SOURCE APPORTIONMENT BY CHEMICAL MASS BALANCE TECHNIQUE OF PM_{10} SOURCES IN EAGLE RIVER AND JUNEAU, ALASKA

FINAL REPORT

Prepared for:

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EXECUTIVE SUMMARY

Eagle River and Juneau, Alaska are non-attainment for the new PM_{10} standard. The objective of this study was to quantitatively apportion the PM_{10} levels in these two airsheds to provide the basis for developing effective state implementation plans. Of particular importance was apportionment of the subcategories of the general crustal dust category which has previously been shown to be responsible for most of the PM_{10}.

The approach used chemical mass balance receptor modeling of high volume PM_{10} quartz fiber filters selected by the Alaska Department of Environmental Conservation based on high PM_{10} days. Previous attempts to apportion these sources with these filters have not provided adequate source resolvability or quantitative accuracy. In this study, high purity quartz fiber filters were used and improved X-ray fluorescence analysis methods to measure elements from Al to Pb, except for Si. In addition, water soluble trace metals were measured and the organic and elemental carbon determined. Of particular importance to resolving and quantifying the impacts of wood smoke was water soluble K. These advances in analysis methods provided the necessary capabilities to accomplish this study's objectives.

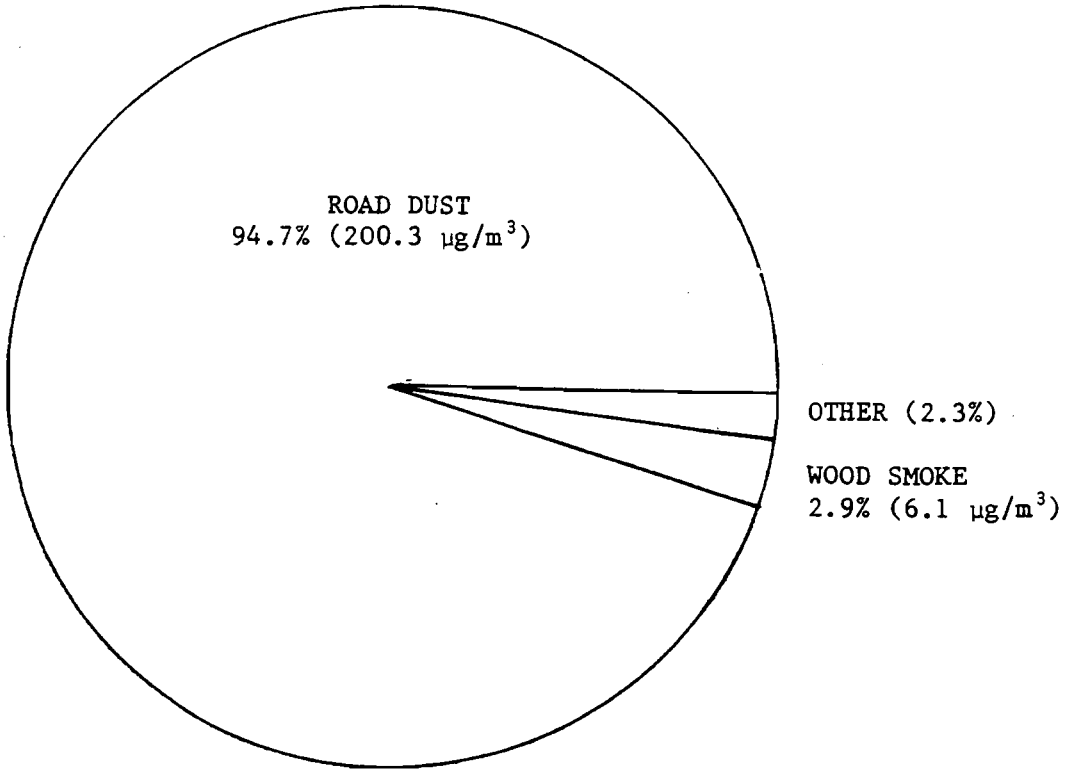
Excellent quality chemical mass balance fits were obtained with all filter samples. Chi square values were all less than 1.5, and all but a few were less than 1.0. R-square values ranged from 0.96 to 1.0 and averaged 0.99. The calculated to measured elemental ratios for the key fitting species were usually within one standard deviation of 1.0, and the residuals for these species were almost always less than two standard deviations. The consistency of the CMB and meteorological data provides a high level of quality assurance and confidence in the final results.

The results of this study are summarized with the pie charts illustrated in Figures A and B. As expected, crustal dust was the largest source of PM_{10} in both Eagle River and Juneau on selected days with high PM_{10} levels. The average spring and fall crustal dust contributions to PM_{10} levels on selected high PM_{10} days was 94.7%. Wind blown river sediment was a minor (1.0%) source of PM_{10} in Eagle River and was resolved only on one day, the day with the highest wind speeds at the Palmer meteorological station. The highest PM_{10} days occurred during calm wind episodes in October. Wood smoke was responsible for only 1.4% (2.1 $\mu g/m^3$) on windy spring days in Eagle River, and 2.9% (6.1 $\mu g/m^3$) on calm fall days.

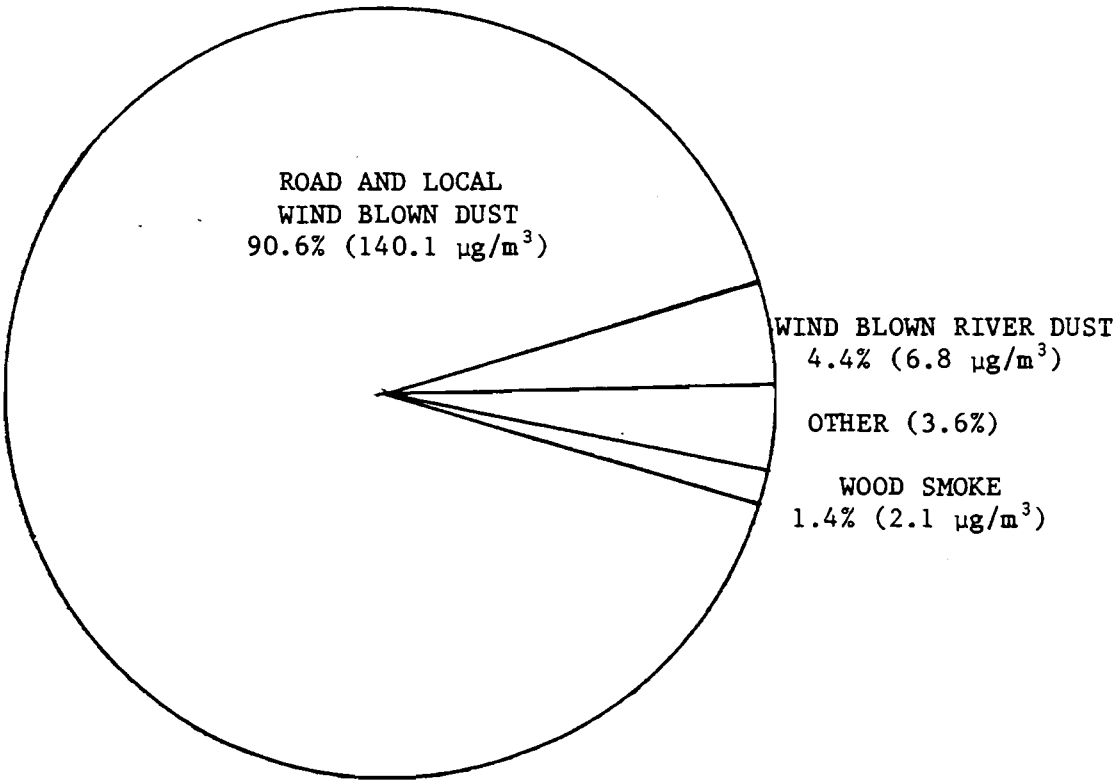
In Juneau, crustal dust was responsible for 69.6% (102.2 $\mu g/m^3$) of the PM_{10}. Essentially, all of this was apportioned to road dust based on meteorology. Wood smoke contributed 13.8% (20.3 $\mu g/m^3$) of the Juneau PM_{10} and varied inversely with the wind speed. The use of water soluble K greatly increased the resolvability of this source and the level of confidence in its contribution.

Figure A

PM_{10} SOURCE CONTRIBUTIONS
(Eagle River)



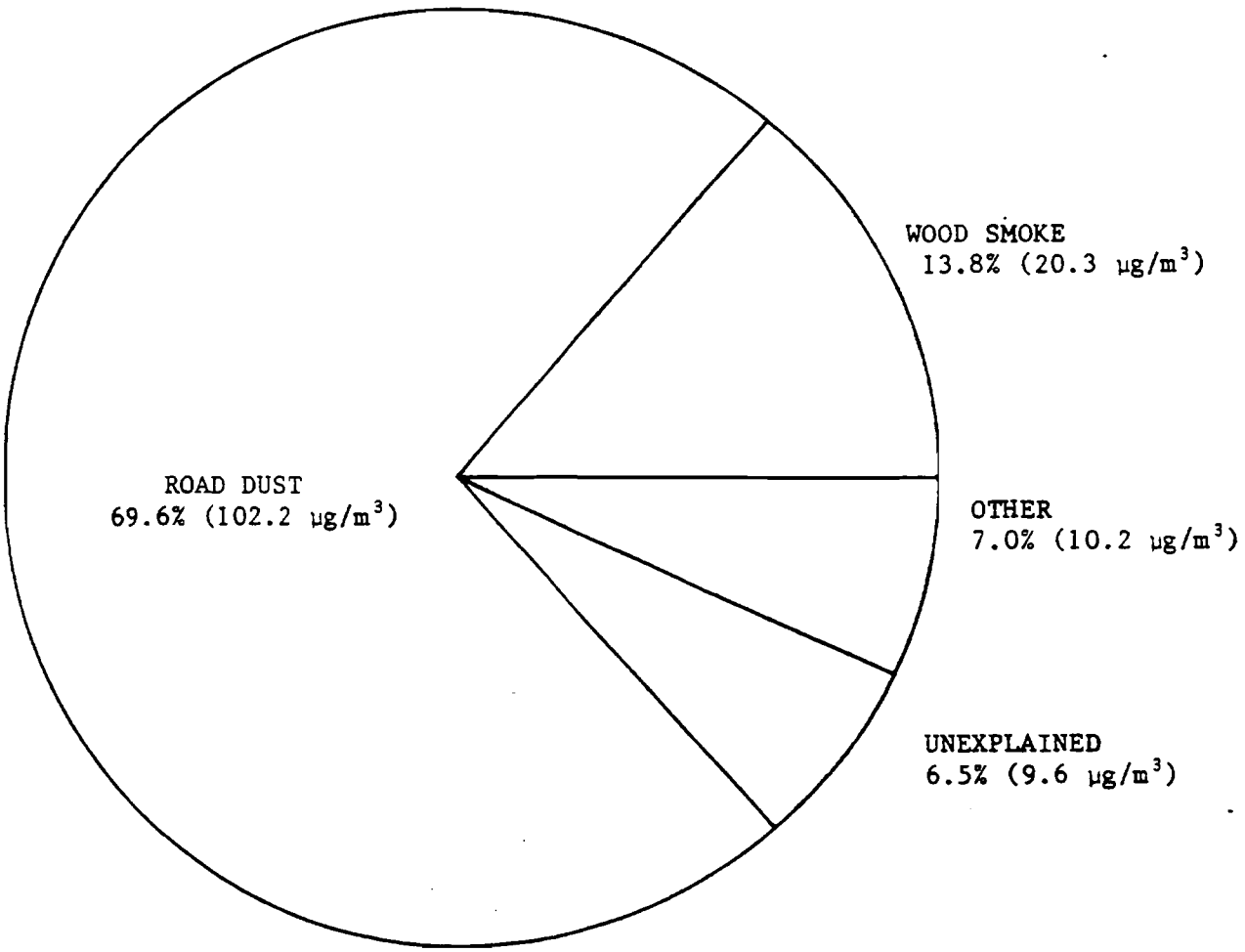
Fall



Spring

Figure B

PM_{10} SOURCE CONTRIBUTIONS
(Juneau)



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1.0 INTRODUCTION

Eagle River and Juneau, Alaska are not in attainment of the new PM_{10} particulate standard. Development of effective control strategies requires an accurate apportionment of the major particulate source's contribution to PM_{10} levels. Previous receptor modeling studies have shown that crustal dust types of sources are the primary problems in Eagle River[1], while wood smoke, transportation, and marine aerosol sources, in addition to the crustal dust, can all be significant contributors in Juneau.

The primary apportionment objective in the Eagle River airshed is to quantify the major crustal dust subcategories. While this is also important in Juneau, resolving the impacts from the other sources from possible interferences is more important because of their expected larger relative contributions.

There are eight possible major crustal source subcategories in the Eagle River airshed:

- Paved freeway road dust
- Paved local streets
- Unpaved roads
- Paved parking lots
- Unpaved parking lots
- River sediment
- Gravel
- Exposed unvegetated soils.

A previous receptor model feasibility study concluded that these eight sources could not be resolved using just chemical mass balance methods[2]. The results did indicate, however, that there was a possibility that the river sediment could be resolved from the other

sources under ideal conditions. In the Juneau airshed, the main source resolution problems were associated with resolving such sources as wood smoke, distillate oil, and motor vehicles.

The approach taken in this study was to use chemical mass balance receptor modeling to apportion the major source categories and subcategories where possible, and then use meteorological regime stratification methods to further resolve the impacts of these major categories.

2.0 EXPERIMENTAL

2.1 Source Apportionment Methodology

The CMB receptor model is based on the conservation of relative aerosol chemistry from the time a chemical species is emitted from its source to the time it is measured at a receptor. That is, if p sources are each emitting M_j mass of particles, then

$$m = \sum_{j=1}^{p} M_j \tag{1}$$

where m is the total particulate mass collected on a filter at a receptor site. This assumes the mass deposited on a filter is a linear combination of the mass contributed from each of the sources.

The mass of a specific chemical species, m_i, is given by

$$m_i = \sum_{j=1}^{p} M_{ij} = \sum_{j=1}^{p} F'_{ij} M_j \tag{2}$$

where M_{ij} is the mass of element i from source j, and F'_{ij} is the fraction of chemical species i of the mass from source j as collected at the receptor. It is usually assumed that

$$F_{ij} = F'_{ij} \tag{3}$$

where F_{ij} is the fraction of chemical species i emitted by source j as measured at the source; that is, the relative fraction of chemical species i of the source mass at the receptor is assumed to be the same as the relative fraction of i of the source mass at the source. The degree of validity in this assumption depends on the chemical and physical properties of the species and on its potential for atmospheric, in-transit modifications such as condensation, volatilization, chemical reactions, sedimentation, etc.

Accepting equation (3) as valid and dividing both sides of equation (2) by the total mass of the deposit collected at the receptor site, it follows that

$$\frac{m_i}{m} = \sum_{j=1}^{p} F_{ij} \frac{M_j}{m} \tag{4}$$

or,

$$C_i = \sum_{j=1}^{p} F_{ij} S_j \tag{5}$$

where C_i is the concentration of the chemical component i as measured at the receptor and S_j is the source contribution (i.e., ratio of the mass contributed from source j to the total mass collected at the receptor site). In practice, it is S_j, the fraction of particulate pollution measured at a receptor due to source j, which is of primary interest in CMB calculations.

If the C_i and the F_{ij} at the receptor for all p of the source types suspected of affecting the receptor are known, and if $p < n$ (n = number of chemical species quantified), a set of n simultaneous equations exists from which the source contribution S_j for each source may be calculated by least squares methods.

NEA used its own quantitative source apportionment system (QSAS III) to perform initial CMB calculations based on an EVLS regression analysis. QSAS III also includes a number of graphics

routines which aid in the fitting process and in the presentation of results. The CMB calculations were then repeated with Version 6.0 of the EPA CMB program. The EPA-CMB results are presented in Appendix B (1,2).

Implementation of a CMB analysis requires the formation of both ambient and source elemental data sets. The development of these data sets for this study are discussed in detail below.

2.2 Resuspensions

Crustal dust samples collected by the Alaska Department of Environmental Conservation (ADEC) from the Juneau airshed were aerosolized at NEA's laboratory facilities using a moving wedge dust generator. This dust was diluted with filtered air and directed into a closed chamber from which a PM_{10} sample was collected on quartz fiber filters using an Andersen 321B size selective inlet. This sample was weighed to determine the deposit mass per square centimeter, after which a 47 mm diameter disk was removed for subsequent analysis.

Similar samples were collected and aerosolized from the Eagle River area as part of the earlier feasibility study[2].

2.3 X-Ray Fluorescence Analysis

Each filter disk was analyzed nondestructively by X-ray fluorescence (XRF) three times using different excitation conditions to optimize the sensitivity for specific elements as indicated below:

Al,P,Fe	Mo anode, no filter, 15KV, 200 μamps
S,Cl,K,Ca, Ti,V,Cr,Mn,Fe	W anode, Cu filter, 35KV, 200 μamps
Fe,Ni,Cu,Zn Ga,As,Se,Br Rb,Sr,Ba,La Hg,Pb	Mo anode, Mo filter, 50KV, 200 μamps

An ORTEC TEFA III analyzer was used for these determinations. A quality control filter and blank was analyzed with each batch of ten (10) filters. The results for these analyses, as well as NBS standards, are listed in Appendix A.

2.4 Water Soluble Species

The water soluble species were extracted from the filters with 20 ml of deionized water over a twenty-four hour period with agitation. A small aliquot of the filtered solution was deposited in the center of a filter and analyzed by X-ray fluorescence similar to the method used for air particulates.

2.5 Carbon Species Analysis

Organic, elemental, and carbonate carbon (OC,EC,CC) were determined on each quartz filter using a combustion, flame ionization method first developed at the Oregon Graduate Center[3]. The instrument corrects for pyrolysis of organic carbon by using laser reflectance to measure the amount of elemental carbon formed during the vaporization of organic carbon species.

2.6 Ambient Profile Development

High volume PM_{10} samples collected on high purity quartz fiber filters in Eagle River and Juneau were selected by ADEC from samples collected in 1985, 1986, and 1987. Samples collected in Juneau were from two sites: Super Bear Shopping Center (SBA), a commercial area, and the Floyd Dryden School (FDA), a residential area.

The days selected, the PM_{10} levels, and the meteorological characteristics on each of these days are summarized in Tables 1 and 2. All of the Juneau samples were from 1986, with five of the six samples from a three day period in February. Of the fourteen samples selected from Eagle River, four of them were collected in the spring of 1986, while the rest were from pollution episodes in late October of 1985, 1986, and 1987.

Table 1

SUMMARY OF METEOROLOGICAL CHARACTERISTICS
DURING SELECTED JUNEAU SAMPLING DAYS

Date	Site	PM_{10} $\mu g/m^3$	Temp °F	Precp in.*	Juneau WS	Juneau WD	Floyd Dryden WS	Floyd Dryden WD
2/19/86	FDA	188	10	0(0)	12	E	5	SE
2/22/86	FDA	240	20	0(T)	4	E	3	E
2/19/86	SBA	119	10	0(0)	12	E	5	SE
2/20/86	SBA	108	15	0(0)	10	E	2	E
2/22/86	SBA	121	20	0(T)	4	E	3	SE
10/31/86	SBA	106	30	T(0)	.5	NNW	NA	NA

*The value in parenthesis is the precipitation during the preceding day.

Table 2
SUMMARY OF METEOROLOGICAL CHARACTERISTICS
DURING SELECTED EAGLE RIVER SAMPLING DAYS

	PM10	TEMP[a]	PRECP.[b]	ANCHORAGE[c]		FT. RICHARDSON[d]		PALMER FSS[e]		TEMP.[h]
DATE	μg/m³	°F	in.	WS[f]	WD[g]	WS (Range)[f]	WD[g]	WS (Range)[f]	WD[g]	°F
10/28/85	219					2 (0-5)	NE	4 (0-7)	N/S	19
10/29/85	143					0 (0-2)	--	4 (0-7)	N/S	21
10/30/85	154					2 (0-6)	--	3 (0-6)	N/S	21
2/18/86	214	18	0(0)	16	NNE	5 (0-13)	N/NE	40 (30-50)	NE	26
4/19/86	126	37	0(0)	11	N	7 (0-30)	NE	20 (5-30)	NE	40
4/30/86	166	43	0(0)	10	SE	5 (0-18)	SE	10 (5-20)	SE	58
5/16/86	112	47	0(0)	9.5	E	6 (0-20)	V	15 (5-25)	V	57
10/27/86	137	33	0(0)	3.4	SSE	0 (0-3)	--	6 (3-9)	S/SE	34
10/28/86	236	31	0(0)	4.0	NNE	0 (0-3)	--	3 (0-6)	SE	39
10/29/86	317	27	0(0)	2.7	N	0 (0-3)	--	4 (0-7)	SE	37
10/30/86	334	23	0(0)	2.0	NE	0 (0-2)	--	2 (0-7)	N/S	33
10/29/87	132					0 (0-1)	--	2 (0-6)	N/S	32
10/30/87	219					0 (0-2)	--	3 (0-9)	V	32
10/31/87	106					2 (0-13)	N	4 (0-9)	V	26

a. Anchorage weather service, average
b. Value in parenthesis is precipitation the preceeding day
c. Anchorage airport located about 15 miles southwest of Eagle River
d. Fort Richardson located about 8 miles southwest of Eagle River
e. Palmer U.S. Forest Service Station located about 20 miles notheast of Eagle River; 8-16 hr averages
f. Wind speed, miles per hour
g. Wind direction, wind coming from the indicated direction
h. Approximate temperature from two readings

2.7 Source Profile Development

Source profiles for this study were developed during the previous feasibility study[2], the EPA[4], and NEA[5] source profile libraries, and resuspension of new dust samples collected in the Juneau airshed by the ADEC as part of this study. The water soluble components of the dust sources were determined from the resuspended PM_{10} samples collected as part of this study and the previous feasibility study. The water soluble K from wood smoke was taken from Reference 6. All of the marine aerosol species were assumed to be water soluble. The water soluble components in the other source emissions were estimated.

3.0 RESULTS AND DISCUSSION

3.1 Meteorology

The meteorological conditions on the days selected for analysis are summarized in Tables 1 and 2. The temperature and precipitation values are from U.S. Weather Service reports from the Juneau and Anchorage airports. The wind speed and direction values in Juneau are from the airport and Floyd Dryden monitoring site. The wind characteristics in Eagle River are based on readings at the Anchorage airport about fifteen miles southwest of Eagle River, Fort Richardson located about eight miles southwest of Eagle River, and the Palmer Forest Service Station located about twenty miles northeast of Eagle River. Although measurements at these sites are not likely to be the same as would be recorded in Eagle River, they provide an indication of the wind characteristics in Eagle River since these sites are located on both sides of Eagle River.

The filters selected in the Juneau airshed fall into three meteorological-site regimes. One regime is composed of dry, low wind speeds from the east or southeast at the Floyd Dryden site. Another

regime consists of dry days of moderate wind speeds from the east at the Floyd Dryden site. The third regime consists of calm conditions at the Floyd Dryden monitoring site.

There was substantial snow cover in Juneau throughout most of the month of February, 1986. The average temperature during the first part of the month was in the range from 20°F to 30°F, but dropped to about 15°F on February 17, 1986, and didn't increase until after February 24, 1986.

In Eagle River, the selected days fall into two major regimes: one consists of dry, calm October days, and the other dry, windy spring days. The spring days might be further subdivided into days when the winds were predominantly from the north or northeast, and when they were mostly from the south or southeast.

In general, the winds were highest at the Palmer site and lowest at the Fort Richardson site. The dominant wind direction was similar at all sites on windy days, but quite variable on calm days.

There was a trace of snow cover in Anchorage on February 18, 1986, and definite snow cover in April which was gone by April 26, 1986. There was no snow cover in May.

3.2 Ambient Particulate Mass Concentrations

The PM_{10} concentrations are also summarized in Tables 1 and 2. The selected Juneau PM_{10} levels ranged from a low of 106 $\mu g/m^3$ on October 31, 1986 at the Super Bear site, to a high of 240 $\mu g/m^3$ on February 22, 1986 at the Floyd Dryden site. The PM_{10} level at the Super Bear site on the 22nd was only 121 $\mu g/m^3$. The second highest level of 188 $\mu g/m^3$ was also measured at the Floyd Dryden site.

The particulate levels in Eagle River ranged from a low of 106 $\mu g/m^3$ on October 31, 1987, to a high of 334 $\mu g/m^3$ on

October 30, 1986. In Eagle River, the five highest PM_{10} levels were recorded in October during relatively calm wind conditions.

3.3 Ambient Chemistry

The chemical composition of the ambient particulates are summarized in Appendix B which lists the concentration of the species used in the CMB calculations. The number of species that can be used in the CMB calculations is limited to twenty-one. Thus, the species listed are primarily the most important fitting species. All of the species measured by XRF are listed in Appendix C. The water soluble species not listed in Appendix B were below detection limits.

Organic carbon was the most abundant species measured at all locations, and accounted for about 5 to about 25% of the mass. The next two most abundant species were Fe and Al which accounted for almost as much of the mass as the organic carbon. The elemental concentrations reported for the ambient samples have been corrected for deposit mass absorption as well as the normal interferences. The corrections used are identical to those used for the resuspended dust samples so as to minimize any systematic bias between the ambient and source profiles. They are not the same, however, as used for Teflon filters in the earlier feasibility study.

3.4 Chemical Composition of Source Profiles

The chemical characteristics of each source profile used in the CMB fitting are listed in Appendix D and summarized in Table 3. The percent composition listed for these species are generally only relevant to this study in which these analytical methods were used with quartz fiber filters. The primary objective in this case was to minimize differences between the ambient and source profiles. Thus, data corrections were kept to a minimum to avoid systematic bias. As a result, all profiles are based on the source profiles developed from the quartz fiber filters and are applicable only to other quartz fiber filters without further adjustments.

Table 3

SOURCE PROFILE SUMMARY TABLE
(Percent)

Element[a]	Vehicle Exhaust	Residual Oil	Distillate Oil	Wood Smoke	Eagle River Riverbed	Eagle River Rd. Dust Comp.	Gravel Pit	Juneau Rd. Dust Comp.
Al	0.20	0.53	0.42	0.02	6.11	5.67	5.17	1.05
S	1.36	13.3	4.16	0.18	.03	0.08	0	0.14
Cl	0.70	0	1.36	0.51	.08	0.30	.08	0.12
K	0.01	0.28	.01	0.86	1.28	1.02	0.84	1.42
Ca	.09	1.58	0.50	0.07	1.09	1.64	1.13	2.20
Mn	.06	0.05	0.01	-	0.10	0.15	0.14	0.11
V	.003	3.44	0.02	-	.03	0.03	0.03	0.03
Fe	.08	2.97	0.16	-	4.98	5.51	4.53	6.45
Ni	.003	5.36	0.01	-	.007	0.01	0.01	0.01
Br	0.34	.013	0.02	-	0	.0004	.001	.0005
Pb	1.29	0.11	0.52	-	.004	.02	.002	0.02
Naw	.02	3.50	0.47	.08	0	.09	.02	0.08
Clw	0.70	0	1.36	0.51	0	.39	0	0.04
Kw	-	-	-	0.86	.005	.04	.04	0.13
OC	45.61	7.00	14.64	47.50	2.43	6.38	2.78	3.89
EC	38.05	3.1	13.72	12.80	.005	.064	.003	0.10

a. A "w" following the element indicates water soluble.

The water soluble species concentrations for the crustal source profiles were measured; wood smoke is based on the literature[6], and the other sources are based on estimates from the total concentration.

3.5 Source Impacts

3.5.1 Overview

Chemical mass balance source apportionment calculations were performed on the ambient particulate filter data sets using both the EPA Version 6.0 CMB program[7] and NEA's QSAS III CMB program[8]. Individual source apportionment results for each filter are presented in Appendix B. Table 4 shows an example of the QSAS III CMB results presented in Appendix B. In this example, the filter identification numbers (MP140,26091835), particle size (total), sampling site (Juneau), and sampling date (February 19, 1986) are listed at the top of the page. The CMB modeling performance measures are listed just below this information (reduced chi square of 0.717, 11 degrees of freedom), followed by a listing of the fitted sources, their source contributions, and the total mass explained (98.388%). (The source names, codes, and descriptions are listed in Table 5.) In the bottom portion of the table are listed the measured elemental concentrations, their calculated concentrations, and the ratio of the calculated to measured concentrations. Elements actually used in the fitting process are indicated with asterisks.

The results from the EPA CMB regression on the same data set are illustrated in Table 6. The EPA program lists the correlation coefficient (R-square = 0.99), in addition to the other parameters. It also lists uncertainty/similarity clusters. In this example, no sources appear in this section. This is interpreted as meaning that there are no source clusters in this model run that are sufficiently similar to cause the model estimates to have high uncertainties. Occasionally, two clusters may be identical (e.g., having the same source numbers). The duplicate clusters are not relevant and are ignored.

Table 4

SAMPLE ID: MP140 Q6091835 PARTICLE SIZE: TOTAL
FIELD FLAG: MASS FLAG: ANALYSIS FLAGS:
SITE: 2 Juneau, Alaska
SAMPLE DATE: 0 START TIME: .0 DURATION: .0 HOURS
REDUCED CHI SQUARE: .717 DEGREES OF FREEDOM: 11

SOURCE	SIZE	UG/M3	PERCENT
11 MOVES1	T	1.118+- .578	.594+- .309
16 WSmoke	F	7.198+- 3.389	3.829+- 1.813
19 J-LRCD	T	174.928+- 6.951	93.046+- 5.943
24 Sulfat	T	1.728+- 1.177	.919+- .628
TOTAL:		184.971+- 7.844	98.388+- 6.451

SPECIES		MEAS. UG/M3	%	CALC. UG/M3	CALC./MEAS.	
Al	*	10.151+- 1.342	5.399	9.229+- 1.258	.909+- .173	Al
P		< .009		.002+- .002	.000+- .000	P
S	*	.251+- .025	.134	.259+- .037	1.032+- .181	S
Cl		.169+- .013	.090	.246+- .025	1.457+- .190	Cl
K	*	2.474+- .177	1.316	2.485+- .273	1.004+- .132	K
Ca	*	3.315+- .236	1.763	3.679+- .413	1.110+- .147	Ca
Ti	*	.984+- .071	.524	.924+- .051	.938+- .085	Ti
V	*	.048+- .011	.025	.044+- .012	.918+- .337	V
Cr	*	.049+- .004	.026	.053+- .003	1.081+- .112	Cr
Mn	*	.196+- .014	.105	.183+- .009	.929+- .080	Mn
Fe	*	10.665+- .756	5.673	10.418+- .525	.977+- .085	Fe
Ni		.013+- .001	.007	.019+- .002	1.496+- .191	Ni
Cu		.023+- .002	.012	.019+- .002	.855+- .102	Cu
Zn		.040+- .003	.021	.077+- .004	1.922+- .177	Zn
Ga		.002+- .000	.001	.000+- .002	.005+- .716	Ga
As		< .003		.002+- .004	.000+- .000	As
Se		< .001		.000+- .002	.043+-3.341	Se
Br	*	.010+- .001	.005	.006+- .003	.578+- .287	Br
Rb		.015+- .001	.008	.014+- .002	.941+- .150	Rb
Sr		.067+- .005	.036	.068+- .003	1.014+- .091	Sr
Ba		.333+- .048	.177	.318+- .072	.955+- .255	Ba
La		< .063		.024+- .115	.818+-4.219	La
Hg		< .001		.002+- .002	1.366+-1.962	Hg
Pb	*	.051+- .004	.027	.067+- .009	1.310+- .216	Pb
OC	*	12.905+- 1.443	6.864	12.728+- 1.334	.986+- .151	OC
EC	*	2.205+- .671	1.173	1.714+- .629	.777+- .370	EC
Naw		.272+- .110	.145	.976+- .412	3.589+-2.095	Naw
Sw	*	.666+- .154	.354	.666+- .240	1.000+- .429	Sw
Clw		< .065		.054+- .120	.000+- .000	Clw
Kw	*	.217+- .039	.116	.267+- .058	1.230+- .345	Kw
Caw		.169+- .037	.090	.000+- .055	.000+- .323	Caw
Mnw		.017+- .009	.009	.000+- .017	.000+- .966	Mnw
Few		.041+- .020	.022	.181+- .038	4.428+-2.375	Few

MASS 188.0 +- 9.4 * FITTING SPECIES

Table 5

SOURCE PROFILES

Source Code	Source Name	Source Description
1	ER-FRW	Eagle River Freeway Road Dust
2	ER-LPS	Eagle River Local Paved Road
3	ER-LUS	Eagle River Local Unpaved Road
4	ER-PPL	Eagle River Paved Parking Lot
5	ER-UPL	Eagle River Unpaved Parking Lot
6	ER-GRP	Eagle River Gravel Pit
7	ER-RVB	Eagle River Riverbed Sample
8	ER-RDC	Eagle River Road Dust Composite
9	LeadedT	Leaded Gasoline - FTP
10	DieselT	Diesel - FTP
11	MOVES1*	Trans. - MOVES with Tire Wear
12	MOVES2*	Trans. - MOVES without Tire
13	ResOilT	Residual Oil Combustion
14	DisOilT	Distillate Oil Combustion
15	MarineT	Marine Aerosol
16	WSMOKE	Residential Wood Combustion
17	JSMOKE	Juneau Wood Combustion Composite
18	OJRDC	Juneau Composite Road & Soil
19	J-LRCD	Juneau Loop/Cinema Dr. Paved Roads
20	J-RVSD	Juneau Riverside Dr. Paved Road
21	J-UPCM	Juneau Unpaved Road Dust Composite
22	J-RVBD	Juneau Riverbed @ Mendenhall V
23	J-RDC	Juneau Road Dust Composite
24	Sulfat	Sulfate - S, SO_4, Sw

*Composite MOter VEhicle Signature that is based on weighted emissions from motor vehicle fleet.

Table 6

RESULTS FOR CMB SITE: MP140 YEAR: 86 DATE: 0219 VERSION: 6.0
COARSE PARTICULATE FRACTION
SAMPLING DURATION: 0 HRS. WITH START HOUR: 0
R-SQUARE: .99
CHI SQUARE: .72
DF: 11

#	TYPE	UG/M3		%	
11	MOVES1	1.042+-	.575	.554+-	.307
16	WSmoke	7.232+-	3.390	3.847+-	1.813
19	J-LRCD	174.875+-	6.978	93.018+-	5.951
24	Sulfate	1.732+-	1.176	.921+-	.627
	TOTAL:	184.881+-	7.071	98.341+-	6.191

UNCERTAINTY/SIMILARITY CLUSTERS: SUM OF CLUSTER SOURCES

COARSE SUSPENDED PARTICULATE

SPECIES		INCL	MISS FLG	MEAS. UG/M3		PERCENT		CALC. UG/M3		RATIO R/U	
13	Al	*		10.15100+-	1.34200	5.39944+-	.76318	9.22652+-	7.07081	-.1	Al
15	P			<	.00458	<	.00487	.00194+-	.00217	-.3	P
16	S	*		.25120+-	.02522	.13362+-	.01499	.25814+-	.03722	.2	S
17	Cl			.16860+-	.01354	.08968+-	.00848	.24522+-	.02521	2.7	Cl
19	K	*		2.47420+-	.17660	1.31606+-	.11470	2.48434+-	.27289	.0	K
20	Ca	*		3.31520+-	.23610	1.76340+-	.15345	3.67820+-	.41271	.8	Ca
22	Ti	*		.98440+-	.07101	.52361+-	.04596	.92346+-	.05071	-.7	Ti
23	V	*		.04770+-	.01134	.02537+-	.00617	.04375+-	.01224	-.2	V
24	Cr	*		.04860+-	.00403	.02585+-	.00250	.05251+-	.00350	.7	Cr
25	Mn	*		.19650+-	.01404	.10452+-	.00911	.18244+-	.00875	-.8	Mn
26	Fe	*		10.66480+-	.75640	5.67274+-	.49229	10.41471+-	.52463	-.3	Fe
28	Ni			.01290+-	.00156	.00686+-	.00090	.01927+-	.00175	2.7	Ni
29	Cu			.02260+-	.00206	.01202+-	.00125	.01930+-	.00175	-1.2	Cu
30	Zn			.04000+-	.00316	.02128+-	.00199	.07648+-	.00413	7.0	Zn
31	Ga			.00240+-	.00112	.00128+-	.00060	.00001+-	.00175	-1.2	Ga
33	As			<	.00163	<	.00173	.00176+-	.00351	.0	As
34	Se			<	.00058	<	.00062	.00002+-	.00175	-.3	Se
35	Br	*		.00960+-	.00141	.00511+-	.00079	.00528+-	.00258	-1.5	Br
37	Rb			.01490+-	.00180	.00793+-	.00104	.01399+-	.00175	-.4	Rb
38	Sr			.06730+-	.00510	.03580+-	.00325	.06824+-	.00350	.2	Sr
56	Ba			.33340+-	.04761	.17734+-	.02683	.31828+-	.07170	-.2	Ba
57	La			<	.03130	<	.03331	.02448+-	.11543	-.1	La
80	Hg			<	.00082	<	.00087	.00176+-	.00175	.4	Hg
82	Pb	*		.05100+-	.00451	.02713+-	.00276	.06588+-	.00896	1.5	Pb
83	OC	*		12.90520+-	1.44290	6.86444+-	.84076	12.70665+-	1.33589	-.1	OC
84	EC	*		2.20550+-	.67080	1.17313+-	.36160	1.68929+-	.63004	-.6	EC
91	Naw			.27190+-	.10980	.14463+-	.05885	.97576+-	.41148	1.7	Naw
92	Sw	*		.66550+-	.15400	.35399+-	.08381	.66550+-	.24005	.0	Sw
93	Clw			<	.03240	<	.03448	.05321+-	.11959	.2	Clw
94	Kw	*		.21720+-	.03901	.11553+-	.02154	.26733+-	.05760	.7	Kw
95	Caw			.16910+-	.03711	.08995+-	.02025	.00000+-	.05456	-2.6	Caw
96	Mnw			.01740+-	.00945	.00926+-	.00505	.00000+-	.01679	-.9	Mnw
97	Few			.04080+-	.02012	.02170+-	.01076	.18047+-	.03760	3.3	Few
1	TOTAL			188.00090+-	9.40120	100.00000+-	7.07194	184.88110+-	.00018	-.3	TOTAL

MEASURED AMBIENT MASS (UG/M3): FINE: .0+- .0 COARSE: 188.0+- 9.4 TOTAL: 188.0+- 9.4

When clusters appear in this section, they are identified by their source code numbers associated with their profiles. The clusters are formed if two criteria are met: 1) two or more source components in an eigenvector derived from the singular value decomposition exceed 0.25, and 2) the t-statistic for any one of these source types is less than or equal to 2.0. These uncertainty/ similarity clusters are caused by excessive similarity (collinearity) among the source profiles in the cluster or by high uncertainties in the individual source profiles. The standard errors associated with the source contribution estimates of sources identified in a cluster are usually very large, often too large to allow an adequate decision to be made.

If collinearity is the cause of these excessive uncertainties, then the uncertainty of the sum of the source contributions for a cluster may be smaller than the uncertainty of any single source contribution in the cluster. The sum of source contributions and the standard error of the sum is expressed in the final column of this display.

The column labeled RATIO R/U contains the ratio of the difference between the calculated and measured concentration (residual) divided by the uncertainty of the residual. The lower the ratio, the better the model has explained the species. For example, a residual of 2.0 indicates that the residual is two times greater than the uncertainty in the residual, and that the calculated value is greater than the measured value.

The CMB results presented in the Appendices represent the best model solution as determined by an interactive procedure which optimizes the following model performance parameters:

- Source contributions should be positive and greater than their uncertainties. The T-statistic value should be greater than 2.0.

- R-square values should be greater than 0.8.

- Reduced chi square should be minimized and generally less than 2. A value greater than 4 indicates that the model has not explained the ambient data well.

- The calculated to measured concentration ratio for individual elements should approach 1.0 within the listed uncertainty.

- The percent elemental mass explained should approach 100% within the uncertainty.

- The degrees of freedom should be maximum, preferably greater than 5.

- Source contribution estimates should approximate the measured mass concentrations.

In this process, the optimum CMB fit is selected only on the basis of these criteria and independent of other data. In this way, other information such as meteorological data, can be used as an independent evaluation to check the validity of the CMB calculations.

In the example illustrated in Tables 4 and 5, 98.4 ± 6.5% of the mass was explained by the sources indicated. A reduced chi square value of .72 was obtained with eleven degrees of freedom (DF). The calculated to measured elemental ratios were generally equal to 1.0 within their listed uncertainties for the fitting elements. The largest deviations from 1.0 were elements below the analytical detection limit. The R-square value is 0.99.

Figure 1 shows an alternate representation of the same source apportionment results listed in Tables 4 and 6. The solid line represents the measured ambient elemental concentration. The asterisks indicate calculated elemental concentrations for fitting species used in the CMB regression calculations; the open circles indicate the calculated concentrations for species not used in the least squares fitting process.

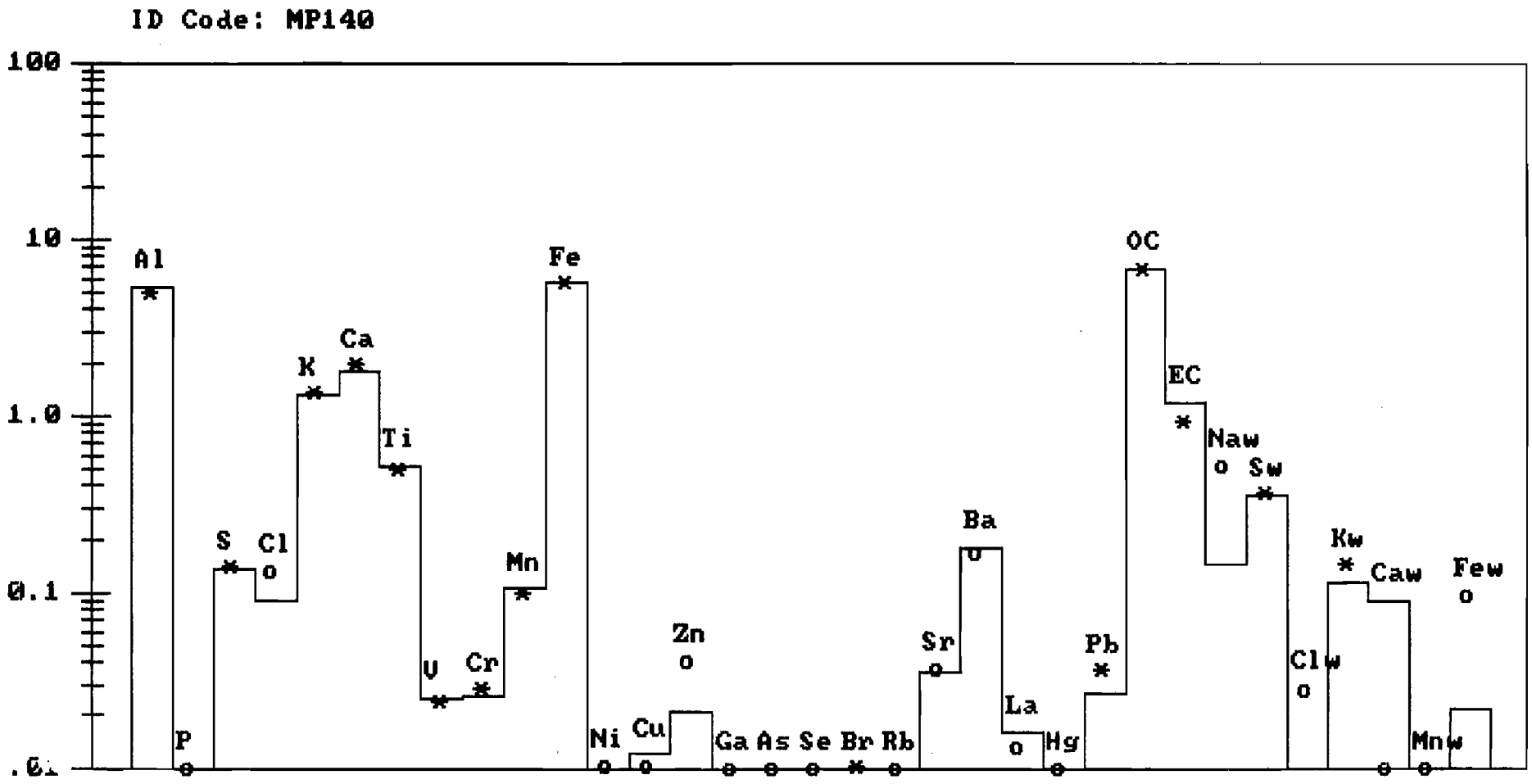

ID Code: MP140
100
10
1.0
0.1
.01
Al
P
S
Cl
K
Ca
Ti
V
Cr
Mn
Fe
Ni
Cu
Zn
Ga
As
Se
Br
Rb
Sr
Ba
La
Hg
Pb
OC
EC
Naw
Sw
Clw
Kw
Caw
Mnw
Few

Figure 1.

3.5.2 Quality of CMB Results

The quality of the selected CMB fits in Appendix B are excellent based on the R-square and chi square criteria. The average R-square value is 0.99 and ranged from 0.96 to 1.0. The average chi square values are 0.64 for the Juneau samples, and 0.81 for Eagle River. The Juneau chi squared values ranged from 0.16 to 1.45, and the Eagle River values ranged from 0.46 to 1.07. The degrees of freedom ranged from 7 to 11, and the number of fitting species ranged from 12 to 15. The ratio of calculated to measured elemental concentrations were generally within one standard deviation of 1.0 for the fitting species, and almost always within two standard deviations. The mean percent mass explained in the Juneau airshed was 93.5 ± 6.6%, while the average in Eagle River was 79.5 ± 5.5%. The excellent fits, as indicated by the above noted criteria, as well as the fact that most of the major species have been measured, indicates that another source category is not missing in the Eagle River airshed but the unexplained mass is due to either a systematic bias in the deposit mass determination of either the Eagle River ambient or source samples and/or the loss of mass in the storage and/or transport of the filters. In either case, the relative source contributions would not be affected other than each being reduced by a constant fraction. The average Eagle River results reported have been corrected for this by normalizing the results to 100%.

3.5.3 Average Source Contributions

The average source contributions are listed in Appendix C and summarized in Tables 7 and 8.

The largest source category in the Mendenhall Valley was road dust which accounted for 69.6% of the mass. Wood smoke was the next largest contributor at 13.8%, followed by sulfate, distillate oil, and vehicle exhaust. The average wood smoke source contributions were nearly the same at both sites (15 $\mu g/m^3$) on the two days when samples were collected at both sites. The motor vehicle contributions

Table 7

AVERAGE PERCENT SOURCE CONTRIBUTIONS
IN JUNEAU, ALASKA

Source Category	Mendenhall* Valley	Super Bear Center	Floyd Dryden School
Vehicle Exhaust	1.61 ± 0.95	5.37 ± 2.16	1.03 ± 0.43
Distillate Oil	1.79 ± 1.14	2.68 ± 1.20	-
Wood Smoke	13.79 ± 4.80	17.32 ± 3.85	6.73 ± 2.23
Composite Road & Soil	4.13 ± 4.13	6.20 ± 0.59	-
Loop Rd./Cinema Dr. Rd.	38.42 ± 17.72	34.38 ± 2.33	46.52 ± 2.97
Road Dust Composite	27.00 ± 17.17	21.96 ± 1.46	37.07 ± 2.47
Sulfate	3.55 ± 0.96	4.58 ± 1.04	1.48 ± 0.62
Unexplained	6.50 ± 3.57	7.51 ± 1.80	7.17 ± 1.74
Mass ($\mu g/m^3$)	147.0	214.0	86.0

a. Average of the individual days analyzed from the Super Bear and Floyd Dryden monitoring sites.

Table 8

AVERAGE PERCENT SOURCE CONTRIBUTIONS
IN EAGLE RIVER, ALASKA[a]

(Normalized)

Source Category	Spring & Fall	Spring	Fall
Vehicle Exhaust	0.52 ± 0.14	0.33 ± 0.26	0.87 ± 0.15
Distillate Oil	0.22 ±(0.09)	0.88 ±(0.32)	-
Wood Smoke	2.55 ± 0.62	1.36 ± 1.02	2.92 ± 0.74
Local Unpaved Rd.	6.14 ±(0.32)	-	8.07 ±(0.43)
Gravel Pit	7.13 ±(0.38)	-	9.39 ±(0.53)
Riverbed	1.04 ±(0.86)	4.38 ±(3.24)	-
Road Dust Composite	80.46 ± 8.78	90.62 ± 6.49	77.26 ± 11.55
Marine Aerosol	0.11 ± 0.06	0.45 ± 0.21	-
Sulfate	0.79 ± 0.18	1.32 ± 0.44	0.63 ± 0.18
Unexplained	0 ± 2.24	0 ± 1.58	0 ± 4.32
Mass ($\mu g/m^3$)	195.88	154.52	210.93

a. Uncertainties listed are standard deviations of the mean. The values listed in parentheses are the uncertainties when only one value was observed.

on these two days at the Super Bear site was 3.9 and 6.8 $\mu g/m^3$, two to four times greater than measured at the Floyd Dryden School. Road dust, on the other hand, was almost two times higher at the School (176 $\mu g/m^3$) than at the Super Bear site.

Crustal dust was also the largest source of PM_{10} in Eagle River. The average impact for all the days selected was 94.8%. This percent contribution was relatively constant with season, averaging 94.7% in the fall selected samples and 95.0% in the samples selected from the spring. This is consistent with previous studies in which about 90% of the mass was also attributed to this type of source[1].

The next largest source contribution was wood smoke (2.55%), followed by sulfate, vehicle exhaust, and distillate oil.

4.0 MODEL VALIDATION

4.1 Overview

Chemical mass balance receptor model calculations are performed on individual filter data sets. These calculations yield the most probable source contributions based on ambient and source aerosol chemistry. Because these calculations are generally made independently of meteorological characteristics, local traffic patterns, etc., the validity of the CMB results can be evaluated by comparing them with these independent airshed and source characteristics.

This is particularly important in this study because of the need to use both the meteorological characteristics and emission inventory data to validate and/or apportion major source categories to sub-categories.

The objective of this section is to evaluate the source apportionment results relative to the complete airshed data base and model evaluation statistics.

4.2 Quality of CMB Results

The quality of each CMB source apportionment calculation is evaluated on the basis of the percent of total mass explained, R-square, chi square, t-statistic, source uncertainty clusters, elemental ratios, and residuals. The mass explained, R-square, chi square, and elemental ratio values for each CMB calculation are presented along with the source impact results in Appendix B, as well as the average values.

As already noted, the source profile fits to the elemental patterns were excellent considering the number of species fit, and the fact that the data is based on quartz fiber filters. The average chi squares were less than 1.0, and the average R-square was 0.99. In addition, the average percent mass explained in Juneau was 93.5%. The percent mass explained in Eagle River with the source fits selected was only 80%. The low percent mass explained in Eagle River is not thought to be due to a missing source but due to a systematic bias between the source profiles and the ambient data or the loss of material from the ambient filter. This bias and the justification for normalizing the source impacts to 100% is based on the following:

1. All of the major chemical species have been measured and apportioned.

2. There are no other major source categories either in the airshed or upwind.

3. The match of the ambient chemical profile is excellent as demonstrated by the goodness-of-fit criteria and illustrated with the histogram plots.

4. Previous studies have shown that crustal material was responsible for 90% of the PM_{10} mass.

5. The lowest percent mass explained is for samples collected on high wind speed days in the spring when large particle wind blown dust is expected to be enhanced, and fine particles depleted due to their removal from the airshed.

6. Wood smoke and other sources of high uncertainty represent a small portion of the PM_{10} and potential systematic uncertainties in their source profiles cannot account for the unexplained mass.

7. A much higher percent of the mass can be explained if the gravel pit profile is used, but the fit is not as good as when the composite road dust is used.

   An example of this is illustrated in Table 9, which compares two fits using different crustal dust profiles. The top fit is the one selected. The alternate fit explains 104.5 ± 7.7% of the mass, but the chi square is substantially higher than the fit chosen, and the ratio of calculated to measured species concentrations were closer to 1.0 for the selected fit. This pattern was consistent for all of the Eagle River source profiles and may indicate a larger influence from this source than is indicated by the composite road dust source profile.

4.3 Source Resolvability

Source resolvability and limit of detection have not been well defined in receptor modeling, but are of particular importance in this study.

A source is generally considered to be resolved and above its detection if the best fit calculates that the source's contribution is greater than its uncertainty. If a source contribution is less than its uncertainty, it is assumed to be below its level of detection and equal to zero. This is the approach recommended by the EPA and the results presented in the report are based on this assumption.

In the case of wind blown river sediment, it's impact was greater than it's uncertainty on only one day, February 18, 1986. On that day, it's contribution was 26.5 ± 22.0 $\mu g/m^3$ (12.4 ± 10.3%) and resolved from the much larger contribution from the Eagle River composite road dust. There is, however, a reasonable probability that the contribution was substantially higher or lower than indicated based on the relatively large uncertainty. Similar results were obtained on other days of high wind, but the contribution was less than its uncertainty and not included in the final fit. On these high wind speed days when it was not fit, the uncertainties were similar, i.e., 10 to 20 $\mu g/m^3$ or about 10% of the PM_{10}. Based on these results, it is assumed that on high wind speed days, the river bed

Table 9

SAMPLE ID: MP146 Q5045528 PARTICLE SIZE: TOTAL
FIELD FLAG: MASS FLAG: ANALYSIS FLAGS:
SITE: 1 Eagle River, Alaska

SAMPLE DATE: 10/28/85 START TIME: .0 DURATION: .0 HOURS
REDUCED CHI SQUARE: .835 DEGREES OF FREEDOM: 7

Source	Size	$\mu g/m^3$	Percent
8 ER-RDC	T	174.545 ± 8.662	79.762 ± 5.619
9 Leaded	T	.960 ± .247	.439 ± .115
10 Diesel	T	1.851 ± 1.709	.846 ± .782
16 WSmoke	F	7.483 ± 3.988	3.420 ± 1.830
24 Sulfat	T	.298 ± .809	.136 ± .370
TOTAL		185.137 ± 9.725	84.602 ± 6.136

Alternate Fit

REDUCED CHI SQUARE: 1.279 DEGREES OF FREEDOM: 7

Source	Size	$\mu g/m^3$	Percent
6 ER-GRP	T	213.498 ± 11.593	97.562 ± 7.201
9 Leaded	T	.999 ± .256	.457 ± .119
16 WSmoke	F	13.492 ± 3.898	6.165 ± 1.808
24 Sulfat	T	.788 ± .889	.360 ± .407
TOTAL		228.777 ± 12.265	104.544 ± 7.664

dust contribution limit of resolvability or detection would be about 10 to 20 $\mu g/m^3$ or about 10% of the PM_{10}.

It is important to note, however, that on days when the river sediment was not resolved, its contribution has been included in the general crustal category.

In addition, different crustal dust sources were used to obtain the best fit on different days. The particular source fit represents all of the crustal sources that could not be resolved[2]. The use of a specific source within an unresolvable source category or the composite source allows for greater source resolvability in other categories and a consistent application of the methods selection criteria. Thus, even though three different crustal dust sources were resolved at different times in the Mendenhall Valley, they should all be considered as part of the larger, unresolvable crustal dust category.

4.4 Major Source Impacts

4.4.1 Eagle River Crustal Dust

The largest source impact in Eagle River was crustal dust which accounted for over 90% of the PM_{10}. Based on the CMB results, the average wind blown river sediment dust contribution was only 1.0%. The only day in which the use of this source provided the best fit was on February 18, 1986. On this day, the river sediment source contribution was estimated to be 12.4 ± 10.3%, but a similarity cluster was indicated. Alternate fits were tried but the fitting parameters were not as good.

Based on the meteorology for this day, it is the most likely day on which one would expect an impact from the river sediment. On this day, the highest winds were recorded at the Palmer and Anchorage stations. The average wind speed at Palmer was about 40 miles per hour and ranged from 30 to 50 miles per hour. The winds

at all three monitoring sites were consistently out of the northeast, which would put Eagle River downwind of the main river beds.

It is not surprising that the river sediment was not fit on the October days since the wind speeds recorded at all three monitoring sites were well below the approximately 10 to 15 miles per hour required to generate wind blown dust.

Although the winds on the other spring days were adequate to generate river sediment dust, this source could not be resolved based on the fitting parameters. The lower limit of detection for this source based on these fitting criteria is estimated to be about 10% in the presence of the other crustal sources.

On the low wind speed October episode days, the crustal dust source would consist of only traffic generated road and parking lot dust. The crustal dust in the spring would include local (not river bed) wind blown dust. These results are illustrated with the pie charts shown in Figure 2.

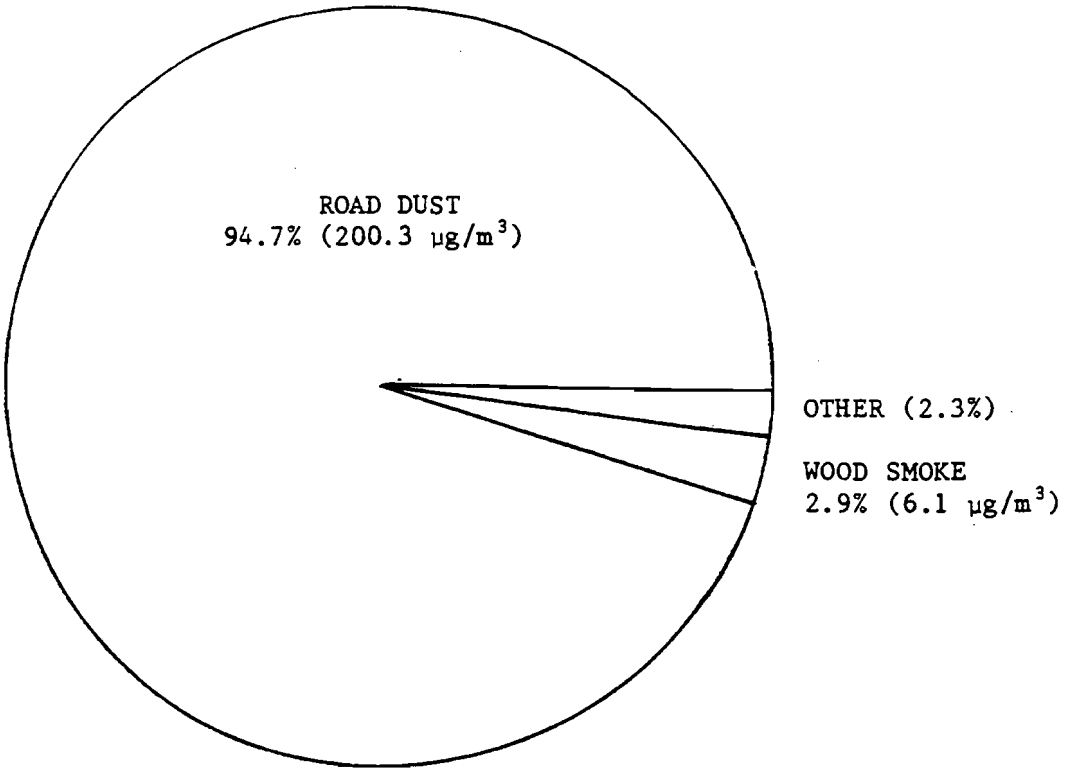
4.4.2 Juneau Crustal Dust

Crustal dust was also the largest source of PM_{10} in Juneau, accounting for 69.6% (102.2 $\mu g/m^3$) of the mass as illustrated in Figure 3. This general category is subdivided by the CMB calculations into composite road and soil dust (4.1%), composite road dust (27.0%), and Loop Road/Cinema Drive road dust (38.4%). Although each of these three source categories fit best at times according to model parameters, they really can't be considered as resolvable.

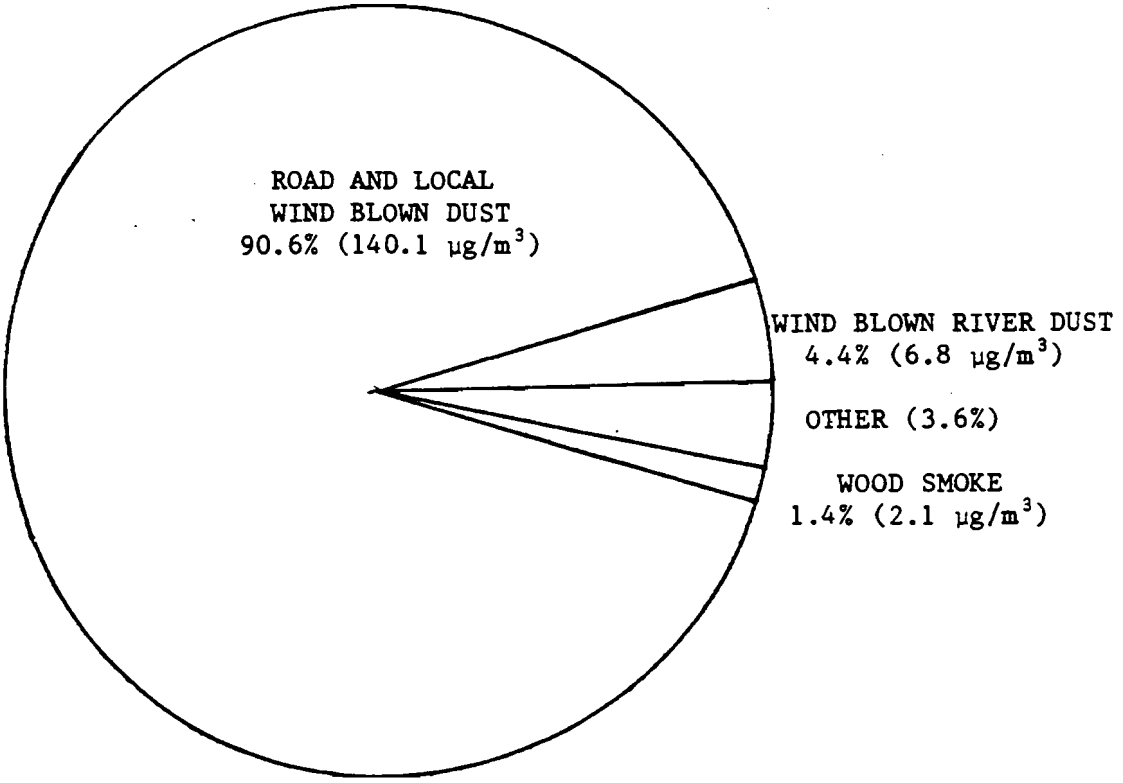
On two of the days sampled (February 22 and October 31), the average wind speeds were under five miles per hour, indicating that wind blown dust was probably not a significant source on these days. The average wind speeds on the other two days selected (February 19 and 20) were between ten and twelve miles per hour at the

Figure 2

PM_{10} SOURCE CONTRIBUTIONS
(Eagle River)

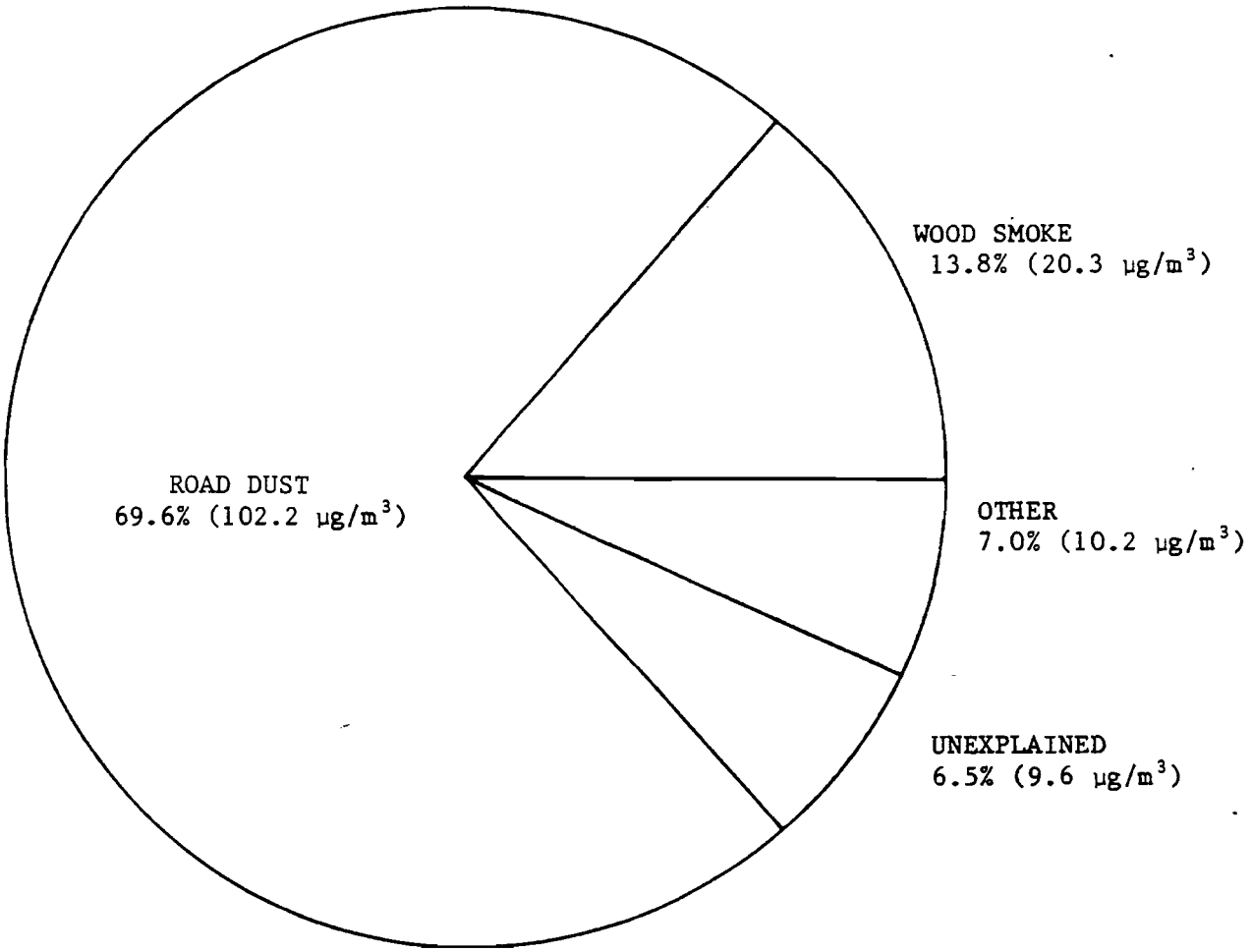


Fall



Spring

Figure 3
PM_{10} SOURCE CONTRIBUTIONS
(Juneau)



Juneau airport, but only two to five miles per hour at the Floyd Dryden monitoring site. This also would suggest that there was little wind blown dust in the vicinity of the Floyd Dryden site, but there may have been some at the Super Bear monitoring site. Based on this meteorology, it is assumed that all of the crustal dust at the Floyd Dryden site is due to road dust. The portion of crustal dust at the Super Bear site due to wind blown dust is uncertain. Because of the marginal dust generating wind speeds measured at the Juneau airport, the substantially lower wind speeds measured at Floyd Dryden School and the absence of wind data for the Super Bear monitoring site, all of the crustal dust in the Mendenhall Valley on the days selected is assumed to be due to road dust.

4.4.3 Juneau Wood Smoke

Wood smoke was the second largest source of PM_{10} in Juneau. This source accounted for 13.8% (20.3 $\mu g/m^3$) of the PM_{10}. The wood smoke impacts were about the same at both monitoring sites on the two days samples were selected from both sites. The impacts were over three times higher on the low wind speed day (24 $\mu g/m3$) than on the moderate wind speed day (7 $\mu g/m^3$). Although the average temperature on the low wind speed day (February 22nd) was about 10 F higher than on the high wind speed day, the higher wind speed is expected to be the dominating influence by providing better ventilation.

This same influence of wind speed is also observed when comparing the wood smoke impacts at the Super Bear site. In this case, the wood smoke impact increases from 6.9 $\mu g/m^3$ on the highest wind speed day (February 19) to 36.5 $\mu g/m^3$ on the lowest wind speed day (October 31).

The consistency of this pattern, along with the use of water soluble K, has greatly increased the resolvability of this source and our overall confidence in this source's contribution.

4.4.4 Other Juneau Sources

The vehicle exhaust, distillate oil, and sulfate contributions accounted for only about 7% of the average Juneau PM_{10}. The impacts of these sources were substantially higher at the Super Bear site than at the Floyd Dryden site as would be expected from the greater vehicle traffic, etc., in the vicinity of the Shopping Center.

Marine aerosol was not identified on any of the days selected. This is consistent with the wind direction during the days sampled which was generally from the east.

Residual oil was also not identified as a significant contributor to PM_{10}. In this case, the V and Ni indicators, which are relatively unique for this source, allows an upper limit to the impact of this source to be set at about 0.2 $\mu g/m^3$.

The source contributions in Mendenhall Valley have not been normalized to 100% because the unexplained mass is small relative to the overall uncertainty.

5.0 CONCLUSIONS

Crustal dust was the largest source of PM_{10} in both Eagle River and Juneau on selected days with high PM_{10} levels. The average spring and fall crustal dust contributions to PM_{10} levels on selected high PM_{10} days was 94.7%. Wind blown river sediment was a minor (1.0%) source of PM_{10} in Eagle River and was resolved on only one day, the day with the highest wind speeds at the Palmer meteorological station. The highest PM_{10} days occurred during calm wind episodes in October. Wood smoke was responsible for only 1.4% (2.1 $\mu g/m^3$) on windy spring days in Eagle River, and 2.9% (6.1 $\mu g/m^3$) on calm fall days.

In Juneau, crustal dust was responsible for 69.6% (102.2 $\mu g/m^3$) of the PM_{10}. Essentially, all of this was apportioned to road dust based on meteorology. Wood smoke contributed 13.8% (20.3 $\mu g/m^3$) of the Juneau PM_{10} and varied inversely with the wind speed. The use of water soluble K greatly increased the resolvability of this source and the level of confidence in its contribution.

6.0 REFERENCES

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