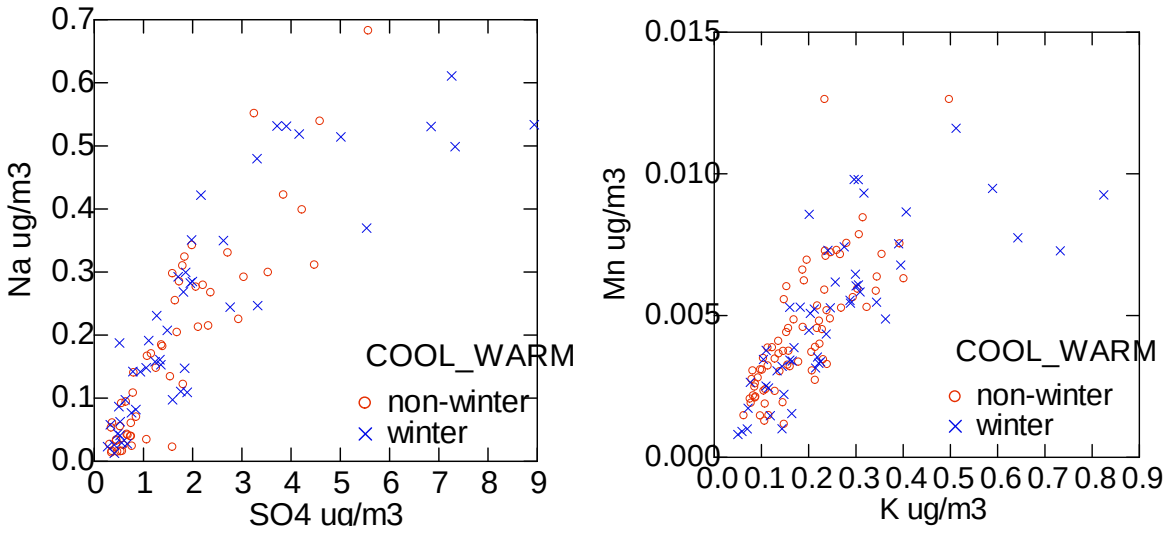


Figure 3-3. Scatter plots of sulfate (SO_4^{2-}) and sodium (Na, right) and manganese (Mn) and potassium (K, left).

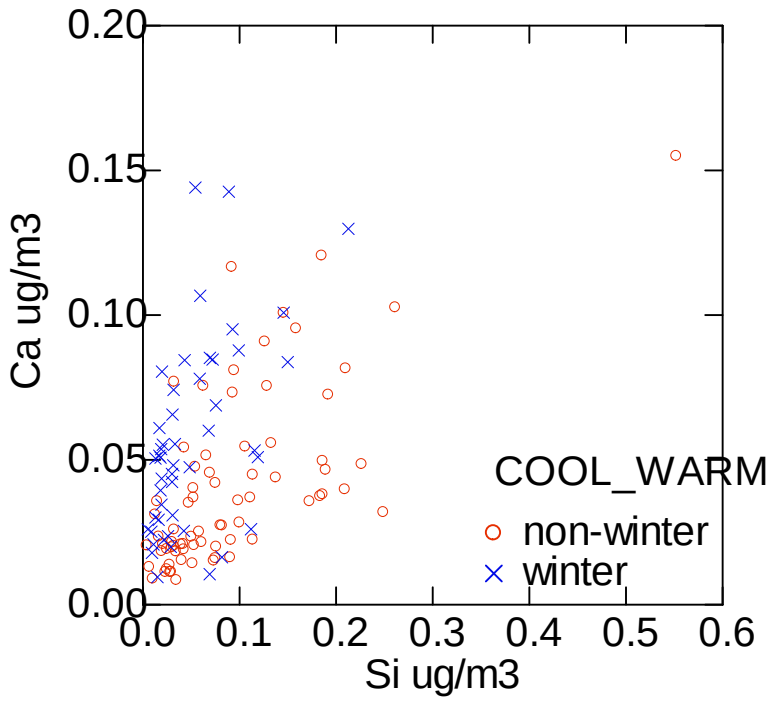


Figure 3-4. Scatter plot of calcium (Ca) and silicon (Si), during winter (November through February) and the rest of the year, for the period of December 2004 to March 2006. The relationship between the species improves when excluding winter months; however, there is still scatter present indicating a calcium source other than road salt.

Time series are also useful to understand how source contributions are expected to change with time. The levoglucosan time series in Figure 2-2 shows a strong seasonal difference with concentrations near zero during the summer. Levoglucosan is a chemical species associated with wood-burning. The time series indicates that wood-burning source contributions should also have a strong temporal trend. Wood combustion is commonly used for power generation by industries in Prince George, including pulp and saw mills. However, if levoglucosan was emitted from these sources, the concentrations would be higher than observed during the summer because industries operate all year. Residential wood-burning for home-heating purposes has a strong increase during the winter, indicating that the dominant source of levoglucosan emissions is this type of wood-burning. Levoglucosan is widely used as a source tracer for wood combustion (Sheesley et al., 2003; Sheesley et al., 2007; Zheng et al., 2007; Gorin et al., 2006), and typically can have a lifetime of days in the atmosphere (Fraser and Lakshmanan, 2000).

The molar ratios of sulfate and nitrate to ammonium ion were also examined. These ratios can provide some insight into secondary PM formation. Sulfate and nitrate react with ammonium to produce ammonium sulfate ($(NH_4)_2SO_4$) and ammonium nitrate (NH_4NO_3), which are in particulate form. Ammonium will first react with sulfate until it is fully neutralized ($(NH_4)_2SO_4$) before reacting with nitrate. For fully neutralized sulfate to form, the molar ratio between ammonium and sulfate must be 2 to 1. If the molar ratio exceeds this level, the remaining ammonium is available to react with nitrate. As shown in **Figure 3-5**, the molar ratio is generally less than 2 with the ratio peaking during the winter at around 2.5. This indicates that some ammonium nitrate may form in the winter, but in general, all the ammonium will react with sulfate. The ambient $PM_{2.5}$ composition agrees with this finding because sulfate makes up a large fraction of the PM mass with minimal nitrate present, even in the winter. Concentrations of sulfate were examined at several sites outside the Prince George downtown area to understand the importance of secondary sulfate transport. Sulfate concentrations at three sites located approximately two, four, and nine miles from the downtown Plaza 400 site were compared with the Plaza 400 concentrations. As shown in **Figure 3-6**, sulfate levels drop off significantly with very little distance from downtown, indicating the majority of sulfate measured at the Plaza 400 site comes from local sources.

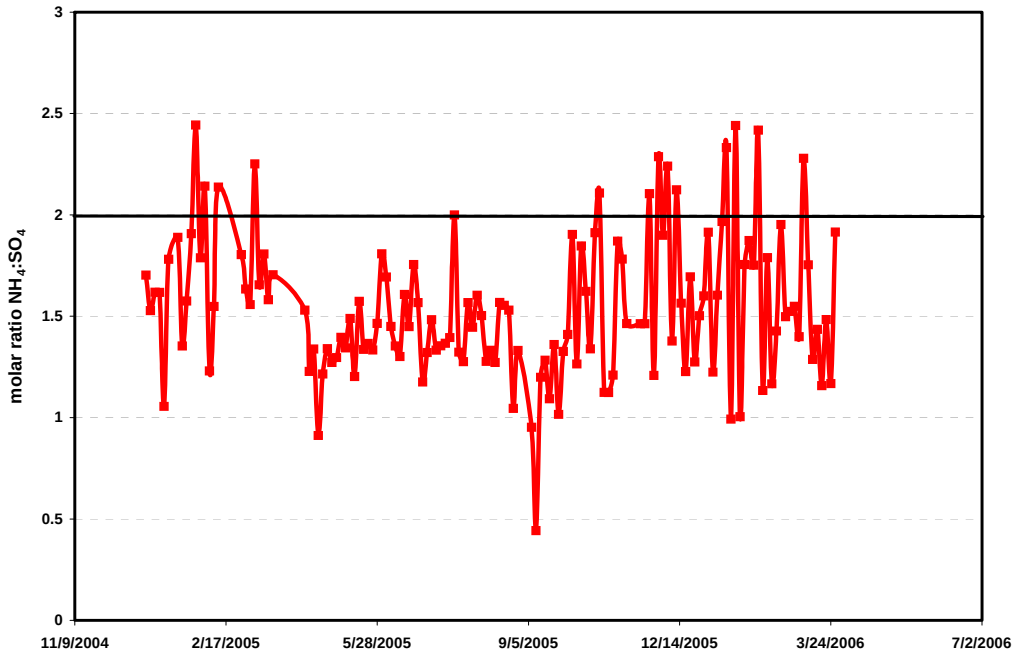


Figure 3-5. Molar ratios of ammonium to sulfate at the Prince George Plaza 400 site (December 2004 to March 2006).

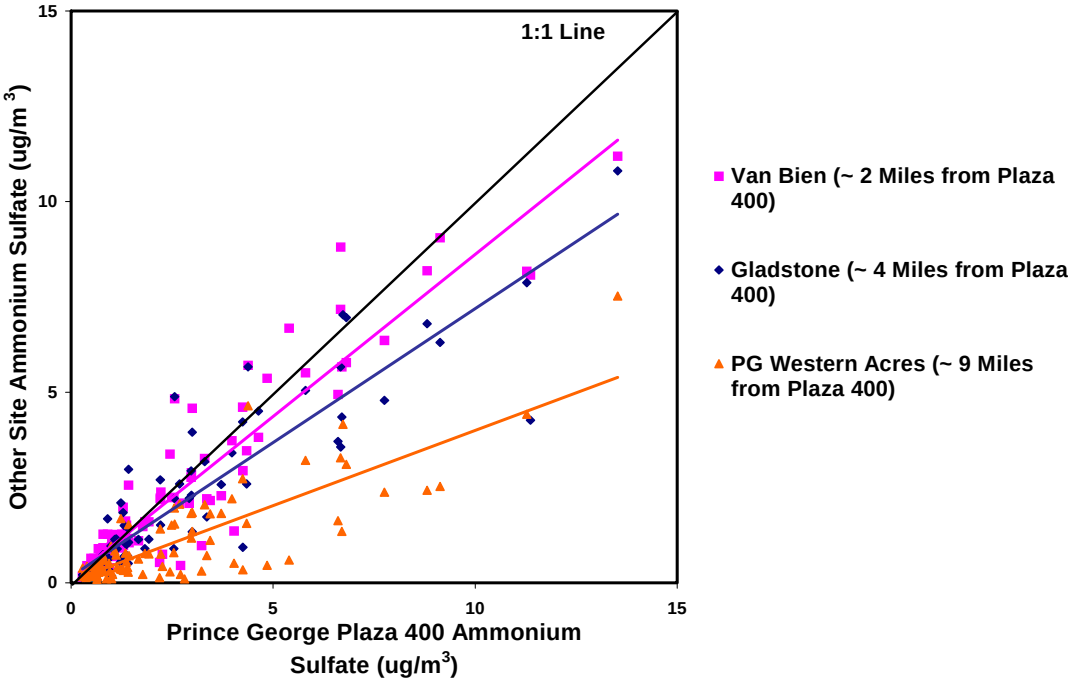


Figure 3-6. Comparison of ammonium sulfate concentrations measured at the Prince George Plaza 400 site to other sites located outside of the Prince George downtown area. Sulfate concentrations drop off quickly with distance from Plaza 400.

3.2 EMISSION INVENTORY ANALYSIS

The 2000 emission inventory was examined for Prince George to get a better understanding of primary sources in the area. Although pollutants directly emitted into the atmosphere react and are transported, it is expected that source apportionment will implicate sources identified as important $PM_{2.5}$ emitters using the emission inventory. Examining emission inventories is also crucial for conducting CMB. As discussed previously, sources need to be identified prior to running CMB because source profiles are a required input for the model.

The $PM_{2.5}$ emission inventory was first examined by emission category including point, road dust, area, and mobile sources. As shown in **Figure 3-7**, the majority of primary $PM_{2.5}$ emissions in Prince George are from point sources. Because point sources were identified as large emitters of $PM_{2.5}$ in the area, this emission category was further examined. As shown in **Figure 3-8**, pulp mills and saw mills dominate $PM_{2.5}$ emissions for point sources. Therefore, profiles for these sources need to be included when running CMB and it is expected that these sources will be identified as significant $PM_{2.5}$ sources from the source apportionment analysis. It should be noted that mobile source emissions appear to be underestimated in the emission inventory shown in Figure 3-7. Local rail yards and tracks are located close to the Prince George urban area. Additionally, highways 16 and 97 run through downtown Prince George. Despite the findings of the emission inventory, vehicle-related emissions are ubiquitous in urban areas and mobile source profiles should be included when conducting CMB source apportionment (Watson et al., 2001). Other important $PM_{2.5}$ sources identified with the Prince George emission inventory are road dust and space heating. Approximately 80% of $PM_{2.5}$ emissions in the area source category come from space heating. A recent survey in Prince George showed that 15 - 20% of home-heating needs in the area are met with wood-burning appliances (Ministry of Water, Land and Air Protection, 2004).

Secondary PM formed from nitrate and sulfate may also affect $PM_{2.5}$ levels in Prince George. As a result, emission inventories for NO_x and SO_x were also examined (**Figure 3-9**). Examining the SO_x emission inventory is especially important since a large fraction of the $PM_{2.5}$ mass in Prince George is made up of sulfate. As shown in Figure 3-9, the SO_x inventory is dominated by only two types of sources: pulp mills and oil refineries. It is, therefore, expected that any sulfur in the Prince George area comes from these sources or is transported into the area. However, the analysis of sulfate levels discussed in Section 3.1 indicates that the majority of sulfate comes from local sources. Therefore, it is expected that local pulp mills and oil refineries are the major sources of sulfate in the area. In comparison, SO_x and NO_x emissions are spread out over several sources. The majority of these emissions are coming from the pulp mills and heavy- and light-duty motor vehicles.

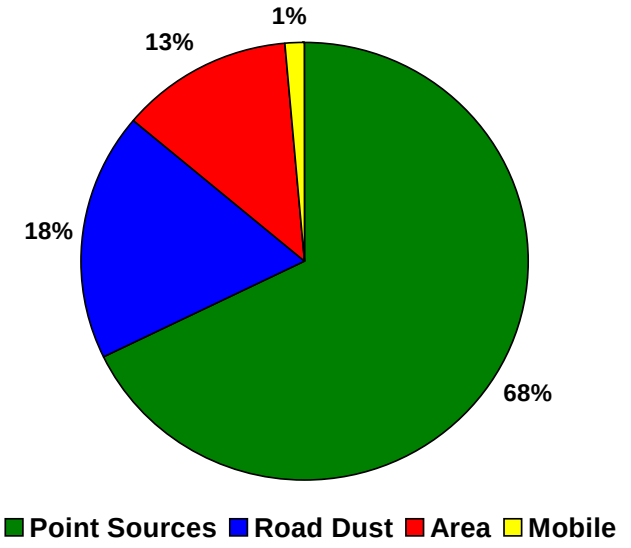


Figure 3-7. Prince George $PM_{2.5}$ emission inventory (2000).

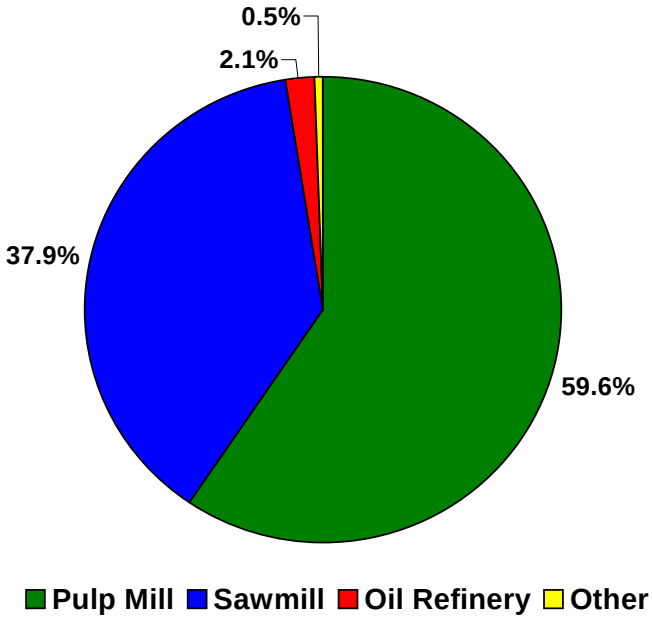


Figure 3-8. Prince George $PM_{2.5}$ emission inventory for point sources (2000).

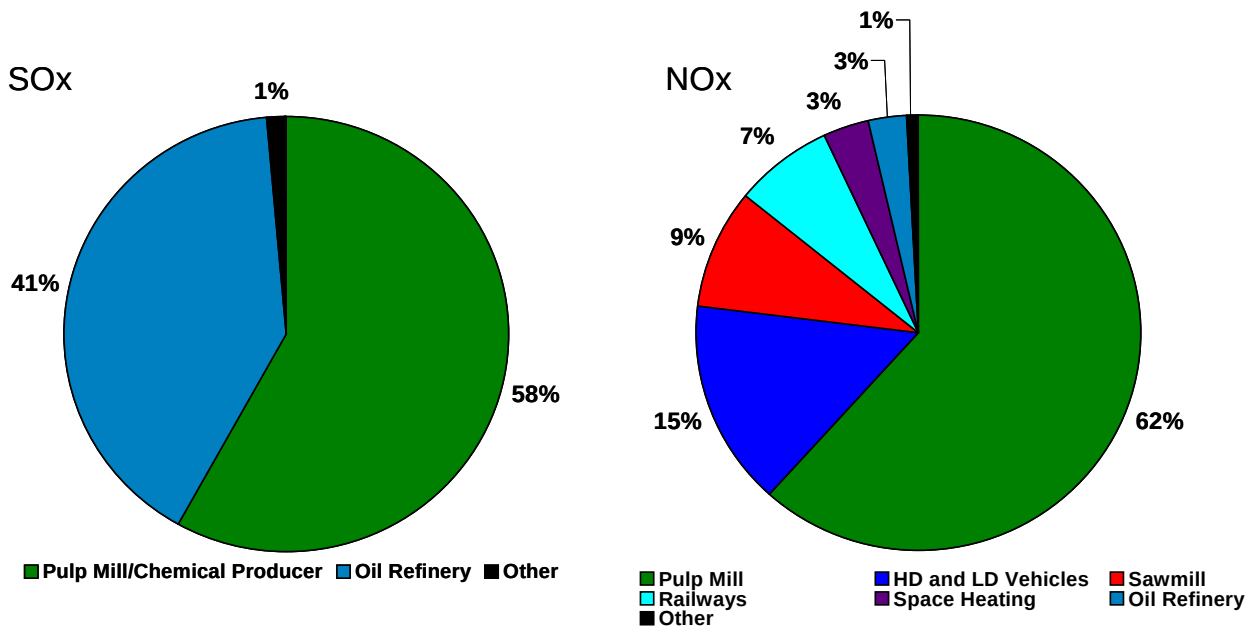


Figure 3-9. SO_x and NO_x emission inventories for Prince George (2000).

3.3 METEOROLOGY

Hourly wind roses for the Plaza 400 site are shown in **Figure 3-10**. The wind roses show data measured from December 2004 through March 2006. $PM_{2.5}$ measurements were made during the same time period. The hourly wind roses show calm (generally less than 2 m/s) southwesterly winds during the night. The winds transition from the southwesterly direction to the southeasterly direction during the late morning with wind speeds increasing (2 m/s to 15 m/s). The transition back to south westerly winds occurs in the late afternoon. Although the dominant wind directions are from the southwest and southeast (~15% of the time), winds from the northeast are present during all hours (~10% of the time). Winds were also examined on a seasonal basis (**Figure 3-11**). Winds in Prince George are calm and generally less than 5 meters per second. Winds are dominated by the southerly direction over all seasons; however, winds from the northeast are more prevalent during the winter and springtime.

The relationship between the concentrations of the continuous data and wind direction were determined by non-parametric regression with a Gaussian kernel. An example of the non-parametric regression is shown in **Figure 3-12** for nitrous oxide. Results of the non-parametric regression are shown in **Figure 3-13** for $PM_{2.5}$. Higher $PM_{2.5}$ levels occur when winds are from the east and the southwest. Additional results for SO_x, H_2S, and NO_x can be found in the Appendix. Higher SO_x and H_2S concentrations occurred with winds from the east. NO_x concentrations had no correlation with wind direction.

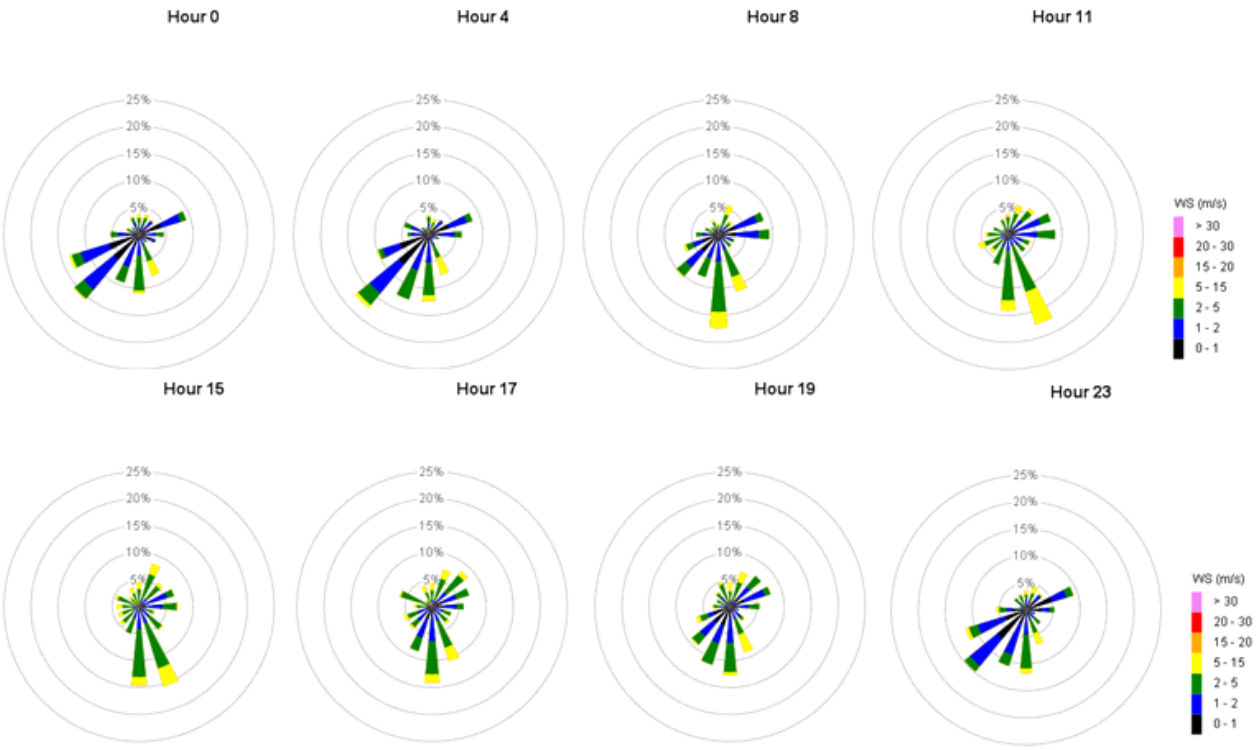


Figure 3-10. Hourly wind roses for the Prince George Plaza 400 site (December 2004 to March 2006).

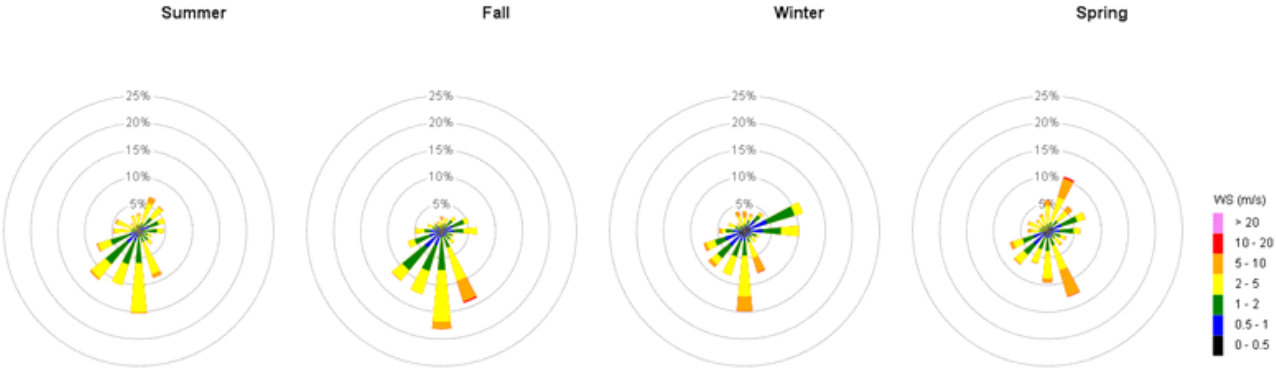


Figure 3-11. Seasonal wind roses for the Prince George Plaza 400 site (December 2004 to March 2006).

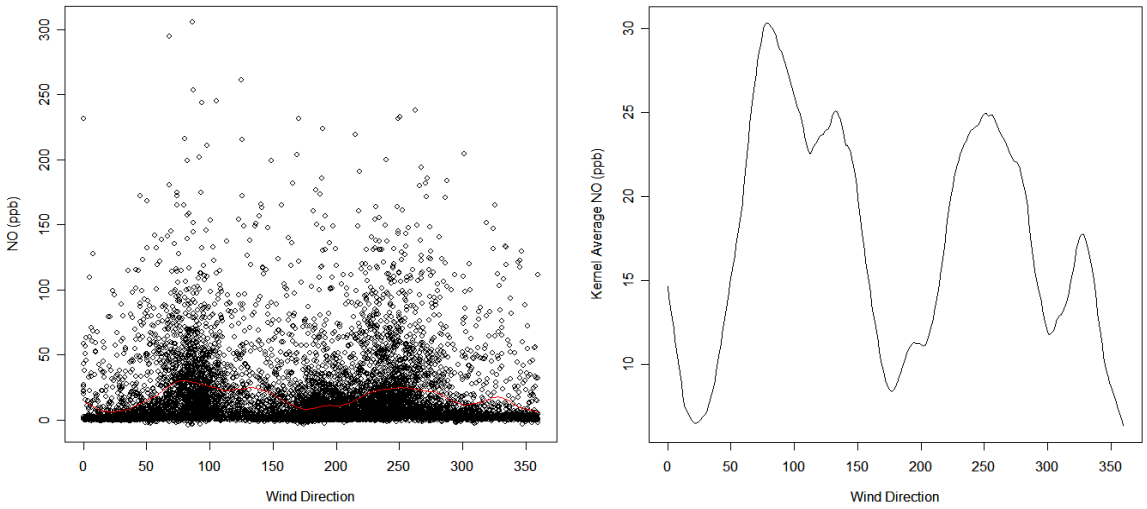


Figure 3-12. Example of non-parametric regression using nitrous oxide concentrations. NO concentration as a function of wind direction (left) and NO results averaged with the Gaussian kernel as a function of wind direction (right).

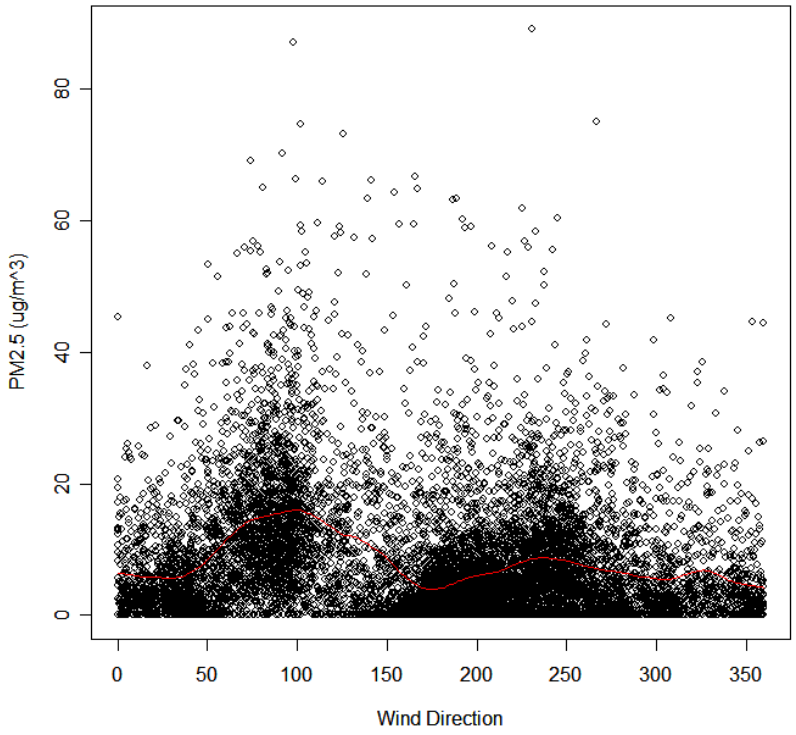


Figure 3-13. Results of the non-parametric regression analysis with wind direction and $PM_{2.5}$ data.

4. CMB SOURCE APPORTIONMENT

CMB was conducted on the speciated $PM_{2.5}$ data collected in Prince George with the U.S. Environmental Protection Agency's (EPA) CMB model: EPA CMB 8.2. The following subsections describe the CMB method, source profile and species selection, and results from the CMB analysis including sensitivity results and wind sector analysis.

4.1 CMB METHODS

The CMB model solves a series of linear equations with a weighted least squares solution in which each equation represents the concentrations of a chemical species at the receptor as the sum of the product of source contributions and source profiles. As a result, the model requires concentrations measured at the receptor and source profile species abundances (i.e., the fractional amount of the species from each source) along with their associated uncertainties as input. For each species *i*, the concentration of *i* measured at the monitoring site is the sum of source contributions from source *j* (*Sj*) times the fraction of *Sj* composed of species *i* (*Fij*) for *n* sources (Equation 4-1). To obtain a unique solution, the number of chemical species must be greater than the number of sources (*n*).

$$C_i = \sum_{1}^{n} F_{ij} S_j \qquad \textbf{(4-1)}$$

Equation 4-1 is solved by minimizing the weighted sums of the squares of the differences between the measured and calculated values of the model inputs (C_i and F_{ij}) (Watson et al., 1984; Britt and Leuke, 1973). The solution algorithm is an iterative process that determines a new set of source contributions based on the source contributions determined from the previous iteration. Data uncertainties for the model input are used to weight the importance of the input values on the solution as well as to calculate uncertainties in source contributions. The solution to the CMB model was developed and tested by Watson et al. (1984) and provides realistic estimates of uncertainties and contributions because it incorporates uncertainties from both the concentration and source profile input data and gives greater influence to species with smaller uncertainties.

In addition to source contribution and uncertainty values, the CMB model calculates various performance measures including percent of mass apportioned, chi-square, and r-square values. The chi-square is the weighted sum of squares of the differences between calculated and measured fitting species concentrations. Ideally, no difference would exist between calculated and measured values with a chi-square value of zero. Values greater than four indicate that one or more species concentrations are not well explained by the determined source contributions (Watson et al., 1997). The r-square is the fraction of the variance in the measured concentrations that is explained by the variance in the calculated concentrations. Values less than 0.8 indicate that the variance is not well explained (Watson et al., 1997).

4.2 SOURCE PROFILES

One of the inputs required to run CMB is a set of source profiles. Profiles need to be obtained for all sources that are potentially impacting the monitoring site. Based on the emission inventory analysis, pulp mill, saw mill, mobile source, road dust/soil, and wood burning profiles need to be included. Additional sources that may impact the site are road salt, asphalt paving, and secondary formation (ammonium sulfate and ammonium nitrate).

Emissions measured at the local Northwood pulp mill were used to compile a pulp mill profile (Jacques Whitford Environment Limited, 2003; Crooks et al., 2003). The Northwood mill is located to the northeast of the Plaza 400 site (Figure 2-1) and is the largest mill in Prince George. Emissions were measured at several sources within the pulp mill including smelters, lime kilns, power boilers, and recovery boilers. The source profile was developed by summing the emissions across all sources for individual species and normalizing by the total mass emitted, giving a weight percent by mass. Ions including sulfate were not measured at Northwood. Sulfate mass fractions were estimated with a sulfur-to-sulfate ratio derived from measurements taken at two pulp mills in Alberta, Canada: DMI and Weyerhaeuser (Kharrat, 2000). OC and EC mass were not measured at Northwood and, therefore, carbon mass was not included in the pulp mill profile. This is a limitation and sensitivity analyses need to be conducted with this profile. It is critical that if future source profiles are taken, carbon analysis be included. Standard deviations of mass fractions were calculated across the individual sources and used as the profile uncertainties.

A local saw mill profile was not available for use in this study. Instead, a hog fuel boiler profile obtained from a study conducted in Missoula, Montana (Carlson, 1990), was used. Hog fuel boilers were identified as a major $PM_{2.5}$ source for saw mill operations in Prince George (personal communication with Mark Graham). Sulfur is present in this hog fuel boiler profile, and may not be fully representative of the local area boilers, or may include additional processes not utilized in local area operations. An asphalt profile was obtained from the California Air Resources Board (CARB) for use in this study. A suitable oil refinery profile typical of the processes and oil used locally was not found, and since the key tracers for refining operations, nickel and vanadium, were nearly always below detection, this source contribution is likely small and difficult to quantify. Mobile source profiles for light-duty gasoline vehicles (LDGV) and heavy-duty diesel vehicles (HDDV) were included in the analysis and were obtained from the Northern Front Range Air Quality Study (NFRAQS) study in Denver, Colorado. A road dust profile was obtained from a study conducted in Seattle, Washington (Maykut et al., 2003). This profile has been used in other studies in southern British Columbia and Washington State, and may have an enhanced sea salt or coastal influence compared to what may be observed at Prince George. These profiles are not necessarily representative of the local sources in Prince George; as a result, sensitivity analyses were conducted for these profiles.

The wood-burning profile in this study was determined by combining burning emissions measured by wood type (Fine et al., 2004) and results from a wood-burning survey taken in Prince George (Ministry of Water, 2004). Survey results included the breakdown of wood type used for burning in Prince George. Weighted averages of the species-specific emission profiles, based on the survey results, were used to create a profile representative of the area. Other profiles included in the source apportionment were road salt (calcium chloride), ammonium

sulfate, and ammonium nitrate. These profiles were determined based on molecular weights. Additionally, a profile called "other OC" was included to account for carbon that could not be apportioned. The profiles used in the CMB analysis are summarized in the Appendix.

OC mass fractions in all profiles were converted to OM (1.8*OC) fractions in order to produce better mass closure in the CMB results. If f_{OC} is the mass fraction of OC and f_{other} is the mass fraction of the other species ($f_{OC} + f_{other} = 1$), then the fraction of OM (f_{OM}) is calculated with Equation 4-2. If the mass fraction of OC is adjusted, the mass fractions also need to be adjusted for the other species because more mass is included in the total mass (mass other + 1.8*mass OC). The mass fractions for each species z were adjusted with Equation 4-3. Uncertainties for the mass fractions were adjusted in a similar manner so that percent uncertainties did not change.

$$f_{OM} = \frac{1.8}{\frac{f_{other}}{f_{OC}} + 1.8} \quad \textbf{(4-2)}$$

$$f_{z,new} = \frac{f_{z,old}}{(f_{other} + 1.8\, f_{OC})} \quad \textbf{(4-3)}$$

4.3 SPECIES AND DATE SELECTION

The number of species used in the ambient data set for CMB has to be greater than or equal to the number of source profiles included to obtain a unique solution. A total of 11 source profiles were identified for use in the source apportionment; therefore, a minimum of 11 species need to be included. Selected species also need to be representative of the sources included in the model (tracer species) to quantify the source contributions. Species were selected based on their abundance in the source profiles as well as their uniqueness to the sources. Non-molecular weight-based source profiles (i.e., not ammonium sulfate, road salt, etc) are shown in **Table 4-1**; highlighted species were selected for inclusion in the CMB data set. Note the sum of species will not necessarily add to 100%, which may be due to differences in uncertainties in either the measurement of total mass of the source sample or in the individual components. Sulfate, nitrate, iron, and calcium were also selected for use in the source apportionment. Samples that passed data validation checks and had measurements above detection limits were selected for use in CMB. Samples with OC/EC measurement problems were not used for source apportionment.

Table 4-1. Source profiles (% of mass in profile) for pulp mills (from Northwood pulp mill), HDDV (NFRAQS composite), LDGV (NFRAQS composite), asphalt (CARB), road dust (Seattle; Maykut, 2003), wood burning (Fine et al., 2004), and hog fuel boilers (Missoula, Montana; Carlson, 1990). Highlighted species were selected as tracer species for use in CMB. Note the sum of species will not necessarily add to 100%, which may be due to differences in uncertainties in either the measurement of total mass of the source sample or in the individual components.

Species	Pulp Mill	Species	HDDV	Species	LDGV	Species	Asphalt	Species	Road Dust/Soil	Species	Wood Burning	Species	Hog Fuel Boiler
SO4	62.56	EC	73.51	OC	54.86	EC	24	Si	27	OC	83.45	SO4	26.36
S	27.23	OC	19.81	EC	23.55	SO4	23	Al	8.1	EC	22.32	K	22.61
Na	4.90	SO4	0.46	SO4	1.33	Cs	12	OC	6.2	Levo	6.90	S	9
K	2.45	NO3	0.2	Si	1.21	Ca	3	Fe	5.3	SO4	0.65	Cl	3.7
Ca	0.96	Cl-	0.11	Fe	1.2	Co	2	Ca	4.2	Cl	0.42	TC	3.55
Cl	0.92	Ca	0.06	Ca	1.18	Fe	2	K	1.3	Cl-	0.37	Cl2	2.54
Si	0.25	Zn	0.06	Zn	0.91	Mn	0.55	Ti	0.48	NO3	0.26	OC	2.48
Mg	0.17	Fe	0.02	Al	0.19	Ni	0.55	EC	0.28	Si	0.13	Zn	1.49
Zn	0.14	K	0.01	Pb	0.06	K	0.55	Mn	0.12	Ca	0.01	EC	1.07
B	0.10	Al	0	Cu	0.04	Se	0.55	SO4	0.096			Fe	0.67
Mn	0.10	NH4+	0	K	0.01	Zn	0.55	NO3	0.038			Ca	0.44
P	0.09	As	0	Mn	0.01	Ba	0.05	Sr	0.036			Mn	0.2
Al	0.05	Ba	0	Ti	0.01	Br	0.05	Pb	0.027			Si	0.15
Fe	0.05	Br	0	NO3	0	Cd	0.05	Zn	0.017			Pb	0.14
Ba	0.01	Cu	0	Cl-	0	Cl	0.05	V	0.016			NO3	0.14
Sr	0.01	Mn	0	NH4+	0	Cu	0.05	Cu	0.011			Cu	0.14
Cu	0.00	Pb	0	As	0	Pb	0.05	Cr	0.011			Br	0.09
Pb	0.00	Sb	0	Ba	0	Mo	0.05	Rb	0.006			Rb	0.08
Bi	0.00	Se	0	Br	0	Ag	0.05	Ni	0.003			Mg	0.05
Ti	0.00	Si	0	Sb	0			As	0.002			As	0.05
Cr	0.00	Sn	0	Se	0			Se	5.00E-04			Cr	0.03
Hg	0.00	Ti	0	Sn	0			Cl	3.00E-04			Ba	0.03

4.4 CMB RESULTS

CMB was run on 105 samples with the 11 selected tracer species and the 11 selected source profiles. The majority of the mass was successfully apportioned to the 11 sources as shown in **Figure 4-1**. CMB mass closure was more consistent for samples with a larger total $PM_{2.5}$ mass with approximately 80% of the mass apportioned (**Figure 4-2**). Successful apportionment for high $PM_{2.5}$ mass days is important because these are the days when concentrations may exceed desired levels. Results for the samples with a smaller total mass were more variable and ranged from 40-160% mass apportioned (Figure 4-2). Sources that were not included in the CMB analysis are likely the cause of under apportioned mass. Additional performance measures including r-square (R^2) and chi square were examined and were within acceptable ranges ($R^2 \sim 1$ and chi square ≤ 4).

Source contributions were examined on an average basis and are shown in **Figure 4-3**. Results were averaged in a manner consistent with the ambient data composition analysis (Figure 3-1) to allow for comparison. The dominant sources over the entire data set were burning, pulp mill, and LDGV. These results are consistent with the ambient data which is composed mainly of OC and sulfate. Some seasonal differences in source contributions were seen. An increase in wood burning contributions occurs in the winter, consistent with home heating needs. The wood-burning contribution is negligible in the summer, with saw mills (hog fuel boiler) and other OC sources becoming more prominent. Source contributions for saw mills (hog fuel boiler) and HDDV were consistent across seasons and on high $PM_{2.5}$ mass days. Ammonium sulfate source contributions to $PM_{2.5}$ are small and almost negligible during the summer. This is because the majority of sulfate measured was apportioned to the pulp mills. As discussed in Section 3.2, the majority of secondary sulfate is coming from point sources in the air shed rather than being transported into the Prince George area. The additional sulfate in the ammonium sulfate source is likely coming from oil refineries or saw mills. Ammonium nitrate contributions were small as expected with higher contributions in the winter. Source contributions are also shown for select high $PM_{2.5}$ mass days (**Figure 4-4**) and for select summer days (**Figure 4-5**). The composition on the high mass days is consistent; however, differences in summer days are observed. Differences in these days are likely due to shifts in meteorology.

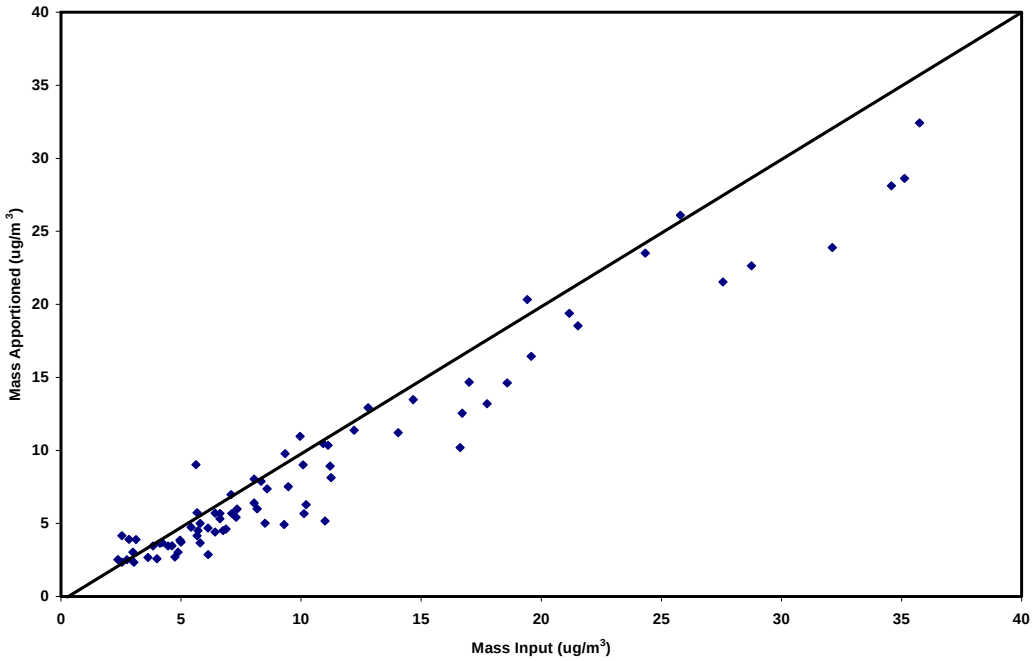


Figure 4-1. Scatter plot of total mass input into the CMB model and total mass apportioned with CMB.

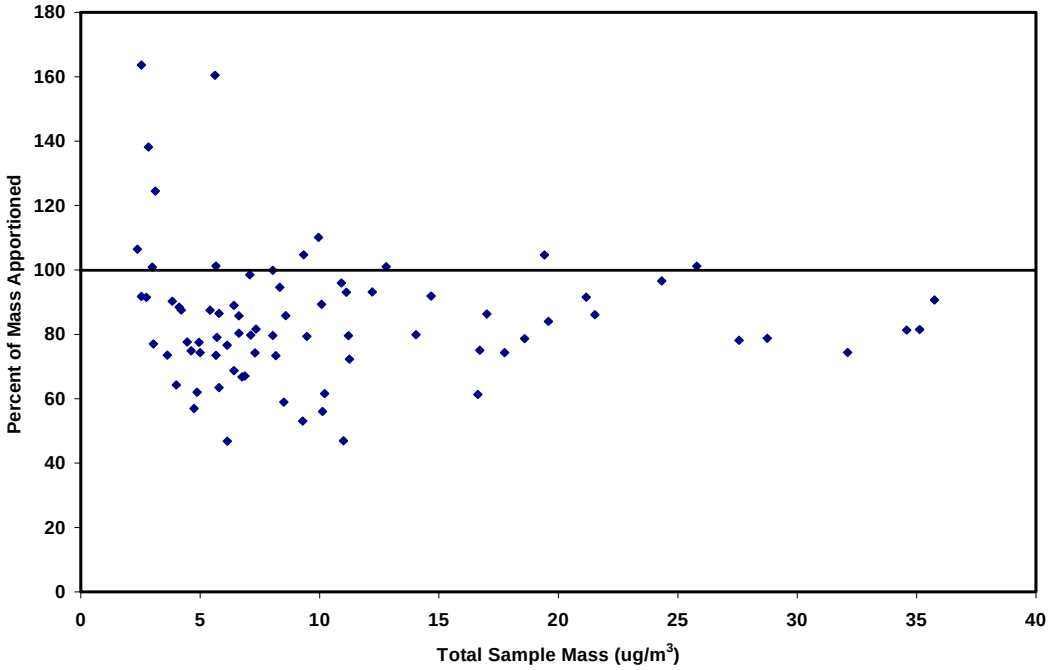


Figure 4-2. Percent of mass apportioned as a function of total sample mass.

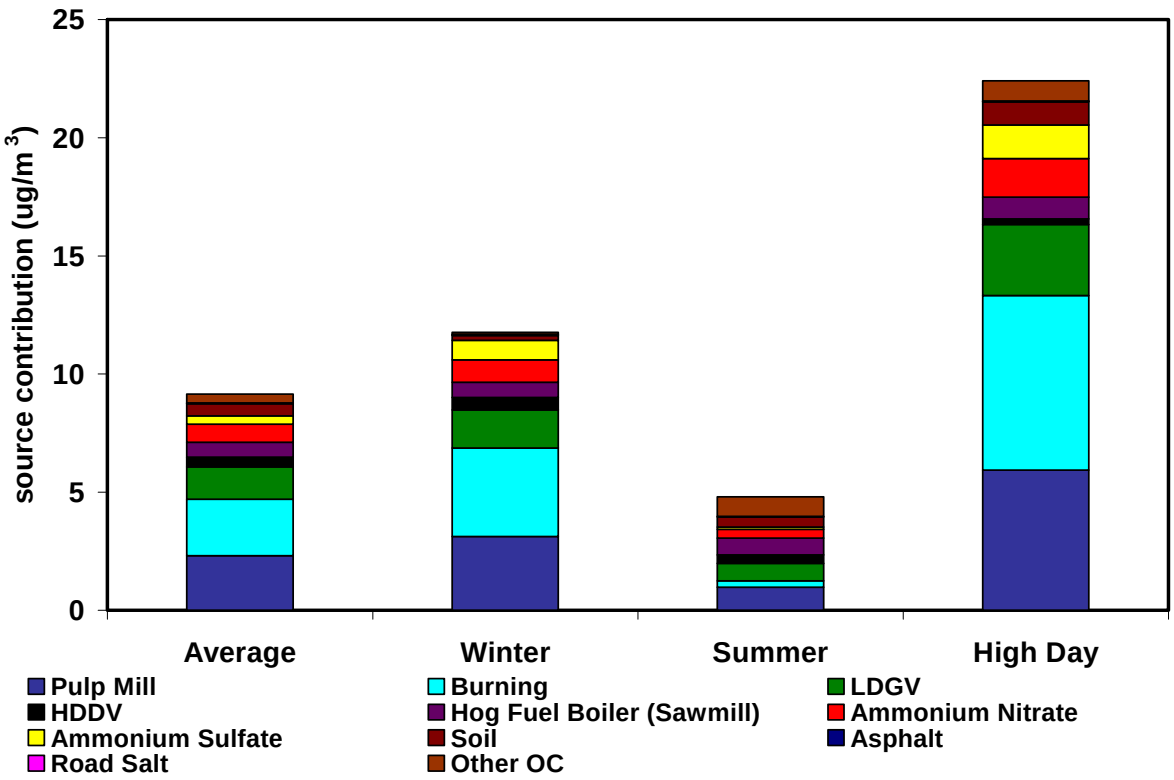


Figure 4-3. Source contributions determined with CMB on ambient data measured at the Plaza 400 site in Prince George (December 2004 to March 2006). Contributions are averaged over all samples (average), winter month samples (winter), summer month samples (summer), and high $PM_{2.5}$ mass samples (high day).

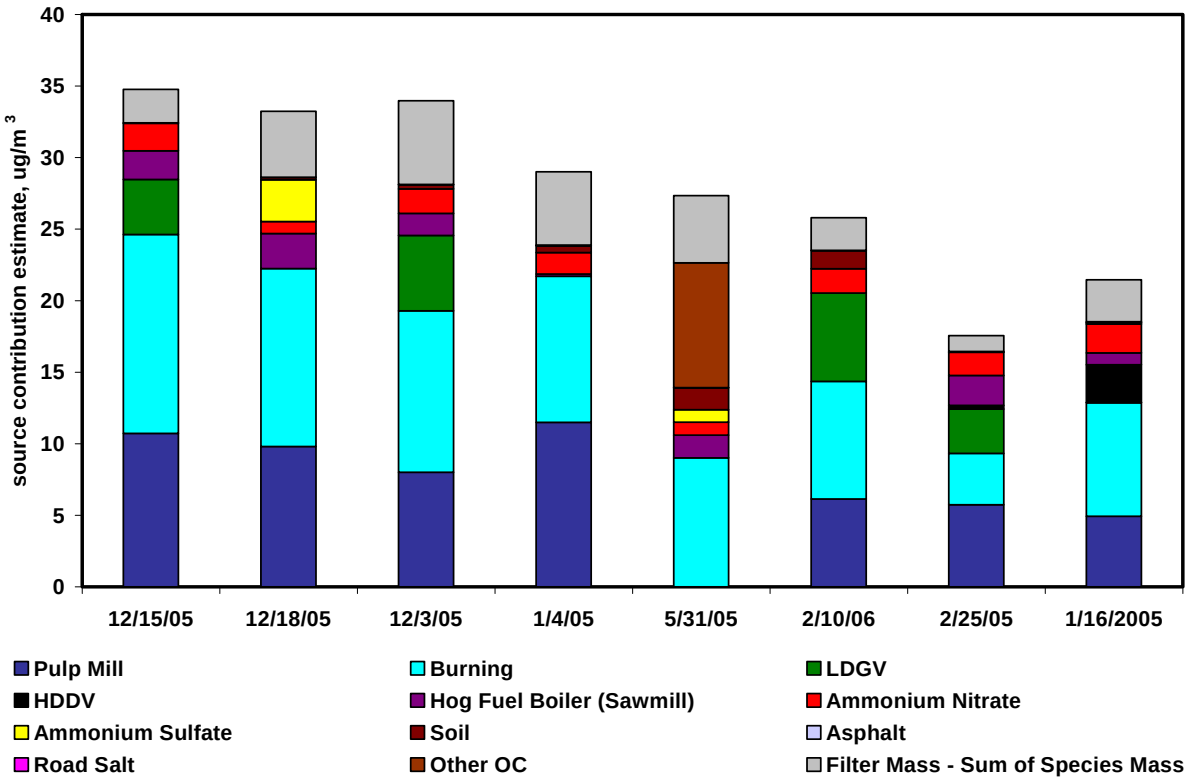


Figure 4-4. CMB $PM_{2.5}$ source contributions from data measured at the Plaza 400 monitoring site in Prince George. Source contributions are shown for select high $PM_{2.5}$ mass days.

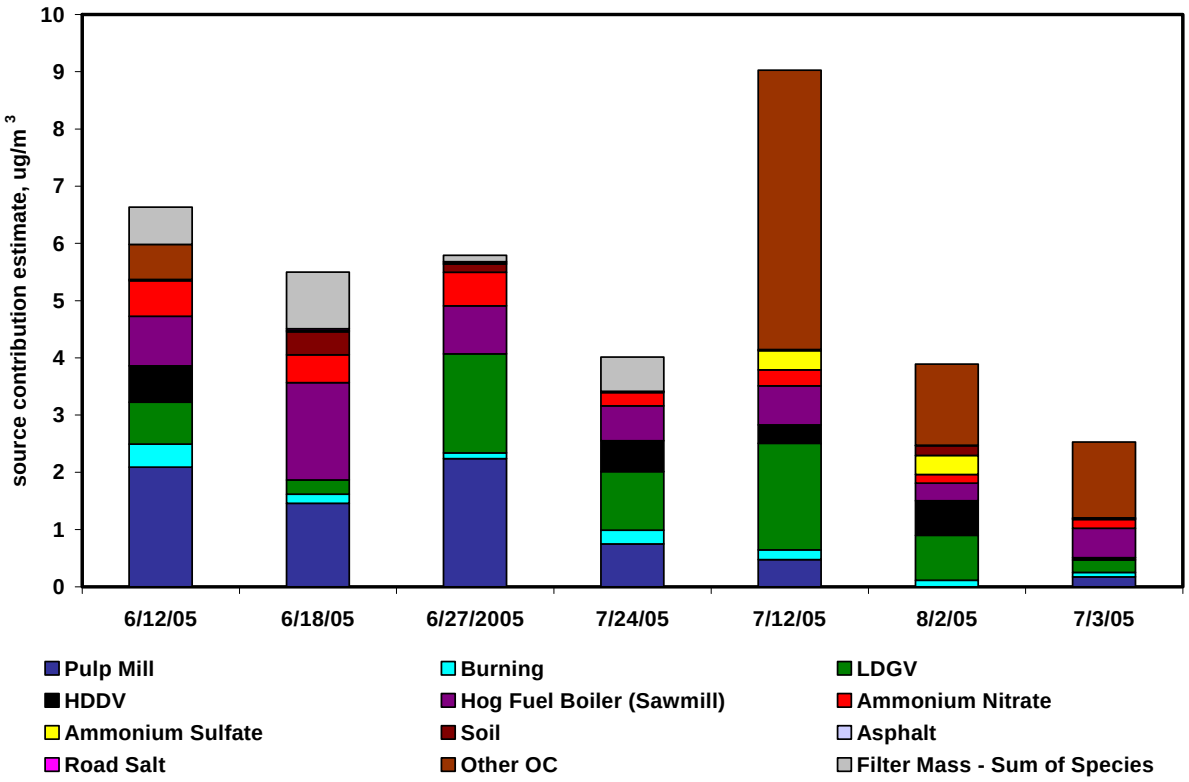


Figure 4-5. CMB $PM_{2.5}$ source contributions from data measured at the Plaza 400 monitoring site in Prince George. Source contributions are shown for select summer days.

Percent source contributions on an average basis are shown in **Figure 4-6**. Percent contributions are similar for the winter days and the high $PM_{2.5}$ mass days. This is expected because most high $PM_{2.5}$ days occur in the winter. The percent contribution for LDGV is very consistent across seasons and on high PM mass days at approximately 15%. The pulp mill contribution is also consistent at approximately 25%. Differences in winter and summer contributions, especially the increased importance of saw mills and other OC sources, become more apparent when looking at the contributions on a percent basis. The actual mass apportioned to saw mills does not change between winter and summer months. Differences in percent contributions are caused by the loss of the wood burning sources. The mass apportioned to the other OC source does change: the increase in the other OC mass during the summer may be caused by wildfires. Source contributions are shown for selected high $PM_{2.5}$ mass days in Figure 4-4. On May 31, 2005, a large fraction of the mass is apportioned to the other OC source and a wildfire event occurred on this date.

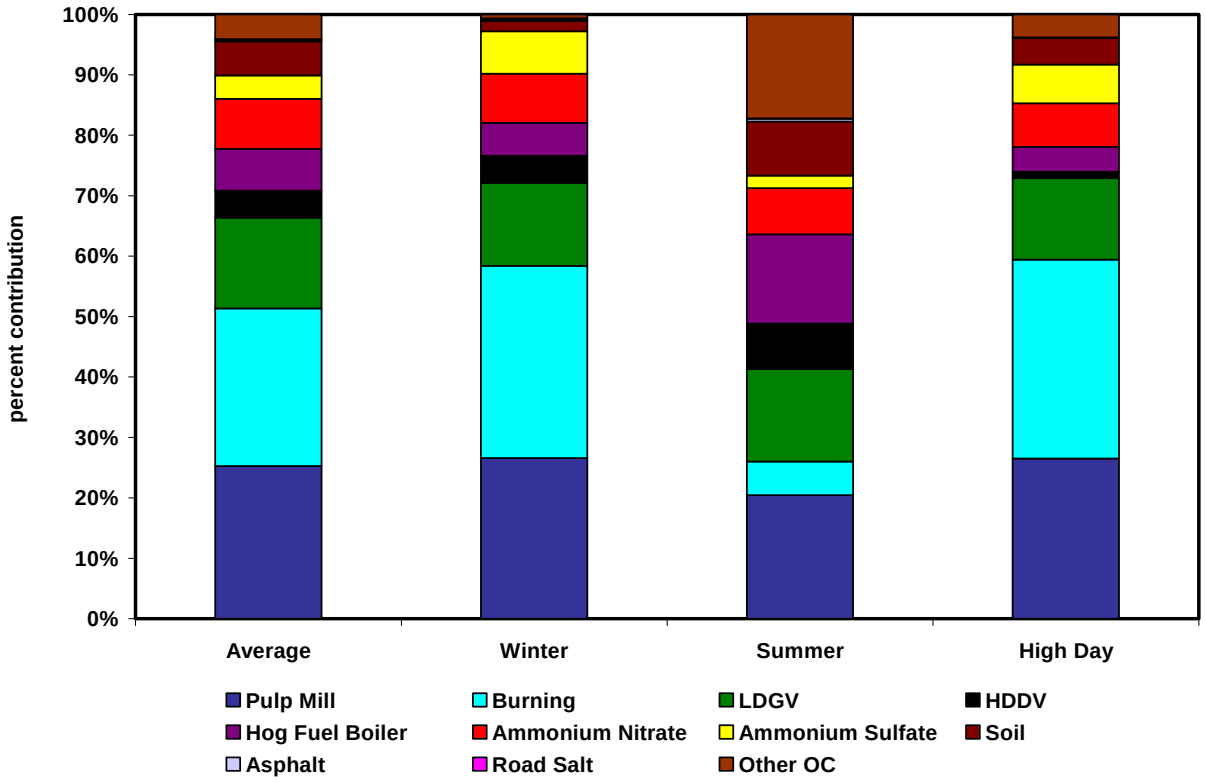


Figure 4-6. Percent contributions of 11 sources to $PM_{2.5}$ levels measured at the Plaza 400 site in Prince George. Contributions are averaged over all samples (average), winter month samples (winter), summer month samples (summer) and high $PM_{2.5}$ mass samples (high day). Note that most of the ammonium sulfate was apportioned to the pulp mill source, with the remaining non-pulp mill sulfate denoted as "ammonium sulfate" in the figure.

Uncertainties (as standard error) in CMB results are summarized in **Table 4-2**. Uncertainties in the CMB results account for uncertainties in ambient concentrations and source profiles as well as collinearity in source profiles. Sources with small source contributions including road salt and asphalt had percent uncertainties near 100%, indicating actual source contributions may be zero. For many of the important sources, uncertainties ranged from 20% to 30%, including pulp mills, secondary sulfate, burning and HDDV. Uncertainties in LDGV and hog fuel contributions were higher at approximately 50 percent. Secondary nitrate and other OC profiles had low uncertainties at 9% and 15%, respectively.

Table 4-2. Average percent uncertainties in source contribution estimates from the CMB analysis.

Source	Average % Uncertainty
Ammonium Sulfate	20
Ammonium Nitrate	9
Soil	20
Pulp Mill	30
Burning	30
HDDV	35
LDGV	50
Road Salt	100
Asphalt	100
Other OC	15
Hog Fuel	50

4.5 SENSITIVITY ANALYSIS

Because several of the source profiles included in CMB may not be representative of the Prince George area, it is important to conduct sensitivity analyses to understand how changes in source profiles can affect the results. Specific profiles targeted in the sensitivity analysis were LDGV, HDDV, wood burning, and pulp mills. Although asphalt and soil (road dust) profiles were not locally measured, these source profiles were not investigated because their contributions were found to be small. The pulp mill profile is representative of the Prince George area; however, OC and EC emissions were not measured. Sensitivity analyses need to be conducted on the carbon mass fractions used in the profile.

LDGV and HDDV profiles were altered by changing the OC/EC ratios. Alternate ratios were taken from vehicle emission measurements from the gasoline diesel split study (Fujita et al., 2005). Extremes of the OC to EC ratios (high and low) observed in the study were used for the sensitivity analysis. Wood-burning sensitivity analyses were conducted with a softwood-only profile (pine) and a hardwood-only profile (oak) from (Fine et al., 2004). Using these profiles tests the extremes of wood burning emissions because softwoods emit a higher percent of carbon than hardwoods. Pulp mill profiles were altered by adding carbon (OC and EC) into the profile to see the effects.

Sensitivity results for LDGV, HDDV, and wood burning profiles are presented in **Figures 4-7, 4-8, and 4-9**, respectively. Each figure shows results for two sensitivity cases, high and low OC/EC fractions for the LDGV and HDDV, and hardwood and softwood cases for wood burning. The figures show the difference in source contributions between the sensitivity case and the base CMB run. Positive values indicate that the source contribution has increased with the sensitivity case and negative values indicate a decrease. Changes in source contribution were averaged over the entire data set, winter month data, and summer month data. Total mass apportioned is also included to show the effect of profile changes on mass closure.

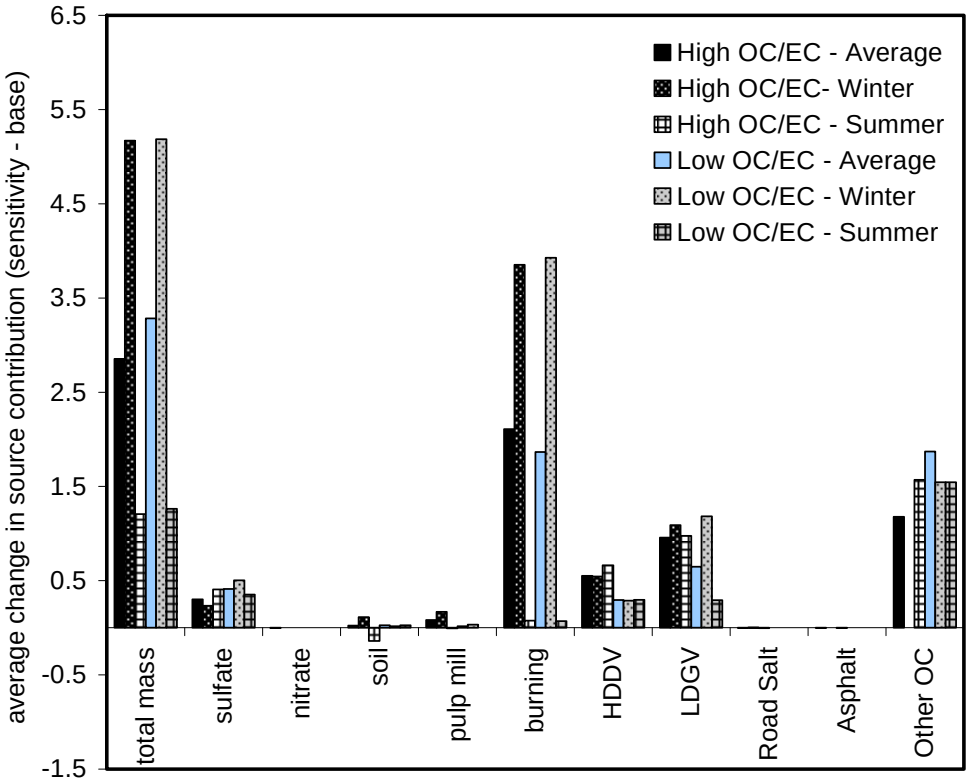


Figure 4-7. Sensitivity results for changes to the LDGV source profile. The figure shows the difference between sensitivity results and base results averaged over all, winter, and summer samples.

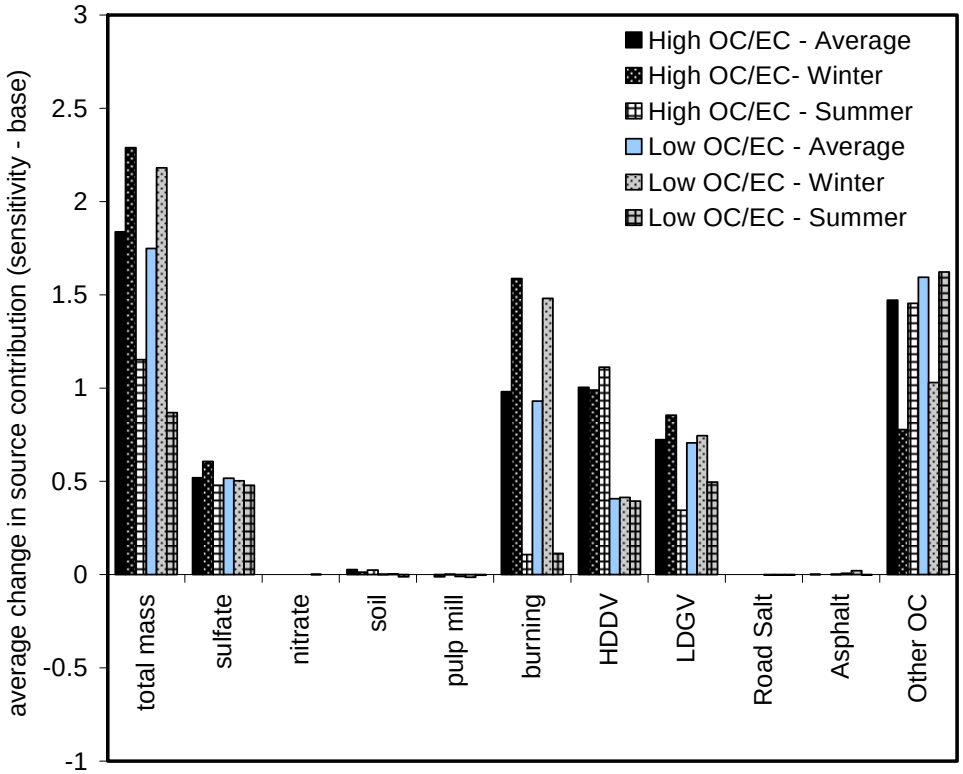


Figure 4-8. Sensitivity results for changes to the HDDV source profile. The figure shows the difference between sensitivity results and base results averaged over all, winter, and summer samples.

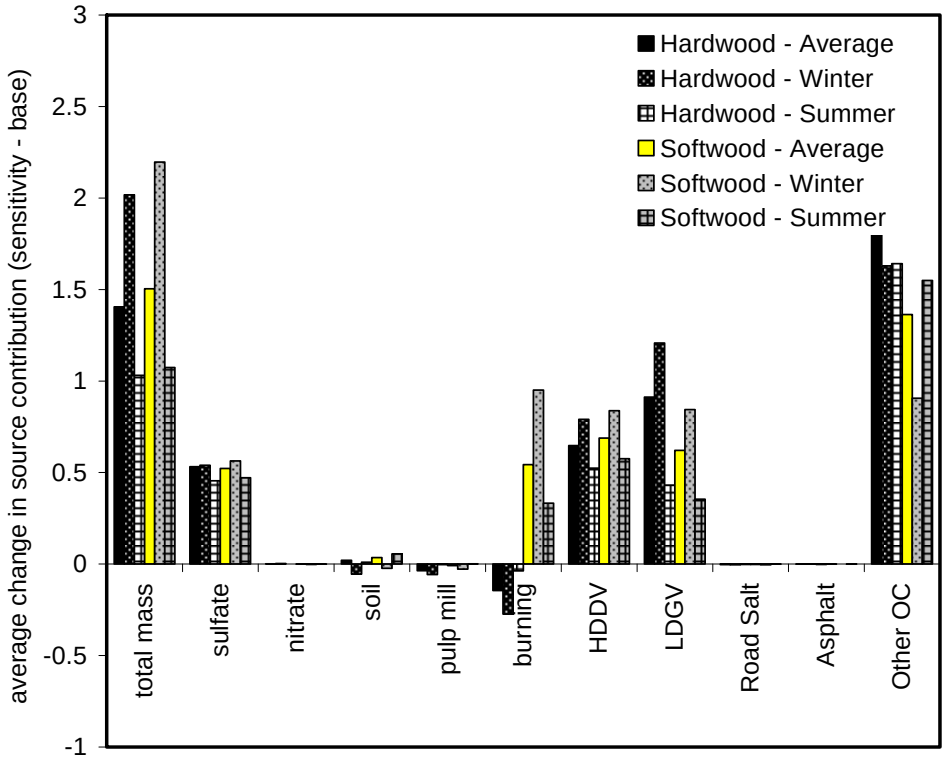


Figure 4-9. Sensitivity results for changes to the wood burning source profile. The figure shows the difference between sensitivity results and base results averaged over all, winter, and summer samples.

Changes observed with the sensitivity analysis were mostly positive, indicating source contributions may be underestimated. For all three sensitivity analyses shown, changes to source profiles mainly affected the carbon sources. This includes burning, HDDV, LDGV, and other OC. Very similar source contribution changes were observed for the LDGV and HDDV sensitivity runs (< 2 $\mu g/m^3$), however, changes observed in the burning source contribution were greater for the LDGV sensitivity case. Results were similar across seasons with burning as the exception. Changes to OC/EC ratios had little effect on burning in the summer while changes were observed in the winter. The wood burning analysis showed increases in LDGV, HDDV, and other OC for both hardwood and softwood profiles. Burning, however, was shown to decrease with the hardwood profile and increase with the softwood profile. Changes in source contributions for the burning sensitivity analysis were generally less than 1 $\mu g/m^3$. Although source contribution masses changed with the sensitivity runs, percent source contributions remained reasonably constant (**Figure 4-10**). The major changes observed were a decrease in the pulp mill source importance with an increased HDDV importance. The importance of wood burning increases for the LDGV case and is less important with the hardwood case. Based on the results of the sensitivity analyses, source contribution masses might be underestimated for burning, LDGV, and HDDV; however, the overall importance of the sources included in the CMB analysis was very stable.

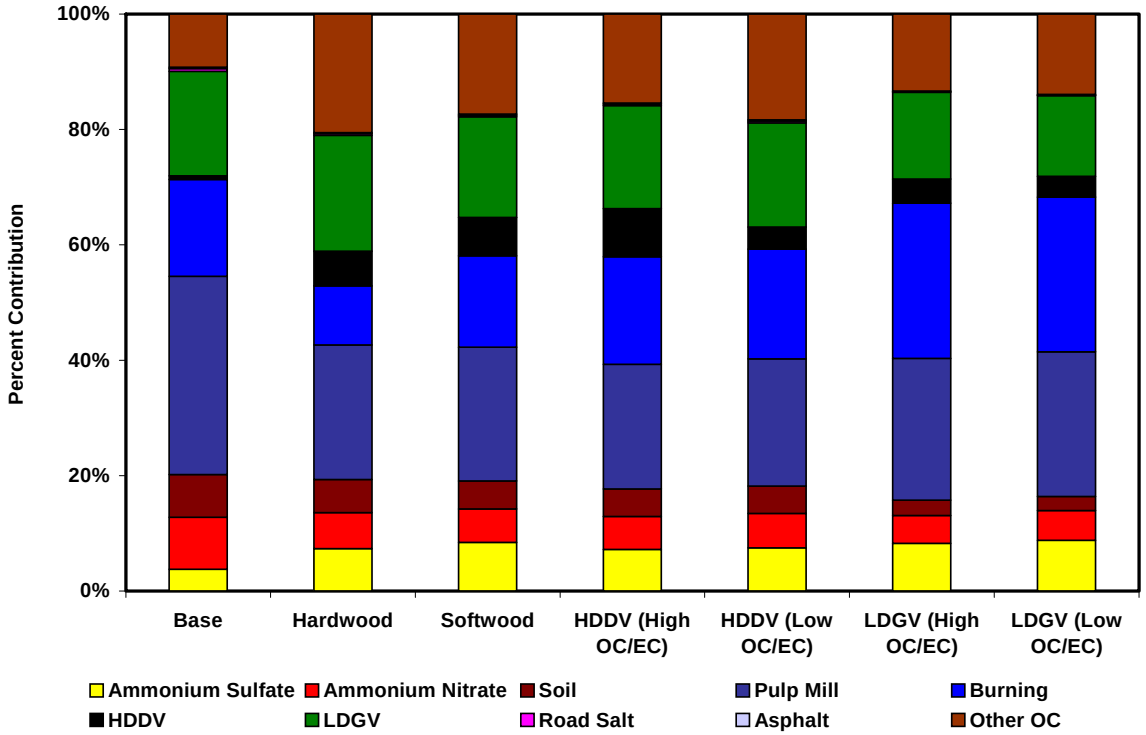


Figure 4-10. Percent contributions for sensitivity CMB runs.

For the pulp mill sensitivity analysis, OC and EC were added to the pulp mill source profile based on source profiles measured at the DMI and Weyerhaeuser pulp mills in Alberta, Canada (Kharrat, 2000). OC and EC mass fractions at DMI varied from 0.6-5% and 0.3-4%, respectively. At Weyerhaeuser, OC and EC mass fractions varied from 6-14% and 0.2-2%, respectively. Based on these guidelines, as a sensitivity test of the CMB results, OC and EC were added to the Northwood pulp mill profile as 5% of the mass, with a 10% uncertainty. The profile provides a distribution of species across the emitted mass, not a measure of the emissions. Thus, when OC and EC are added to the profile, the other species were therefore reduced on a percentage basis to accommodate this "extra" OC and EC mass (and still sum to 100%). Note that OC and EC were not explicitly measured in the Northwood profile, and the amount of mass in the profile from these species is unknown, and as seen by the variation in the other pulp mill profiles, can vary widely. This sensitivity test was conducted based on the observations of OC and EC in other pulp mill profiles. The difference in sensitivity results and base case results are shown in **Figure 4-11**. Changes in source contributions were insignificant (< 0.1 $\mu g/m^3$) for all sources.

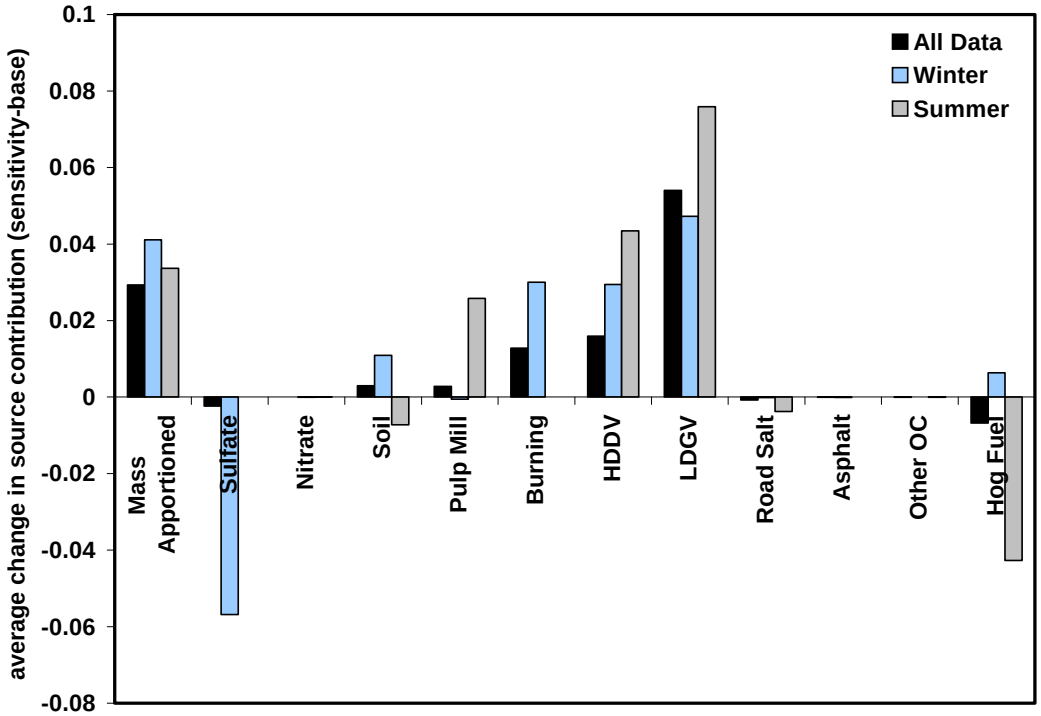


Figure 4-11. Sensitivity results for changes to the pulp mill source profile. The figure shows the difference between sensitivity results and base results averaged over all, winter, and summer samples.

4.6 CMB WITH VOC DATA

Additional CMB runs were conducted with the addition of select VOC species that are representative of gasoline and diesel vehicle emissions. This approach should be considered exploratory, and useful to understand if, when adding these additional constraints, the results vary. Because OC and EC are not exclusively emitted from mobile sources, the addition of unique species may improve mass apportionment to the LDGV and HDDV sources. The select VOC species included were 2,2,4-trimethylpentane (gasoline) and n-decane (diesel). These species, while often used as tracers, are not unique to mobile sources, but are present in all gasoline and diesel fuel combustion. On average, results showed a decrease in mass apportioned to the LDGV source and no change in the HDDV source. Changes in source contribution estimates were less than 1 $\mu g/m^3$, and provide a estimate of the uncertainty in the analysis and ambient data.

4.7 WIND ANALYSIS

The effects of local transport on CMB results can be better understood by examining meteorological data. Wind roses were also examined for select summer days to understand the cause of the different source contributions seen in Figure 4-5. For summer days on which pulp mill contributions were important, the wind direction tended to be northeasterly with higher wind speeds as shown for two days in **Figure 4-12**. Northeast is the direction of the largest pulp mill

in the Prince George area. For summer days on which pulp mill contributions were not important, the dominant wind direction was from the southwest (**Figure 4-13**).

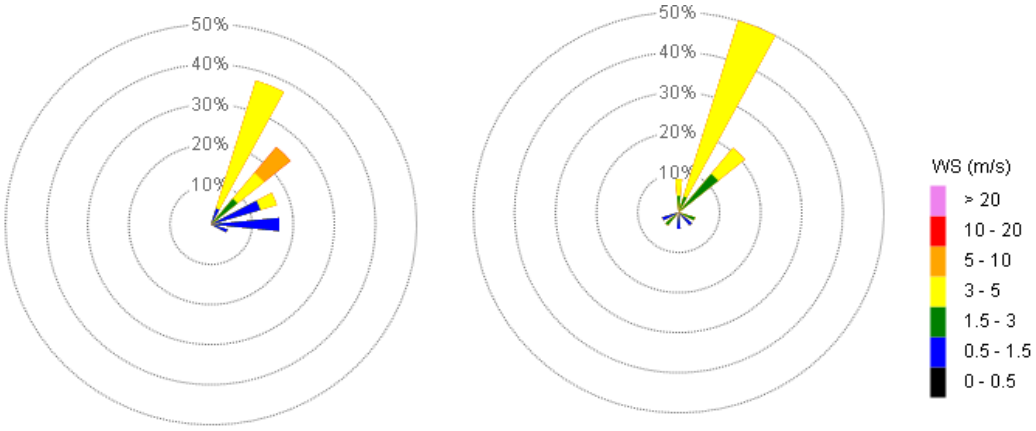


Figure 4-12. Wind roses for select summer days (June 12, 2005, and June 18, 2005) on which pulp mill contributions were important.

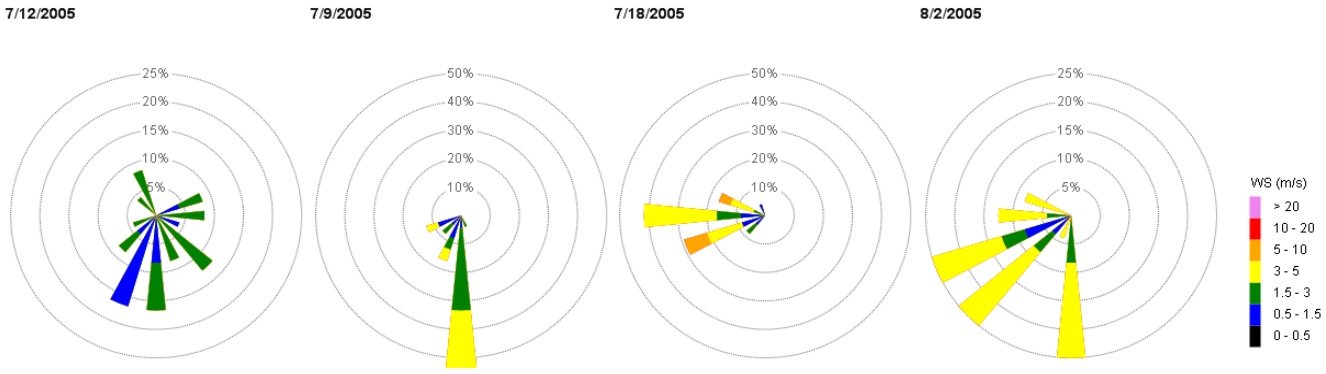


Figure 4-13. Wind roses for select summer days (July 12, 2005; July 9, 2005; July 18, 2005; August 2, 2005) on which pulp mill contributions were small.

5. POSITIVE MATRIX FACTORIZATION

$PM_{2.5}$ source contributions for Prince George were determined using EPA PMF version 1.1. The following sections describe the workings of PMF, data preparation, results, and source identification. Detailed descriptions of PMF can be found elsewhere (Paatero and Tapper, 1994; Paatero, 1997).

5.1 WORKINGS OF PMF

PMF is an advanced multivariate receptor modeling technique that calculates site-specific source profiles with time variations of these sources based on correlations imbedded in ambient data. PMF has been successfully applied to PM data in several studies (Anttila et al., 1995; Begum et al., 2005; Buzcu et al., 2003; Juntto and Paatero, 1994; Kim et al., 2003b; Kim et al., 2004a; Kim et al., 2004b; Kim and Hopke, 2004a, b; Kim et al., 2005a; Kim et al., 2005b; Larsen and Baker, 2003; Lee et al., 1999; Poirot et al., 2001; Polissar et al., 2001; Ramadan et al., 2000; Zhou et al., 2004). Given a data matrix *C* consisting of the concentration measurements of *n* chemical species in *m* samples and their corresponding uncertainties, the objective of PMF is to determine the number of factors *p*, the chemical composition profile of each factor, and the contribution of each factor to each sample. PMF factorizes the data matrix *C* into two matrices according to Equation 5-1:

$$C_{(m\ by\ n)} = G_{(m\ by\ p)}\, F_{(p\ by\ n)} + E_{(m\ by\ n)} \qquad \textbf{(5-1)}$$

where *G* represents the contribution of each factor to each ambient sample and describes the time variations of the factors because each ambient sample is an observation at different times. *F* is a matrix of chemical composition profiles of each factor. *F* and *G* are both forced to be non-negative in order to make physical sense (i.e., factors cannot have negative species concentrations and ambient samples cannot have a negative factor contribution). *E* is an *m by n* residual matrix of random errors. The elements of the residual matrix, e_{ij}, can be defined as show in Equation 5-2:

$$e_{ij} = x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj} \qquad \textbf{(5-2)}$$

where $i = 1,\ldots,m$; $j = 1,\ldots,n$). In PMF, the sum of the squares of residuals, e_{ij}, weighted inversely by the variation of the data points, s_{ij}^2, is minimized according to the following constrained weighted least-squares model, Equation 5-3:

$$\text{minimize } Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \frac{e_{ij}^2}{s_{ij}^2} \qquad \textbf{(5-3)}$$

The objective is to determine the matrices *G* and *F* by minimizing *Q*. Equation 5-1 is solved using a unique iterative algorithm in which matrices *G* and *F* vary simultaneously at each iteration step (Paatero, 1997). Theoretically, if the uncertainties correctly characterize the data and every point is perfectly modeled, *Q* should be approximately the number of species

multiplied by the number of observations, minus the number of factors multiplied by the number of species (i.e., the number of data points). In these analyses, Q from the modeling was required to be within 50% of the theoretical Q to ensure a reasonable fit for all observations.

5.2 USING PMF OUTPUT

Source contributions of each factor can be determined using PMF output, matrices G and F. Each element of the matrix G (g_{ik}) is a normalized source contribution of a factor k for a given sample i. Each element of F (f_{kj}) is a mass contribution of a chemical species j to a factor k. Using matrix F, the reconstructed mass (m_k) for an individual factor i can be calculated as shown in Equation 5-4:

$$m_k = \sum_{j=1}^{n} f_{kj} \quad \textbf{(5-4)}$$

The normalized source contributions of matrix G can then be converted to meaningful mass units by multiplying the individual elements of G and the corresponding factor mass m_k, as shown in Equation 5-5:

$$c_{ik} = g_{ik} * m_k \quad \textbf{(5-5)}$$

Uncertainties in the EPA PMF solution are estimated using a bootstrapping technique, which is a re-sampling method in which "new" data sets are generated that are consistent with original data; each data set is decomposed into F and G matrices, and the resulting F and G matrices are compared with the base PMF run (Eberly, 2005). Instead of inspecting point estimates, this method allows the analyst to review the confidence intervals for each species to obtain more robust profiles. Output of the bootstrapping analysis consists of box whisker plots of species for each profile by both percent of species and concentration. The box shows where the middle 50% of the bootstrap values exist—the tighter the box, the more certainty in the profile, and the more consistent the results are across the bootstraps. In this study, 200 bootstrap runs were performed for the final PMF results.

5.3 DATA PREPARATION

The only required input for PMF is the ambient data set (matrix C) with associated uncertainties. Prior to using the data in PMF, adjustments need to be made to missing or below detection samples. In PMF, each data point is weighed individually, allowing the user to adjust the influence of each point depending on the confidence in the data. This feature is an advantage of PMF because samples with some species missing or below the method detection limit (MDL) can be used in the analysis, with associated uncertainty adjusted so that these data points are given less weight in the model solution. This maximizes the number of samples used in PMF, whereas with CMB, samples with measurements below detection are excluded. Data below MDL were substituted with the maximum MDL reported for the given species divided by two and missing data were substituted with median concentrations (Poirot et al., 2001; Polissar et al., 2001; Song et al., 2001), resulting in a total of 125 samples. The maximum MDL was used for

substitution because use of the sample-specific MDL could introduce a false source of variability in the data. Uncertainties for values below MDL were calculated as 5/6 times the maximum MDL and for missing values as 4 times the median concentration.

5.4 PMF RESULTS

PMF was run using the 125 sample dataset with 7 to 9 factors. Of the $PM_{2.5}$ species measured, a total of 20 were included (**Table 5-1**). Several sensitivity runs were conducted to test the effects of including additional species. This included the incorporation of several polar organics, continuous data, and OC and EC carbon fractions in replacement of total OC and EC. Results were stable across the runs, and the final species list included formate, acetate, phosphate and carbon fractions in addition to those listed in Table 5-1 (excluding total OC and EC). The final PMF solution used was an 8 factor solution. The final number of runs and the species used were based on model performance criteria including the Q-value, convergence, species correlations, and mass recovery (**Figure 5-1**). Ten random runs were conducted for the final number of factors selected to ensure robust results. Over the ten runs, Q values were stable and were within 50% of the theoretical Q values. Residuals of the PMF results were also within recommended bounds (-3 < residual < 3) (Paatero et al., 2003) excluding a few outliers.

Table 5-1. $PM_{2.5}$ species used in PMF.

Aluminum	Copper	Sodium	Sulfate
Arsenic	Iron	Ammonium	Vanadium
Bromium	Potassium	Nitrate	Zinc
Calcium	Levoglucosan	Lead	Elemental carbon
Chloride	Manganese	Silicon	Organic carbon
Acetate	Formate	Oxalate	Phosphate

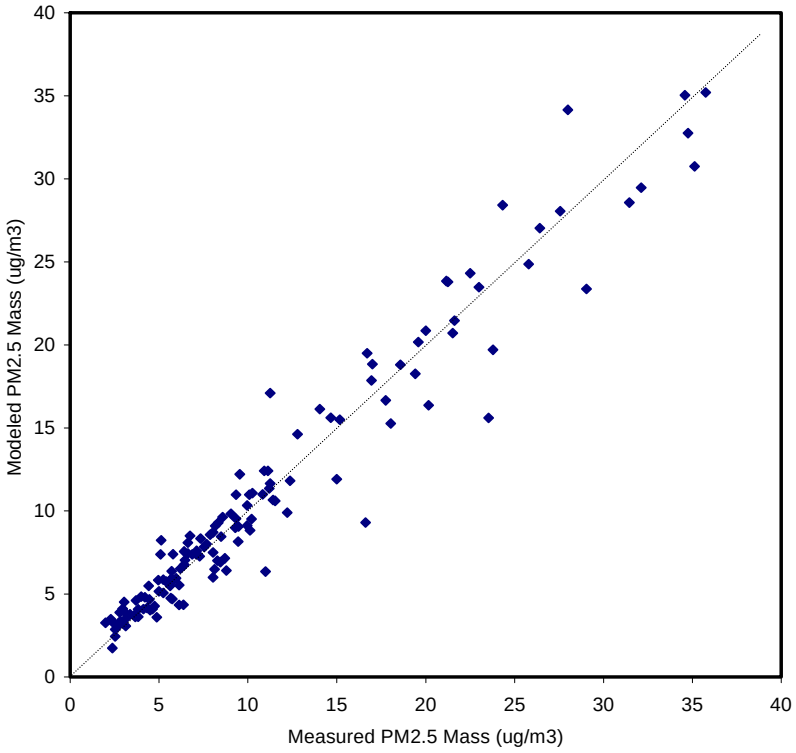


Figure 5-1. Measured versus modeled $PM_{2.5}$ mass ($\mu g/m^3$) from the 8 factor PMF solution.

Factor profiles and time series for the 8-factor PMF solution are shown in **Figure 5-2**. Correlated species were grouped together in factors as indicated in Section 3.1, including sodium/sulfate, potassium/manganese, and levoglucosan/zinc. Silicon and calcium were also found together in the same factor. The source associated with each factor was identified by looking for key chemical species associated with the source in the factor profile. Sources that are expected to be important contributors to $PM_{2.5}$ in Prince George and their associated tracer species were discussed in Section 4.3. Important species include levoglucosan for wood burning, sulfate and sodium for pulp mills, OC for LDGV, EC for HDDV, silicon and calcium for soil, and potassium for saw mills. Using these tracer species, burning, pulp mill, carbon (mobile sources), saw mill, and soil factors were identified. LDGV and HDDV could not be separated out and instead were lumped into one carbon factor. The three unidentified factors included acetate/formate, copper/iron, and chloride. Seasonal differences in the chloride factor mass are significant (shown in **Figure 5-3**). The winter season mass is greater than the rest of the year, which indicates this factor may be road salt. The molar ratio of chloride and calcium in this factor was approximately 10; if this factor were only road salt, the ratio would be 2. This factor is likely road salt with a second chloride source. The copper/iron factor that could not be identified also contains nitrate and ammonium. Secondary nitrate is accounted for within this factor. The acetate and formate were likely grouped into a separate factor because these are polar organics and are measured with a different method than the speciated PM data.

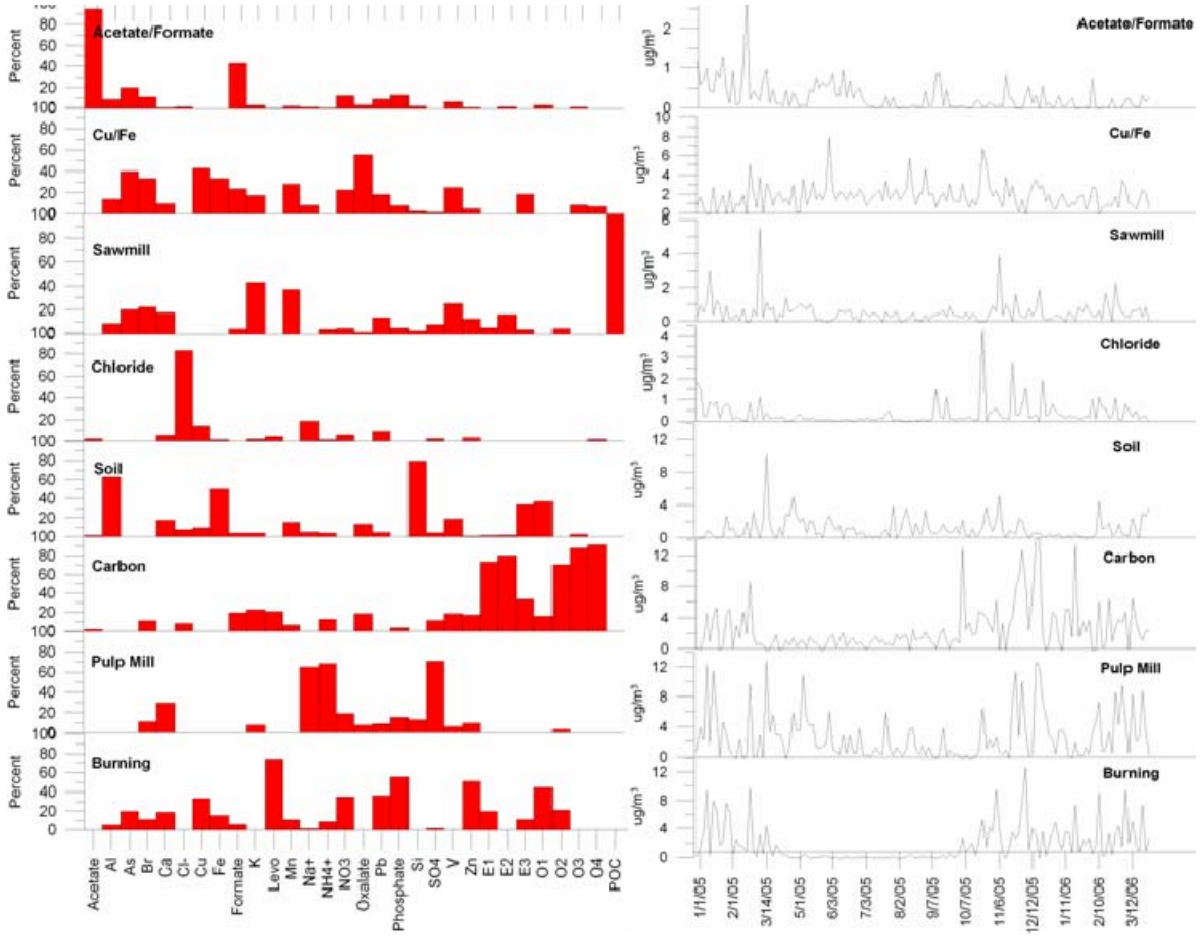


Figure 5-2. Prince George PMF factor profiles and time series for speciated $PM_{2.5}$ data (December 2004 to March 2006).

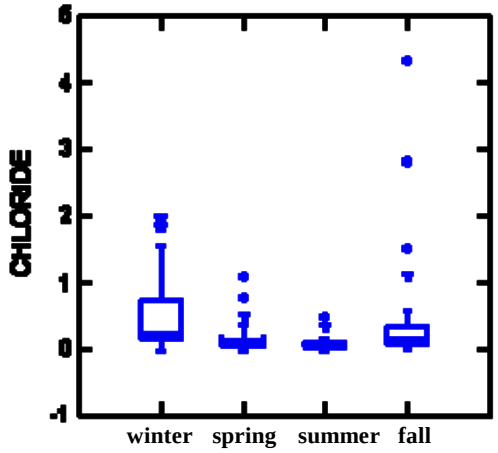


Figure 5-3. Seasonal distributions of the PMF chloride factor mass ($\mu g/m^3$).

The mass composition of the PMF results are shown in **Figures 5-4 and 5-5** averaged over all the data, winter-month data, and summer-month data. The copper/iron factor is shown with nitrate mass subtracted out and nitrate as a separate source. The sum of the copper/iron minus nitrate source and the nitrate source is the total mass contribution from the actual factor identified in PMF. Mass contributions from the pulp mill, carbon factor, and saw mill are consistent at approximately 25%, 20%, and 5%, respectively. The burning factor, as expected, has a larger contribution during the winter and is negligible in the summer. Averaged over all the data, burning contributes approximately 17% to the total mass apportioned. The copper/iron factor contributes a large percent of the mass apportioned, specifically in the summer. This factor becomes more important during the summer because the burning source is no longer present and the overall mass is less. Figure 5-5 shows that the mass apportioned to the copper/iron factor does not increase much during the summer. The soil factor also contributes a large percent of the mass in the summer. The chloride and acetate/formate factors contribute only a small fraction of the $PM_{2.5}$ mass.

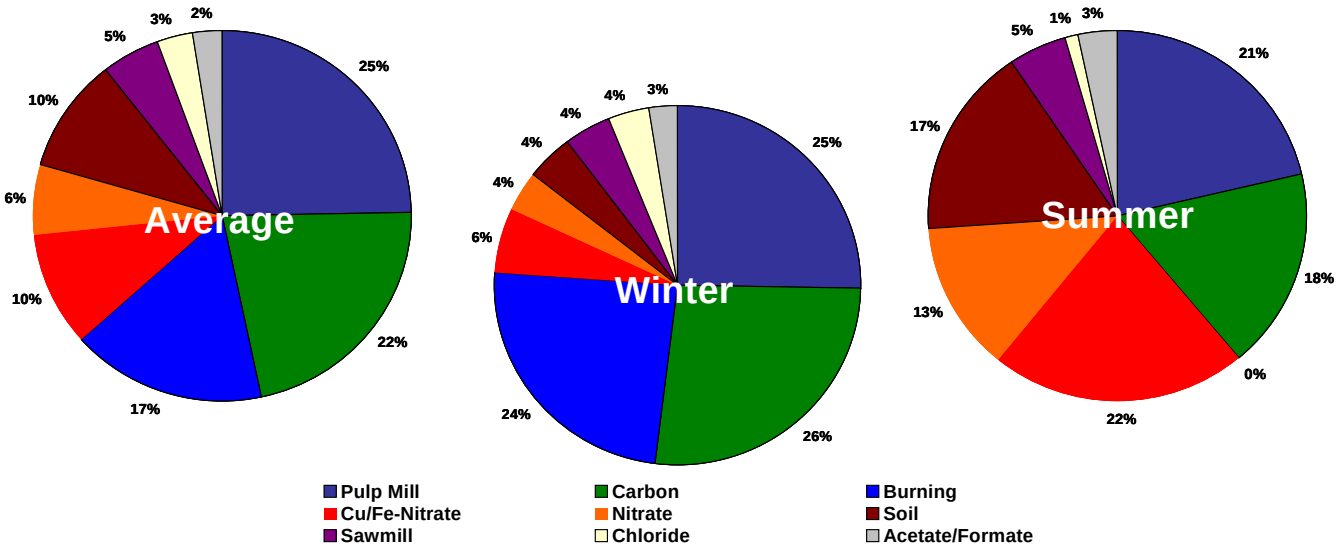


Figure 5-4. Prince George PMF results averaged over all samples (average), winter samples (winter), and summer samples (summer) (December 2004 to March 2006).

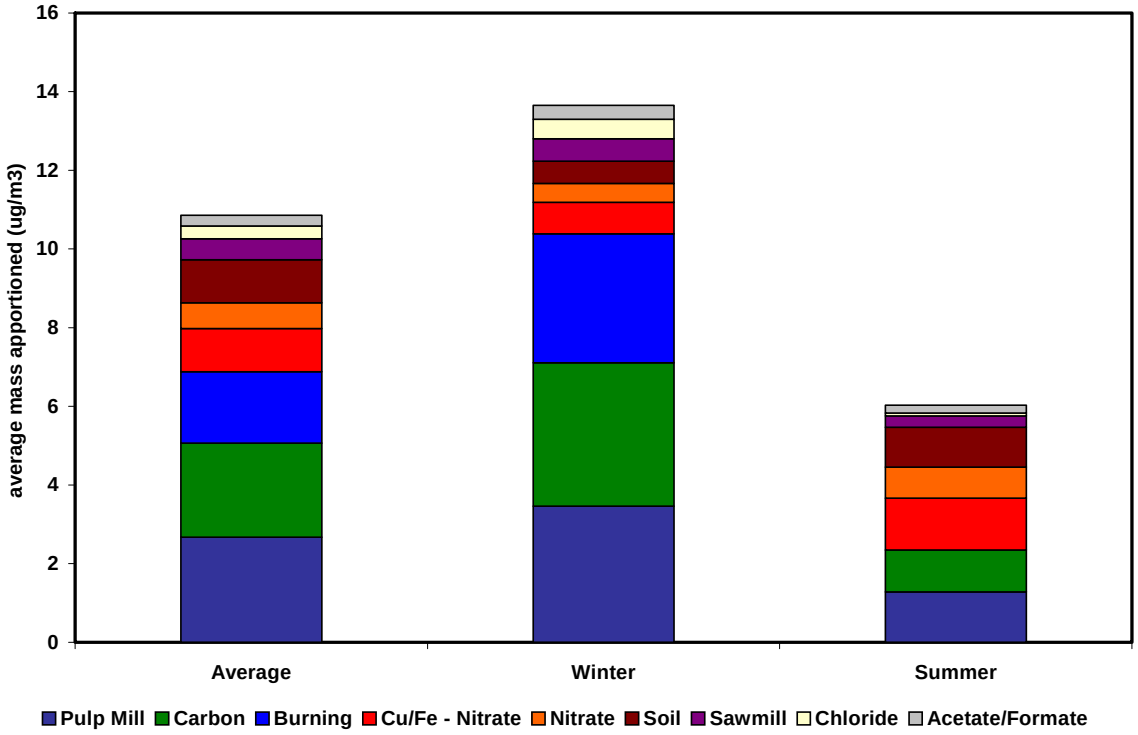


Figure 5-5. Prince George PMF mass composition averaged over all samples (average), winter samples (winter), and summer samples (summer) (December 2004 to March 2006).

5.5 PMF WITH CONTINUOUS DATA

Continuous data including nitrogen oxides (NO_2 and NO), ozone, hydrogen sulfide (H_2S), sulfur dioxide (SO_2), PM_{10}, $PM_{2.5}$, and carbon monoxide (CO) were also measured at the Plaza 400 site. The continuous data set is ideal for use in PMF because several species were measured with a large number of samples and high variability among the species. In addition, source apportionment with the continuous data could provide additional insight into sources and temporal patterns in emissions. PMF was run using all 8 species with 5 factors. Ten random runs were conducted with the 5 factors to ensure robust results. Over the 10 runs, Q values were stable and were within 50% of the theoretical Q values. Residuals of the PMF results were also within recommended bounds, excluding some outliers.

Source profiles and time series from the PMF analysis with continuous data are shown in the Appendix. Factors identified include a PM factor (PM_{10} and $PM_{2.5}$), a sulfur factor (SO_2 and H_2S), a nitrogen oxide (NO) factor, an ozone factor, and a combined CO and NO_2 factor. The sulfur factor contained approximately 15% of the $PM_{2.5}$ mass, similar to the percent of mass apportioned to the pulp mill source (with consideration of uncertainty), giving additional confidence in the results found. Some statistically significant differences in seasonal levels of the factors were observed. The NO factor and combined CO and NO_2 factor showed higher levels in the winter consistent with higher concentrations when mixing heights are low. The ozone factor had higher levels in the spring and summer as expected for this photochemically

produced pollutant. The PM and sulfur factors did not have statistically significant seasonal differences.

5.6 BOOTSTRAPPING

The speciated $PM_{2.5}$ PMF results were bootstrapped using 200 runs. The bootstrapping factors were consistently mapped back to the original PMF factors as shown in **Table 5-2**. The stability of the bootstrap runs shows that the results of the PMF analysis are good. Bootstrap results for the source profiles (25^{th} to 75^{th} percentiles) are shown in **Figure 5-6**. The source profile distributions were small for many factors (pulp mill, soil, chloride, copper/iron, acetate/formate), showing consistent bootstrapping results. Therefore, uncertainties in these source profiles are small. The distributions were larger for the carbon and burning profiles, particularly for the carbon species. This is not unexpected because carbon species have some of the highest relative uncertainties of any fitting species.

Table 5-2. Percent of bootstrap factors mapped back to the original PMF factors from the 8-factor PMF solution.

Factor	Percent of Bootstrap Factors Mapped to Original PMF Factors
Pulp Mill	97
Carbon	85
Burning	95
Copper/Iron	83
Soil	92
Saw mill	87
Chloride	93
Acetate/Formate	97

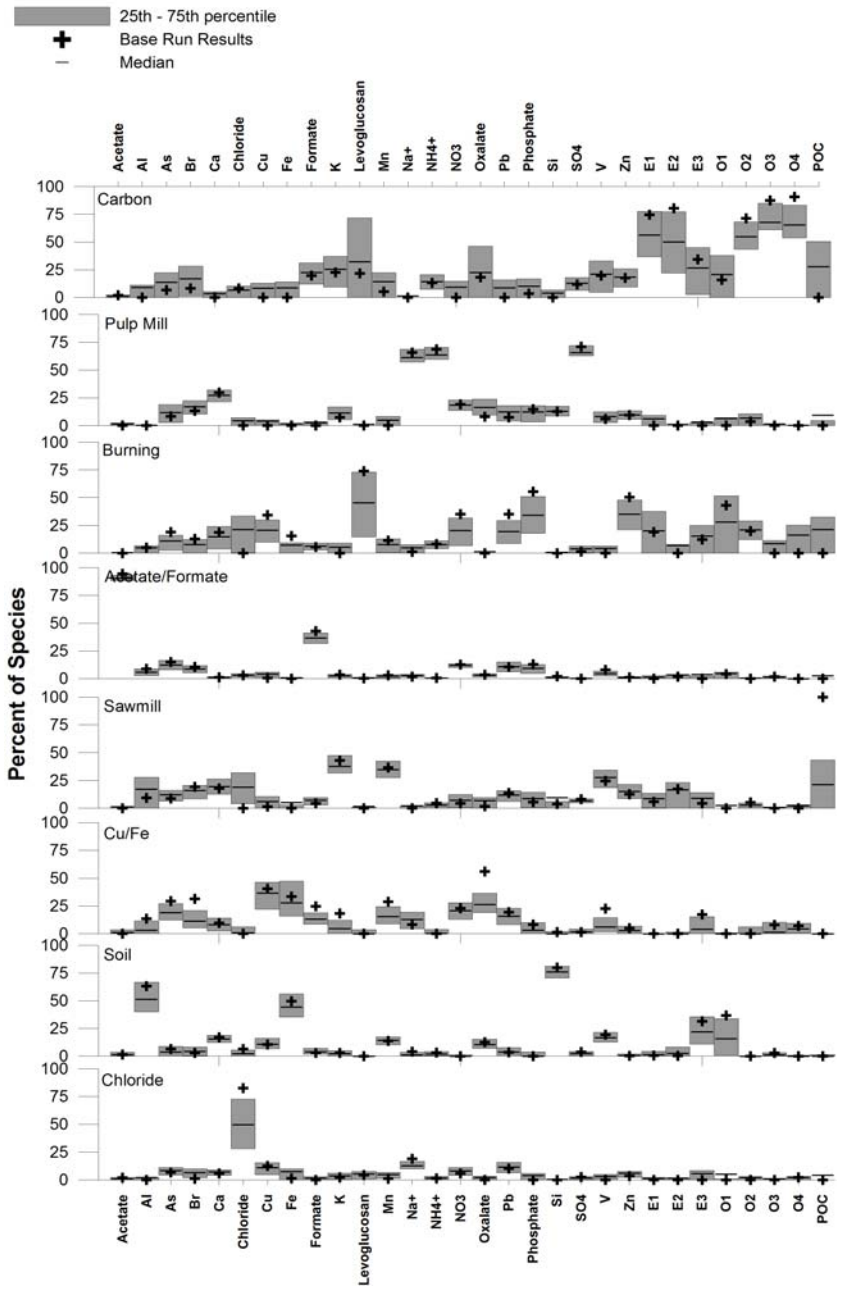


Figure 5-6. Bootstrapping results for the 8-factor PMF solution. The bar charts show the distribution of species percentages in source profiles.

6. COMPARISON OF SOURCE APPORTIONMENT RESULTS

The mass apportioned to each source from the CMB and PMF analyses were compared on a day-to-day and average basis. Source profiles were also compared. Consistency between results produces more confidence in the apportionment.

6.1 CMB AND PMF PROFILE COMPARISON

As discussed previously, CMB requires the input of source profiles whereas PMF does not. Instead, profiles are output from PMF. Comparison of source profiles between the two methods is important because it can provide insight into whether the right sources were input into the CMB model and whether these same sources have been identified using PMF. The comparison of CMB and PMF source profiles is shown in **Figures 6-1 through 6-5**. For soil profiles, the levels of calcium, iron, OM, and silicon were similar between the two methods (Figure 6-1). The major difference is the presence of sulfate in the PMF profile, which is likely secondary sulfate associated with the soil. Pulp mill profiles were also similar with strong agreement in sodium and sulfate mass percents (Figure 6-2). EC and levoglucosan levels were similar in the burning profiles (Figure 6-3), but OM levels were much higher in the CMB profile. The CMB burning profile is for wood burning without any emission controls and this likely accounts for the carbon difference in the two profiles. For the saw mill profiles, the mass percents of EC, sulfate, and potassium were similar, but the OM percents are much higher in the PMF profile (Figure 6-4). The use of a hog-fuel boiler profile in CMB to represent saw mill emissions may account for the difference between these two profiles.

In PMF, a specific source could not be identified for a few factors. One of these factors was carbon. Because motor vehicles are known to be an important source of carbon, the profile from the PMF carbon factor was compared with both the CMB LDGV and HDDV profiles. The OM and EC mass percents in the PMF carbon factor were similar to that of the LDGV profile as shown in Figure 6-5, but slightly pulled in the direction of the HDDV percents. The carbon factor is likely a mix of LDGV and HDDV emissions with a majority of the mass in the factor coming from LDGV. Based on the assumption that the carbon factor is a mix of these two sources only, LDGV and HDDV make up approximately 80% and 20% of the mass, respectively.

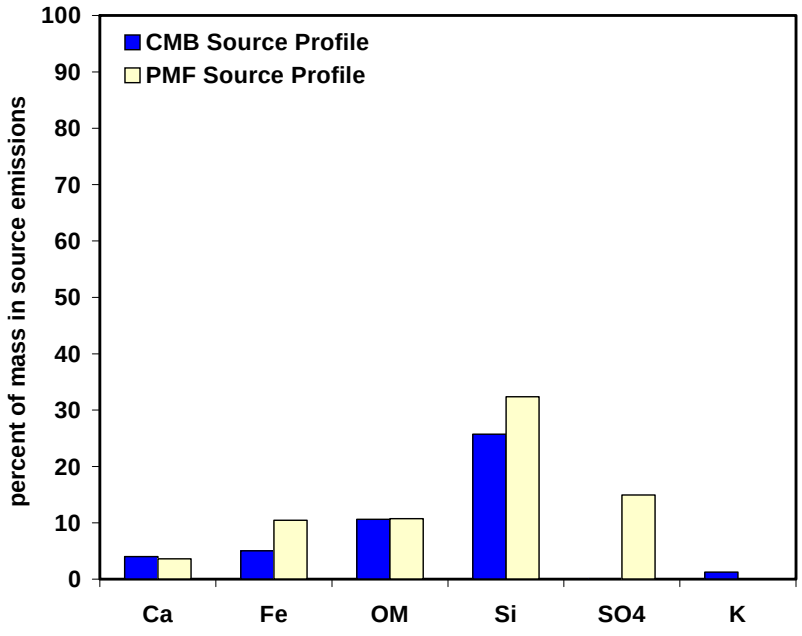


Figure 6-1. CMB and PMF soil profile comparison.

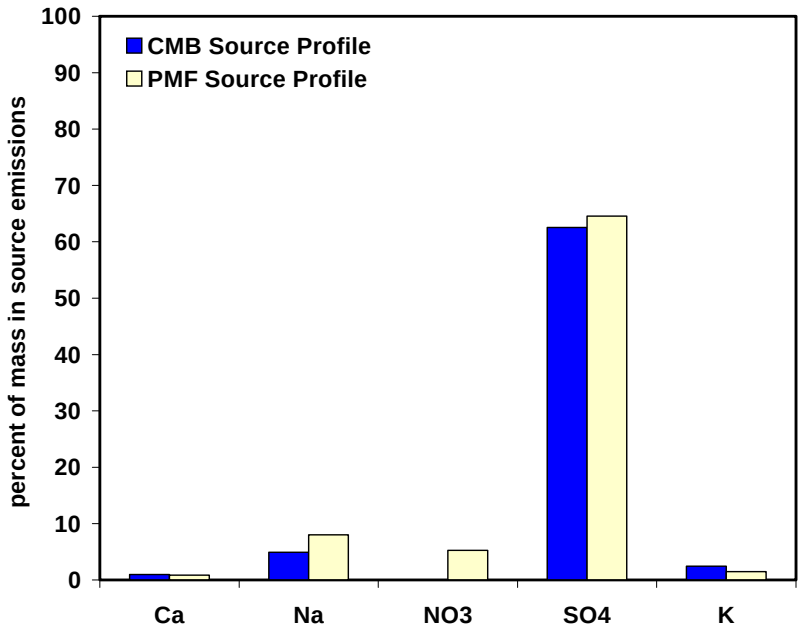


Figure 6-2. CMB and PMF pulp mill profile comparison.

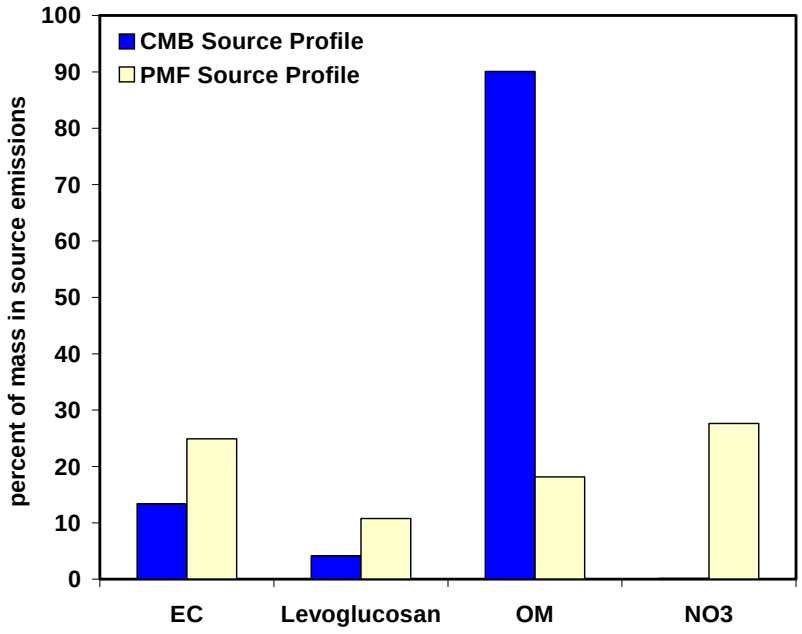


Figure 6-3. CMB and PMF burning profile comparison.

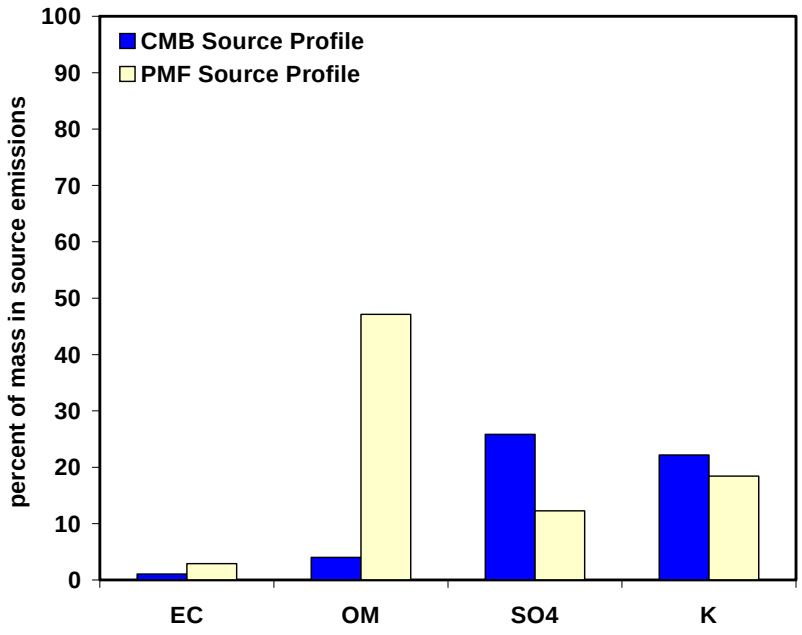


Figure 6-4. CMB and PMF saw mill profile comparison.

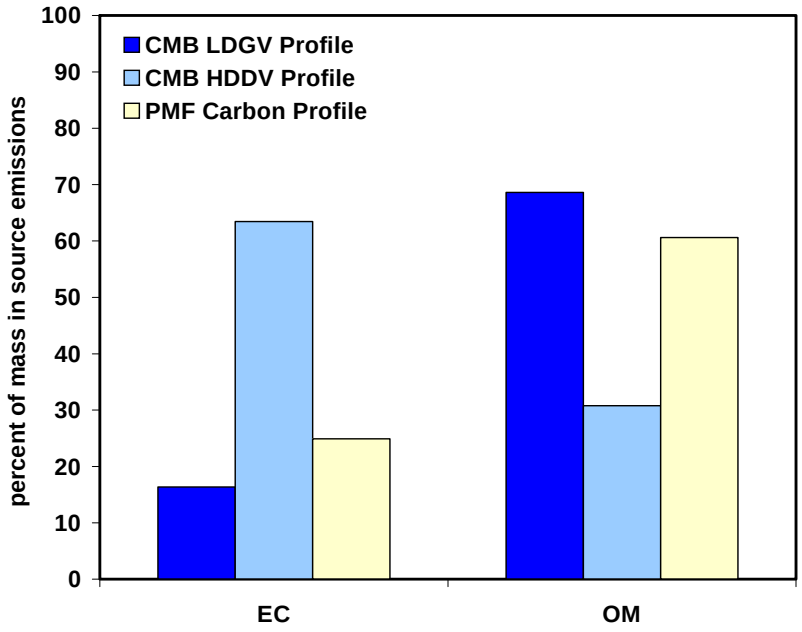


Figure 6-5. Comparison of CMB LDGV and HDDV profiles to the PMF carbon profile. PMF profile percents are similar to those in the CMB LDGV profile.

6.2 COMPARISON OF MASS APPORTIONED

Source contributions determined from the two source apportionment methods were compared on a day-to-day basis as shown in **Figures 6-6 through 6-10**. Comparisons are shown for the soil, pulp mill, burning, saw mill, and motor vehicles sources. As shown in Figure 6-6, soil source contributions with an R^2 value of approximately 0.7 showed a correlation. However, the ratio of mass apportioned to the soil source between CMB and PMF was approximately 0.4 instead of the expected ratio of 1. More mass was apportioned to the soil source in the PMF analysis than in the CMB analysis. The same observation was seen in the pulp mill source contribution comparison (Figure 6-7). The ratio of mass apportioned was approximately 0.8 with more mass apportioned in the PMF analysis. Although PMF mass apportionment was slightly higher, the correlation is very strong between the two methods (R^2=0.97) and the ratio is close to 1. The correlation between burning source contributions is strong with an R^2 value of 0.94 and a ratio close to 1 (Figure 6-8**)**. A strong correlation was not seen between daily saw mill contributions (Figure 6-9). As seen with other sources, more mass was apportioned to saw mills in the PMF analysis than the CMB analysis. For motor vehicles, the source contributions from the PMF carbon factor were compared with the sum of the LDGV and HDDV contributions determined from CMB (Figure 6-10). The relationship is scattered and, in general, the sum of the contributions from LDGV and HDDV was greater than the contributions from the PMF carbon factor. Although the relationships between daily source contributions were scattered for some of the sources, the relationships were strong for those that were identified as important contributors to $PM_{2.5}$ in the individual source apportionment analyses including pulp mills and burning.

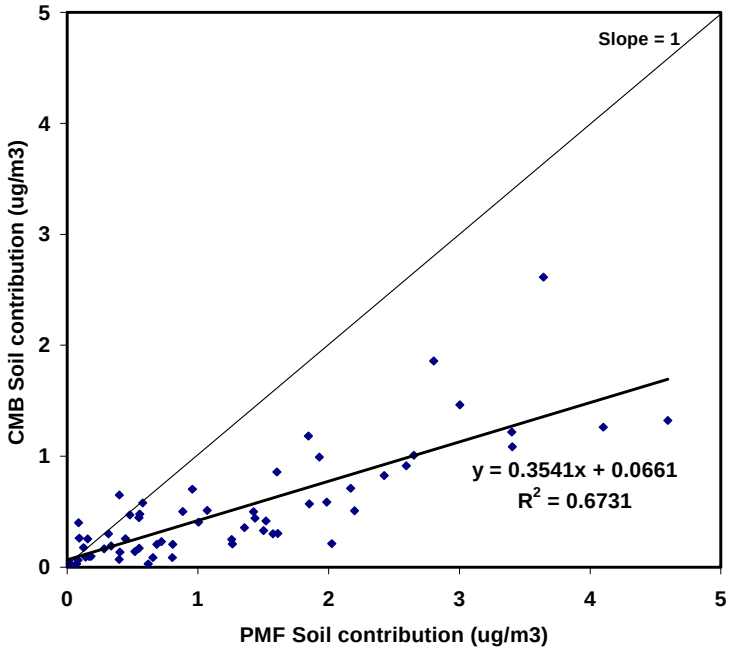


Figure 6-6. Comparison of PMF and CMB mass apportioned to the soil source on a day-to-day basis.

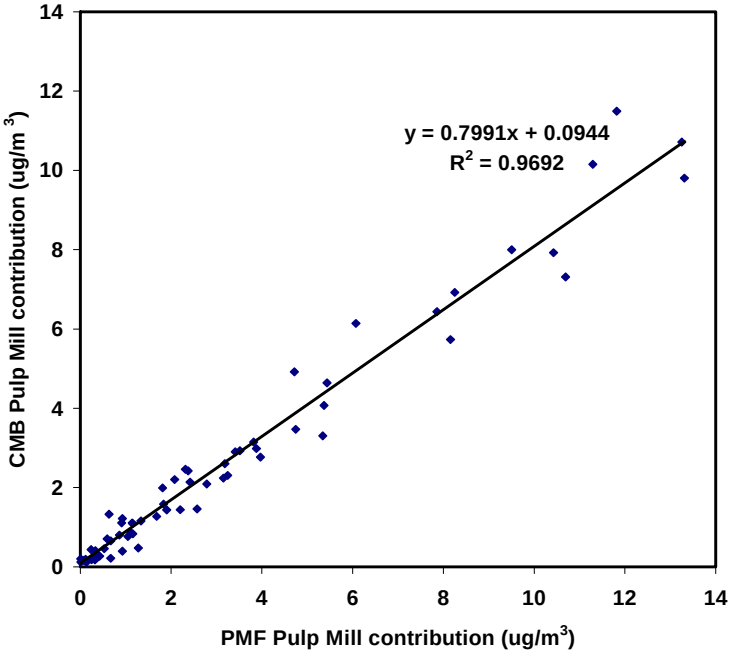


Figure 6-7. Comparison of PMF and CMB mass apportioned to the pulp mill source on a day-to-day basis.

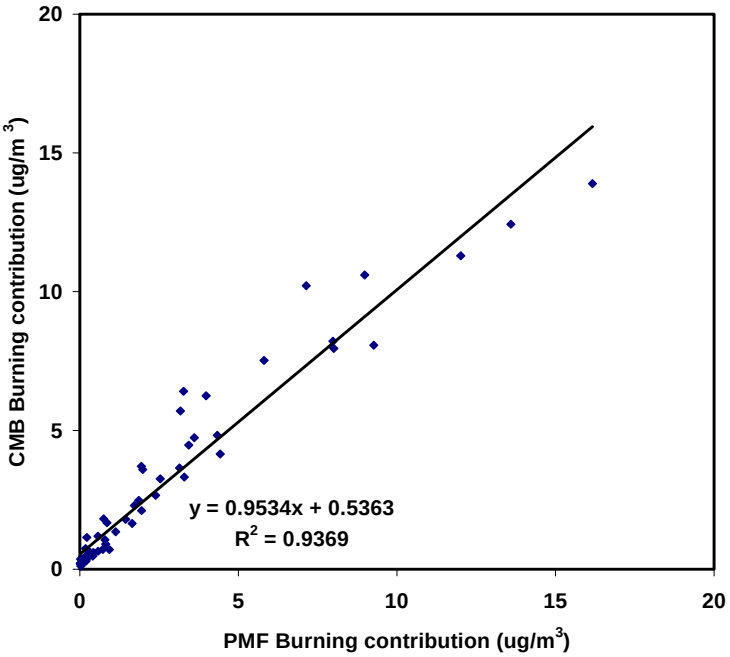


Figure 6-8. Comparison of PMF and CMB mass apportioned to the burning source on a day-to-day basis.

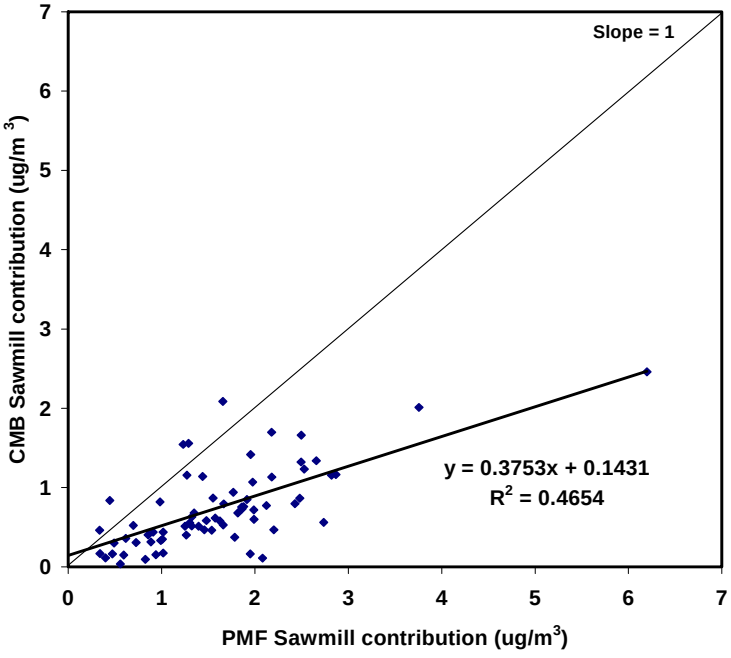


Figure 6-9. Comparison of PMF and CMB mass apportioned to the saw mill source on a day-to-day basis.

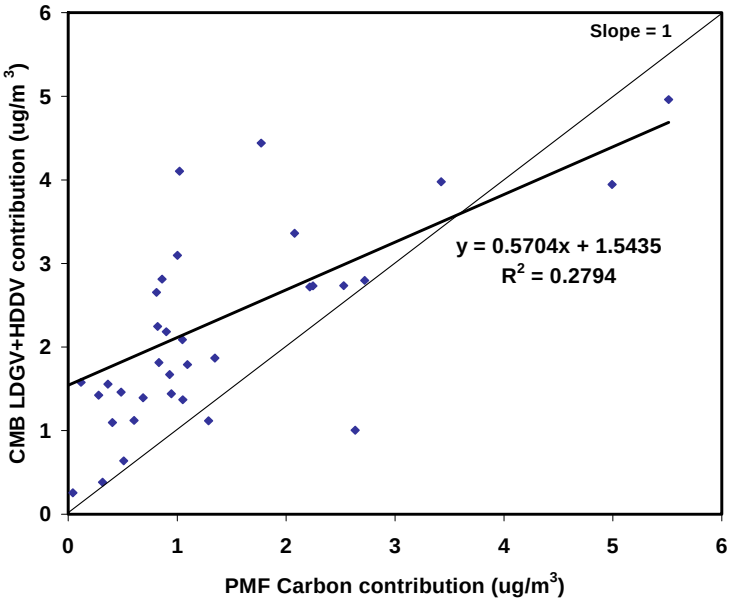


Figure 6-10. Comparison of PMF and CMB mass apportioned to the motor vehicle source on a day-to-day basis. The sum of mass apportioned to the LDGV and HDDV sources are shown for CMB.

Source contributions were also compared between the two methods on an average basis. Results were averaged over all data, winter data, summer data, and the highest $PM_{2.5}$ mass days (20%). Although there was scatter observed in the daily mass comparisons, good agreement between the two methods was seen on an average basis as shown in **Figure 6-11**. The total average mass is slightly different between the two methods because the data sets used were not exactly the same. Results of the comparison are summarized in **Table 6-1**.

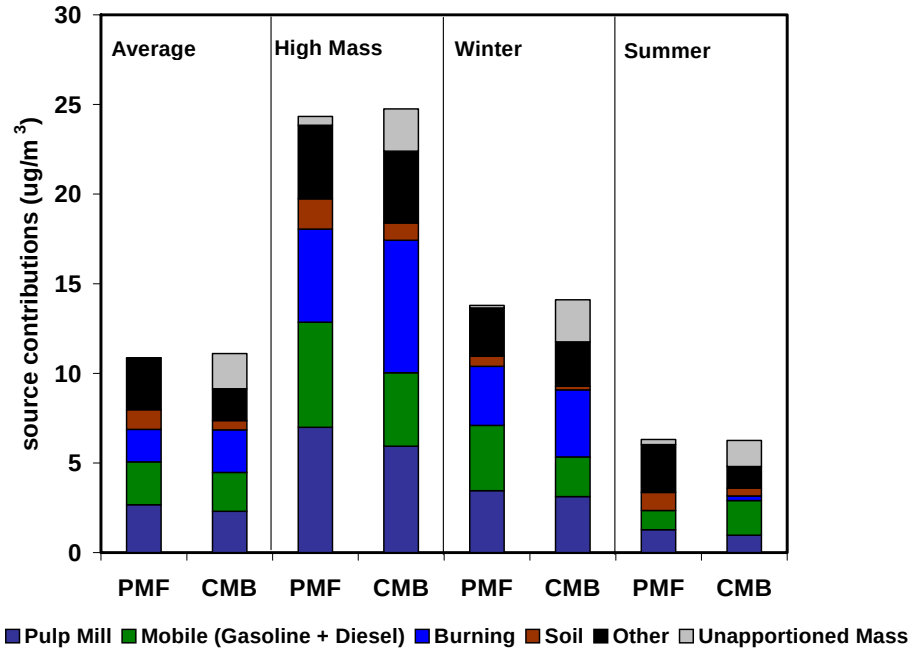


Figure 6-11. Comparison of PMF and CMB source contributions averaged over all data (average), the top 20% $PM_{2.5}$ mass days (high mass), winter days (winter), and summer days (summer).

Table 6-1. Comparison of PMF and CMB source contribution percents averaged over all data (average), the top 20% $PM_{2.5}$ mass days (high mass), winter days (winter), and summer days (summer).

	Average		High Mass Days		Winter		Summer	
	CMB	PMF	CMB	PMF	CMB	PMF	CMB	PMF
Pulp Mill	25	24	27	29	26	25	20	21
Burning	26	18	33	22	32	24	6	0
Carbon (HDDV+LDGV +OtherOC)	24	22	18	24	19	26	40	18
Soil	5	10	4	7	2	4	9	17
Other	20	26	18	18	21	20	25	44

7. SUMMARY

$PM_{2.5}$ has been monitored in Prince George since 1994, and the annual average $PM_{2.5}$ concentrations are the highest in the province. A large monitoring, modeling, and data analysis effort is under way to better understand the sources of $PM_{2.5}$ in the area. This report summarizes the application of two types of source apportionment tools, CMB and PMF, to the Prince George speciated $PM_{2.5}$ data. Review of the emission sources in the area indicated that the most important PM sources were likely to be emissions from the pulp mill, wood burning, and mobile sources. To better quantify wood burning, special measurements were made of levoglucosan, a unique marker. Assessment of the ambient data showed the following:

- Sulfate and OM are the largest contributors to $PM_{2.5}$ year round.
- Both sulfate and OM are significant on the highest $PM_{2.5}$ concentration days, which mostly occur in the winter; two high concentration events occurred in May 2005 when levoglucosan data suggested influence from fires.
- Even though $PM_{2.5}$ concentrations are high in the winter, nitrate concentrations are small and sulfate can be high. Sulfate is mostly local in origin.
- Levoglucosan and OM correlate at high concentrations, suggesting that wood burning is a large contributor to OM (and thus PM).
- Soil elements (silicon, aluminum, iron, calcium) and road salt species (chlorine) account for < 10% of the mass.
- Non-soil calcium is evident and is likely from road salt as well as lime associated with pulp mill operations.

The Prince George air shed is well-suited for receptor modeling/source apportionment because the number of significant sources is relatively limited; the contribution from regional transport of pollutants is relatively small; sources are spread out spatially and have different signatures/unique tracers; and data collected included these tracers (especially levoglucosan). Both models predicted total mass well and both high and low mass days were modeled well (**Figure 7-1**). Results are shown in Figure 6-11 for average, high mass, winter, and summer days. Both models gave consistent results for the largest contributors to $PM_{2.5}$ mass. The CMB and PMF average apportionment of pulp mill emissions, mobile sources, and wood burning combined was 77% and 75% of the mass during the winter and 78% and 75 % of mass during days with the highest 20% $PM_{2.5}$ mass.

Comparison of profiles, model sensitivity tests, wind trajectory analyses, and exploration of continuous data were also conducted to help increase the certainty in our results. In summary,

- Pulp mill emissions, mobile sources, and wood burning are the major contributors to $PM_{2.5}$, both for days on which $PM_{2.5}$ concentrations are highest and on average.
- Prior measures to reduce PM from dust and salt appear to have been effective, as dust and salt are small contributors to PM.

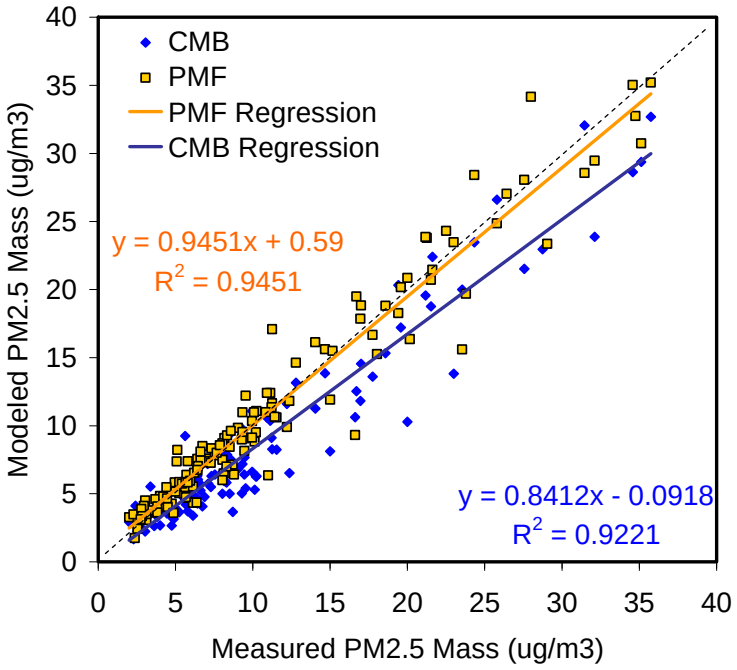


Figure 7-1. Modeled versus measured $PM_{2.5}$ mass from CMB and PMF analysis.

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APPENDIX

SUPPLEMENTARY RESULTS

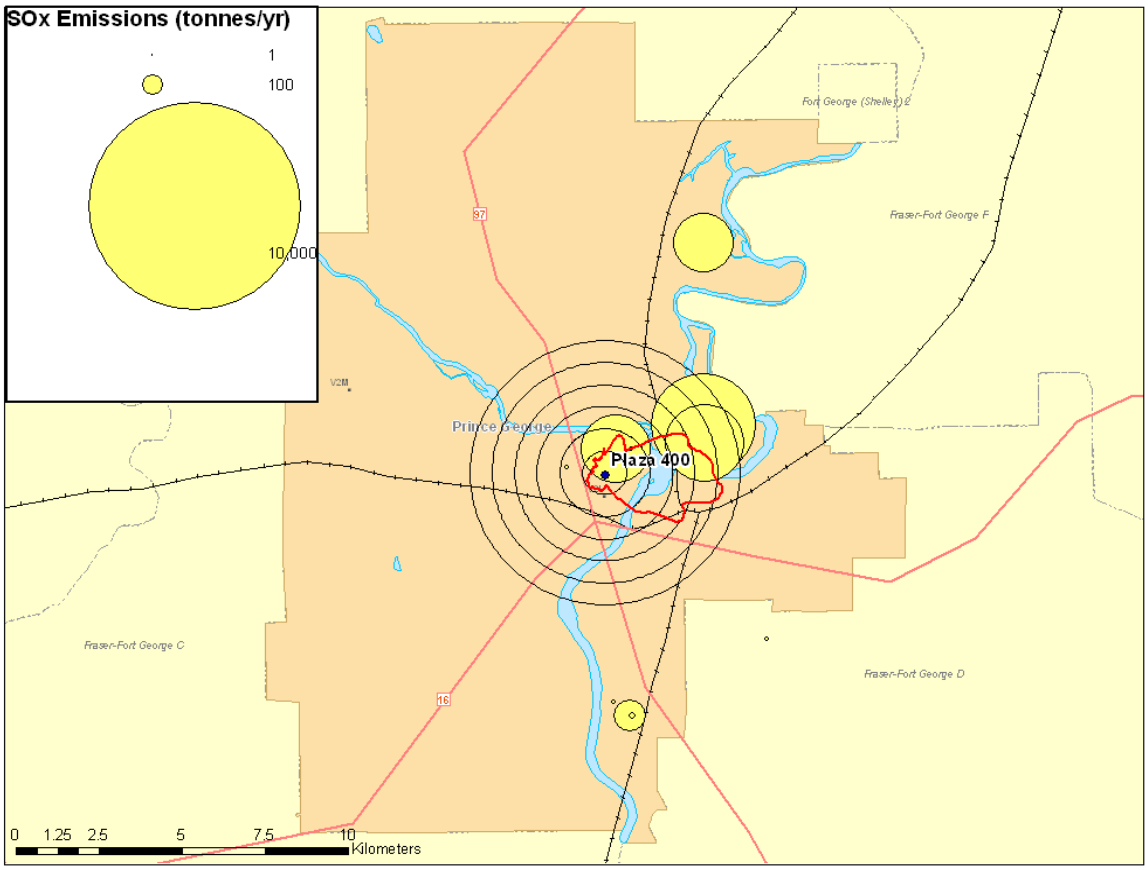


Figure A-1. Results of the non-parametric regression analysis with wind direction and SO_2 data. SO_x point sources are also shown. Each concentric circle represents kernel average of 4 ppb.

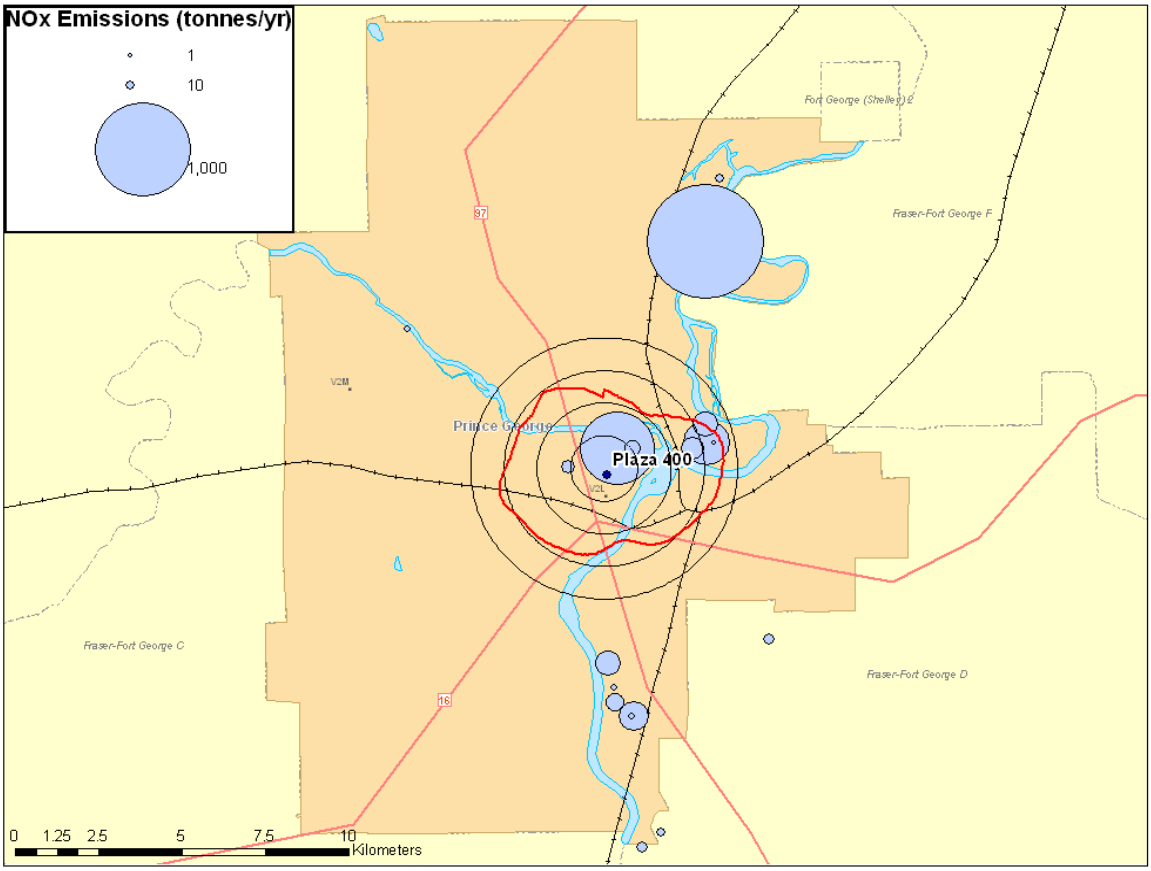


Figure A-2. Results of the non-parametric regression analysis with wind direction and NO_2 data. NO_x point sources are also shown. Each concentric circle represents kernel average of 10 ppb.

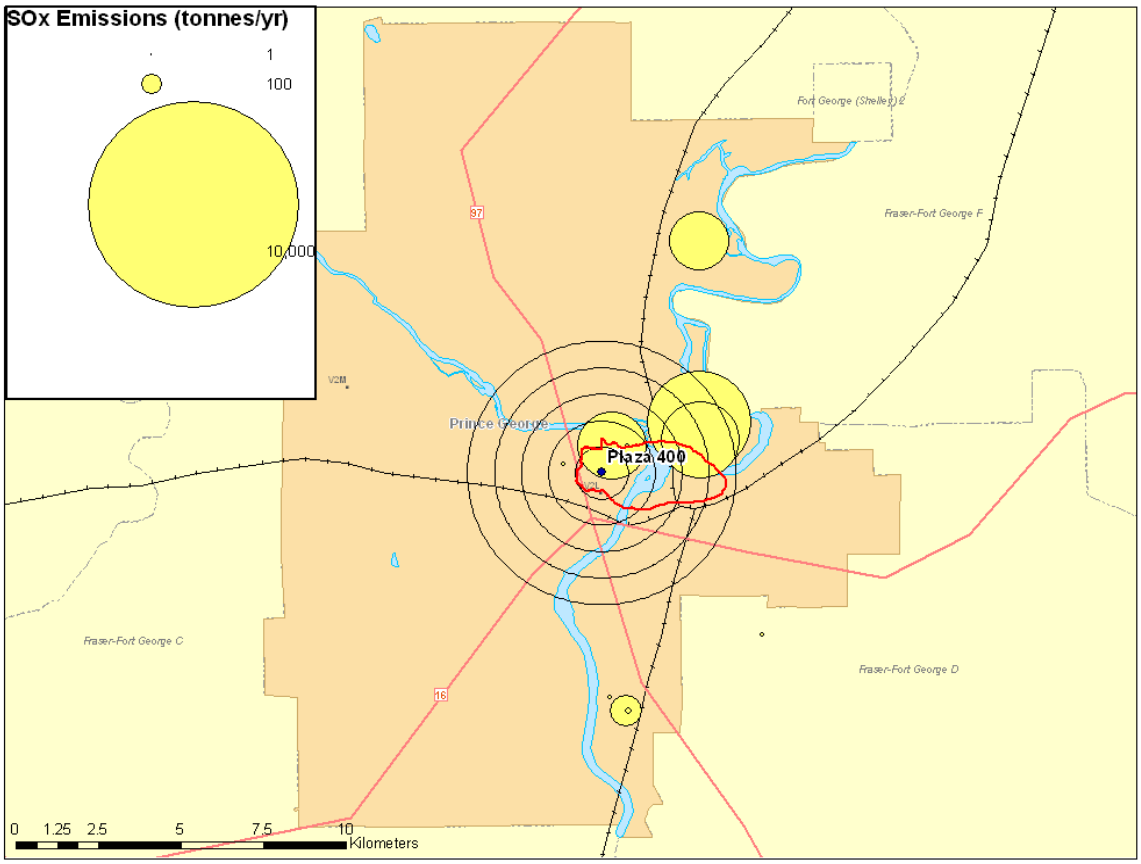


Figure A-3. Results of the non-parametric regression analysis with wind direction and H_2S data. Each concentric circle represents kernel average of 1 ppb. SO_x point sources are also shown.

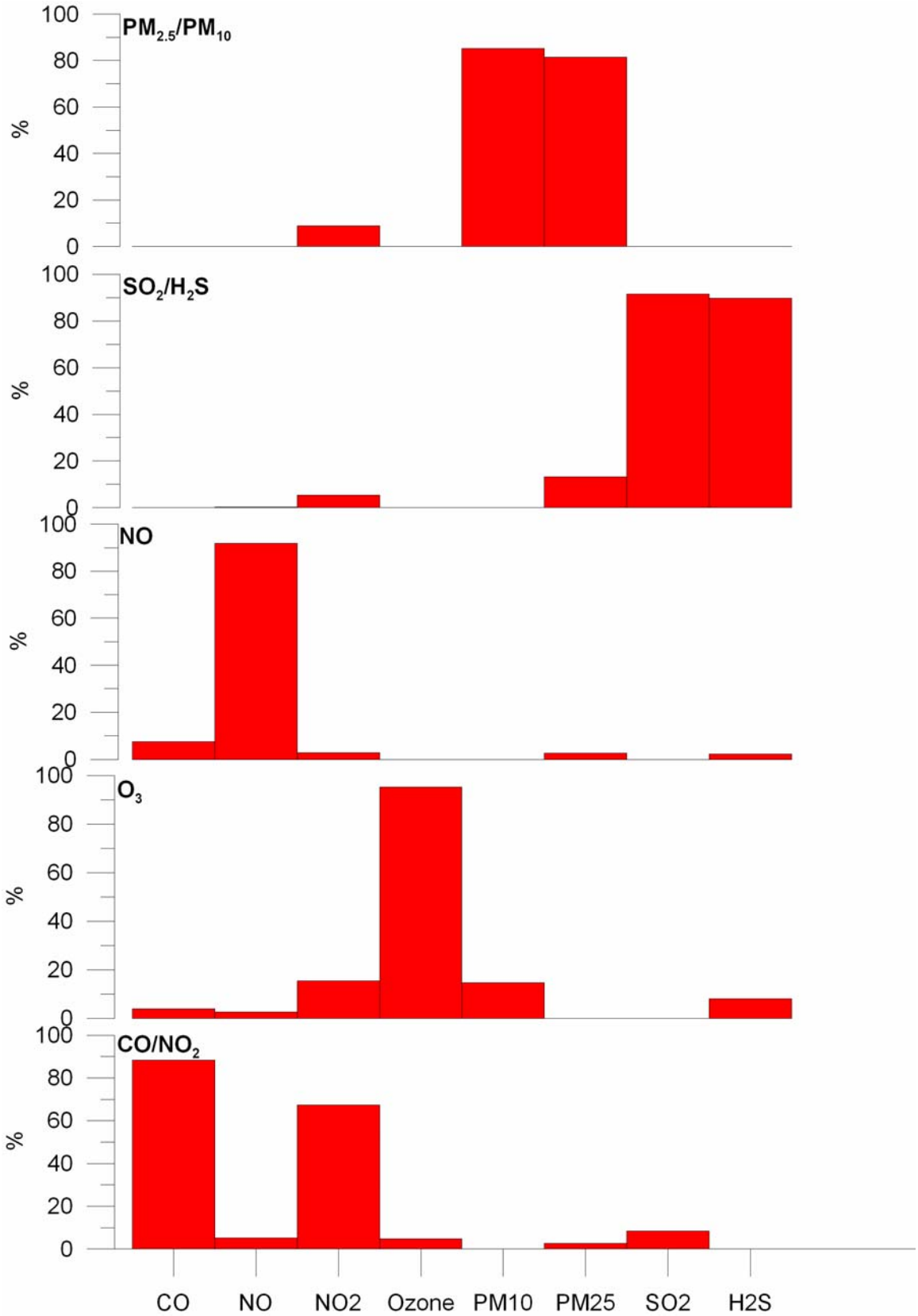


Figure A-4. PMF factor profiles using the continuous data at Plaza site.

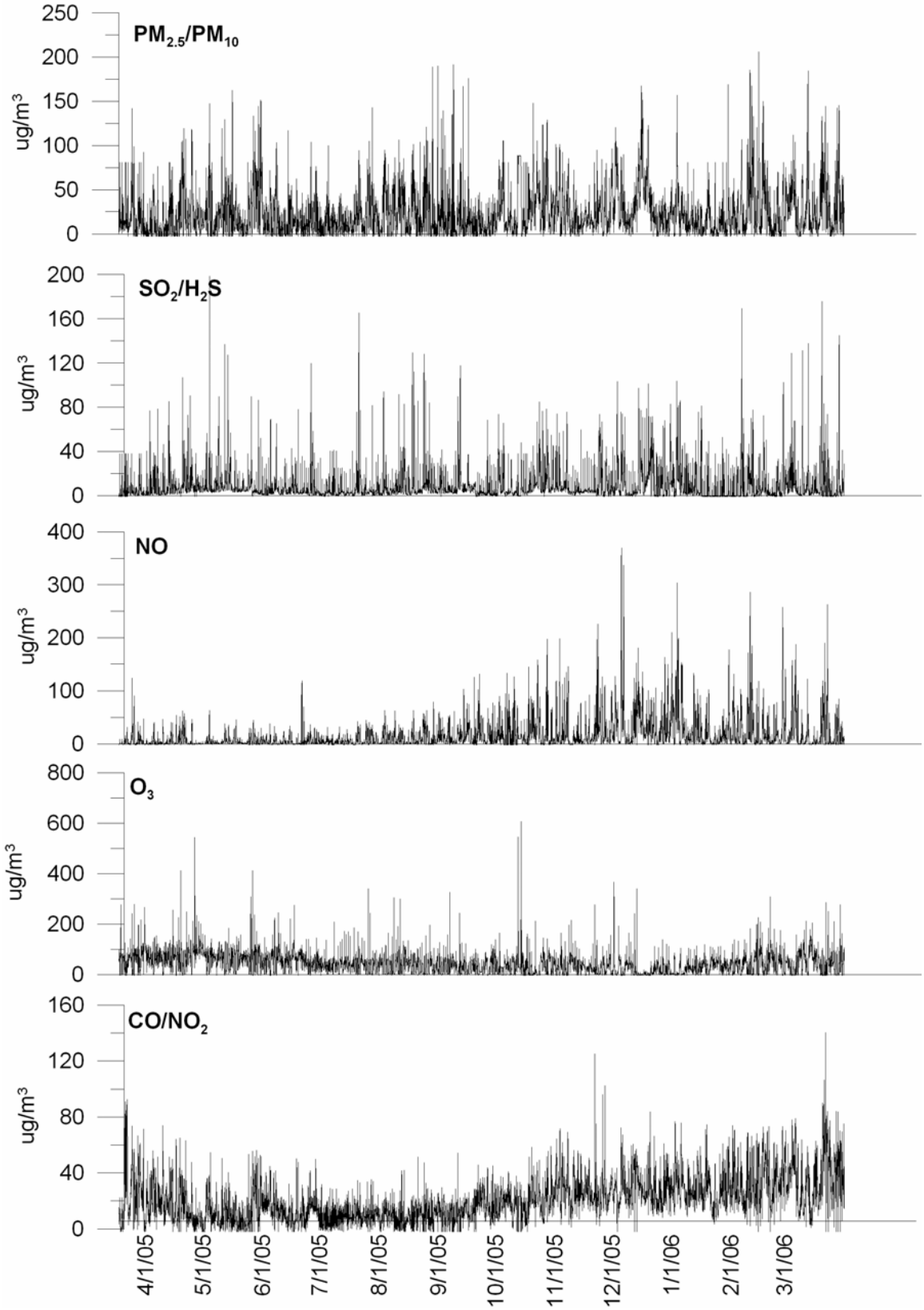


Figure A-5. Time series of PMF factors using the continuous data at Plaza site.