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Chemical mass balance (CMB) source apportionment and organic speciation of PM(2.5) in Missoula Montana including the 2000 wildfire season

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Chemical Mass Balance (CMB) Source Apportionment and Organic Speciation of $PM_{2.5}$ in Missoula, Montana Including the 2000 Wildfire Season

by

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Presented in partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

The University of Montana - Missoula

December 2001

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Chemical Mass Balance (CMB) Source Apportionment and Organic Speciation of $PM_{2.5}$ in Missoula, Montana Including the 2000 Wildfire Season

Director: Garon C. Smith GCS

A yearlong sampling program for $PM_{2.5}$, Semi-Volatile Organic Compounds (SVOCs), and Volatile Organic Compounds (VOCs) was conducted in 2000/2001. The data were used in a Chemical Mass Balance (CMB) Source Apportionment Model (Version 8.0) to apportion the sources of $PM_{2.5}$ in the Missoula Valley. Results showed that wood combustion contributed an average of 41% to the fine fraction throughout the year. The second largest source of $PM_{2.5}$ was diesel (19%), followed by ammonium nitrate (17%), the kraft recovery boilers from Smurfit-Stone Container (14%), other hog fuel boilers (6%), and street sand (5%). Results also showed that $PM_{2.5}$ levels and contributions from sources were consistent on both sides of the Missoula Valley, but VOCs were twice as high in Missoula compared to Frenchtown.

Another aspect of this program was to investigate the organic fraction of the Missoula Valley $PM_{2.5}$ by evaluating a modified Federal Reference Method (FRM) $PM_{2.5}$ sampler. A method comparison was also made between sampling for SVOCs using the modified $PM_{2.5}$ sampler and in using a Hi-volume Polyurethane Foam (PUF) sampler. Results showed that the $PM_{2.5}$ PUF measured more of the lighter SVOCs compared to the Hi-vol PUF sampler. This is most likely the result of the higher flows through the Hi-vol PUF which “strip” the lighter organics from the surface of the filter.

The wildland fires of summer 2000 comprised one of the most severe fire seasons is U.S. history, and had a direct impact on the city of Missoula. Sampling in Missoula was already in progress when the fires began and smoke started rolling into the Missoula Valley. Samples were collected before, during, and after the 2000 fire season, and a detailed characterization of particulate and gaseous emissions from extensive wildland fires was obtained. The 2000/2001 CMB Sampling Program data collected during the 2000 fire season suggest that the main health impacts to downwind populations reside in the fine particulate exposures, with an average of 81% of the Missoula Valley $PM_{2.5}$ resulting from forest fires.

For Emilie.

To infinity and beyond……

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A host of undergraduates worked with me at The University of Montana. Thanks to Joe Benson, Anna Simpson, Mark Mencel, and Baron Arnone for everything. Thanks to the gals in the Chemistry office (Bonnie Gatewood, Barbara McCann, and Rosalyn Chaitoff) and the guys in the lab (Dr. Gus Alnassar, Dr. Tim Looper, David Tooke, and Paul Miller) for the help. Thanks to my committee (Dr. Bill Derrick, Dr. Dick Field, Dr. Ed Rosenberg, Dr. Garon Smith, and Dr. Mark Tinsley) for the guidance.

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TABLE OF CONTENTS

Preface

PART I: THE MISSOULA VALLEY $PM_{2.5}$ SOURCE APPORTIONMENT STUDY

PART II: INVESTIGATION OF THE REALTIONSHIP BETWEEN $PM_{2.5}$, SEMI- VOLATILE ORGANIC COMPOUNDS, AND VOLATILE ORGANIC COMPOUNDS

PART III: AIR SAMPLING STUDY OF THE 2000 MONTANA WILDFIRE SEASON

LIST OF TABLES

Part I

Part II

Part III

LIST OF FIGURES

Part I

Part II

Part III

ABBREVIATIONS

BFB: Bromofluorobenzene.
BGI: Bob Gussman Industries, Inc.
CADMP: California Acid Deposition Monitoring Program.
CEHS: Center for the Environmental Health Sciences.
CFR: Code of Federal Regulations.
CHEER: Coalition for Health, Economic and Environmental Rights.
CMB: Chemical Mass Balance.
DEQ: Department of Environmental Quality.
DFTPP: Decafluorotriphenylphosphine.
EC: Elemental Carbon.
EPA: Environmental Protection Agency.
FID: Flame Ionization Detector.
FRM: Federal Reference Method.
FTS: Flow transfer standard.
GC/MS: Gas Chromatography / Mass Spectrometry.
K-D: Kuderna-Danish Evaporator.
LCS: Laboratory Control Spike.
LMB: Laboratory Method Blank.
LPM: Liters Per Minute.
MCCHD: Missoula City / County Health Department.
MDL: Minimum Detection Limit.
MIR: Minimum Instrument Response.
NAAQS: National Ambient Air Quality Standards.
NIST: National Institute of Standards and Technology.
NOx: Oxides of nitrogen.
NWS: National Weather Service.
OC: Organic Carbon.
PAHs: Polycyclic Aromatic Hydrocarbons.
PC-BOSS: Particle Concentrator – Brigham Young University Organic Sampling System.
$PM_{2.5}$: Particulate Matter smaller than 2.5 microns in diameter.
PM_c: Coarse particulate matter with diameters between 2.5 and 10 μm in diameter.
PM_{10}: Particulate Matter smaller than 10 microns in diameter.
pptv: parts per trillion by volume.
PUF: Polyurethane Foam.
QA/QC: Quality Assurance / Quality Control.
RAMS: Real-time Ambient Mass Sampler.
SCE: Source Contribution Estimates.
SFS: Sequential Filter Sampler.
STD ERR: Standard Error.
SVOCs: Semi-Volatile Organic Compounds.
TC: Total Carbon.
TSP: Total Suspended Particulates.
TEOM: Tapered Element Oscillating Microbalance.
TOR: Thermal Optical Reflectance.
TSTAT: T-statistic.
VOCs: Volatile Organic Compounds.
WINS: Well Impactor Ninety-Six.
XRF: X-Ray Fluorescence.

PREFACE

Introductory Remarks

This thesis is composed of three separate (yet related) research topics. Initially, the Missoula Valley Sampling Program was designed to determine the sources of $PM_{2.5}$ in the Missoula Valley (Part I) as well as investigate the relationship between $PM_{2.5}$ and SVOCs (Part II). During the summer of 2000, a third project emerged when smoke samples from nearby forest fires were collected in the Missoula Valley. These three projects have not only provided information on local air quality issues here in the Missoula Valley, but have also contributed to the advancement of $PM_{2.5}$ sampling.

Purpose of Study

The Missoula Valley $PM_{2.5}$ Source Apportionment Study.

Part I of this thesis identifies the major sources of $PM_{2.5}$ in the Missoula Valley as well as the airborne levels of $PM_{2.5}$, $PM_{2.5}$ constituents, and numerous semi-volatile organic compounds (SVOCs) and volatile organic compounds (VOCs). Ambient air samples were collected for an entire year at two locations in the Missoula Valley. T210hese data were used in an Environmental Protection Agency (EPA) Chemical Mass Balance (CMB) model 8.0 to identify the source contributions to the fine fraction. In the future, this study will be used as guidance in the continuing effort to improve the air quality in the Missoula Valley.

Investigation of the Relationship Between $PM_{2.5}$, and SVOCs.

Part II of this thesis evaluates a new $PM_{2.5}$ sampling methodology that investigates the relationship between $PM_{2.5}$ and the SVOCs that compose them. This part of the research answers the EPA's request to investigate the organic composition of $PM_{2.5}$ so that a more accurate accounting of the mass and risk of airborne particulates can be established. A comparison is made between the SVOCs that compose the $PM_{2.5}$ particles with those that compose Total Suspended Particulates (TSPs) as determined by a Hi-vol PUF sampler.

Air Sampling Study of the 2000 Montana Wildfire Season.

The third part of this thesis presents results of air samples collected before, during, and after the 2000 fire season. It presents not only a mass analysis of the smoke, but also a detailed chemical analysis of the smoke particles as detected by two sites in the Missoula Valley. Smoke particles were also collected and provided to The University of Montana's Center for Environmental Health Sciences (CEHS) for further health effects studies. This portion of the thesis was published in the 2001 proceedings of the Air & Waste Management's Annual Conference in Orlando, Florida.

Overview of Thesis Organization

This thesis is organized into three parts: I, II, and III. Part I contains 5 chapters and discusses the source apportionment program. Part II contains 5 chapters and details the organic composition of airborne particulate matter. Finally Part III presents results of air sampling conducted during the Montana wildfire season of summer of 2000. All of the raw data collected in this sampling program can be obtained from the Missoula Health Department.

Part I

THE MISSOULA VALLEY $PM_{2.5}$ SOURCE APPORTIONMENT STUDY

Chapter 1 Introduction

1.1 Missoula Valley Air Pollution and Project History

The 1967 Montana Clean Air Act authorized local air pollution control programs, and by 1969, the Missoula City-County Health Department (MCCHD) had developed a local air pollution control program and assumed responsibility for most sources of air pollution in Missoula County. Traditionally, the Missoula urban area has a history of exceeding the Montana and National Ambient Air Quality Standards (NAAQS) for particulate and the 8-hour carbon monoxide standard. Prior to 1970, industrial sources were largely responsible for the high levels of particulate measured in the Missoula Valley. By 1974, strict enforcement of emission standards reduced industrial emissions in the valley by over 90%.

After the Arab oil embargo of the 1970's, more people began to heat their homes with wood. In 1974 and 1975, local air quality officials found that wintertime particulate levels were increasing and that Total Suspended Particulate (TSP) collection filters were darker in color than those collected earlier in the decade. They suspected residential wood burning as the source of the increased particulate levels and the cause of the darker filters. During the winter of 1986/1987, MCCHD conducted a Chemical Mass Balance (CMB) study at Rose Park to apportion the sources of PM_{10} (particulate matter less than 10 μm in diameter) in the valley. Residential wood smoke was found to contribute 47%

of the PM_{10}, confirming that residential wood burning had replaced industry as the primary source of particulate pollution in the Missoula Valley.

In 1986, PM_{10} sampling started in Missoula at Boyd Park, with another PM_{10} sampler installed at the Missoula Health Department in 1987. Missoula exceeded the annual average PM_{10} standard in 1986 and exceeded the 24-hour PM_{10} standard several times between 1987 and 1989. To reduce PM_{10} emissions in the valley, both the city and the county adopted regulations on residential wood stoves, outdoor burning, industry, fugitive emissions, street sanding and street maintenance (MCCHD, 1999). In general, PM_{10} concentrations have decreased at all sites since sampling began.

Another CMB source apportionment study, conducted in Missoula during 1995/1996 at Boyd Park, showed that residential wood combustion had decreased by as much as 87% from the 1986/1987 Missoula Rose Park study, while road dust impacts had increased by almost 25%. Motor vehicles were found to be responsible for over half the average PM_{10} in the 1995-96 study (Schmidt, 1996).

On July 18, 1997, the EPA promulgated the new NAAQS for particulate matter creating a new sub-index for fine particulate matter ($PM_{2.5}$), and revised PM_{10} standards that were made more stringent. As a result of these new amendments, the Missoula Valley began monitoring for $PM_{2.5}$ at two locations (Boyd Park and the Missoula Health Department) in early 1999. In 1998, the Smurfit-Stone Container paper mill in Missoula was sued by several groups in the Missoula Valley, including Montana CHEER (Coalition for Health, Economic and Environmental Rights), Native Forest Network, and Cold Mountains, Cold Rivers. This lawsuit accused Smurfit-Stone of violating federal clean air and water standards more than 1,000 times. Instead of going to trial, both sides settled a United States District Court-approved deal in March, 1998, resulting in Stone contributing more than $650,000 for local environmental projects. Out of this fund, $120,000 was earmarked for studies on air pollution in the Missoula Valley. A project was developed at this time to secure the money for funding. After several meetings with the Missoula City-County Health Department, the Missoula Valley Air Quality Advisory Council, Montana CHEER, Smurfit-Stone Container Corporation, and the Missoula County Board of Health during the summer of 1999, the project was refined, revised, and finally approved. The final title of this project is "The Missoula Valley Sampling Program," also known as "The 2000/2001 CMB."

1.2 Airborne Pollutants

All results and conclusions from this program began with the collection of the following airborne constituents: $PM_{2.5}$, semi-volatile organic compounds (SVOCs), and volatile organic compounds (VOCs). A particulate (or aerosol) is a suspension of fine solid or liquid containing many molecules held together by intermolecular forces. $PM_{2.5}$ is typically anthropogenic in origin, resulting either from condensation of hot combustion vapors or from the coagulation of nuclei particles and condensation of vapors onto existing particles resulting in a single unit in suspension. Particles can range in size from a few nanometers (nm) to tens of micrometers (μm). Particles less than 2.5 μm ($PM_{2.5}$) in aerodynamic diameter are generally referred to as "fine" and those between 2.5 μm and 10 μm in diameter are referred to as "coarse" particulate matter. The atmospheric lifetime of such particulates is on the order of days or weeks, allowing them to travel hundreds to thousands of kilometers. Fine particles have been implicated in human health effects. Recent studies have discussed the epidemiology (Dockery *et al.*, 1993; Heath *et al.*, 1995; Pope[1] *et al.*, 1995; Pope[2] *et al.*, 1995; Schwartz *et al.*, 1996; Laden *et al.*. 2000), potential causal mechanisms (Seaton *et al.*, 1995), and the controversy that surrounds the $PM_{2.5}$ health effects debate (Vedal, 1997).

A $PM_{2.5}$ particle can be composed of many different compounds and chemical species. An important component of particulate matter are organic (carbonaceous) compounds. Carbonaceous particles in the atmosphere consist of three components: organic carbon (OC), elemental (also known as soot, graphitic, black, or free) carbon (EC), and carbonates. Particulate organic carbon consists of thousands of separate compounds that contain more than 20 carbon atoms ($>C_{20}$), including *n*-alkanes, acids, waxy materials, and ringed structures (Rogge, *et al.*, 1993). Particulate organic carbon is emitted directly by sources, produced from condensation of low vapor pressure products of gas phase reactions of hydrocarbons onto existing atmospheric particles (secondary), or the reaction product of primarily emitted organic compounds with atmospheric oxidants. Elemental carbon contains pure, graphitic carbon, but also contains high molecular weight, dark-colored, non-volatile organic materials such as tar, biogenics, and coke. It is emitted directly into the atmosphere, predominantly from combustion processes. Carbonate carbon accounts for a negligible fraction of the total carbon in aerosol.

$PM_{2.5}$ is also composed of trace elements and ions. Oxides of aluminum, silicon, calcium, titanium, iron, and other metal oxides generally make up suspended dust, and depends on the geology and industrial processes in the area. Sulfate, in the form of ammonium sulfate ($(NH_4)_2SO_4$), ammonium bisulfate (NH_4HSO_4), and sulfuric acid

(H_2SO_4) are the most common forms of sulfate found in atmospheric fine particles. These water-soluble compounds can be produced from the oxidation of SO_2 gas to sulfate particles. Nitrate, in the form of ammonium nitrate (NH_4NO_3) is the most abundant nitrate compound resulting from a reversible gas / particle equilibrium between ammonia gas (NH_3), nitric acid gas (HNO_3), and particulate ammonium nitrate.

Compared to $PM_{2.5}$, SVOCs are compounds that can exist as either a gas or as a liquid / particle form based on the ambient conditions. One important subgroup of SVOCs are polycyclic aromatic hydrocarbons, or PAHs. PAHs are significant in that they were one of the first atmospheric species to be identified as being carcinogenic and / or mutagenic (Chrisp *et al.*, 1978; Eiceman and Vandiver, 1983; Nikolaou *et al.*, 1984). They are comprised of only carbon and hydrogen, and consist of two of more fused benzene rings in linear, angular, or cluster arrangements which possess substantial resonance energies.

VOCs denote the entire set of vapor phase atmospheric organics with the exception of carbon monoxide (CO) and carbon dioxide (CO_2). VOCs have been shown to be precursors for secondary fine organic carbon particles and also play a role in the formation of fine nitrate and sulfate particles (Darlington, 1997). Some VOCs may cause acute or chronic health problems. For example, benzene has been identified as a human carcinogen.

1.3 Methods of Source Apportionment

Although there are many types of models available to apportion sources of particulate matter (Seigneur *et al.*, 1999), two types of computer models are generally used. Receptor models use both chemical and physical characteristics of particles and gases measured at source and receptor to construct a "best fit" linear combination of source emissions to identify and quantify source contributions to receptor concentrations (Schauer *et al.*, 1996). Dispersion models, or source oriented models, use pollutant emission rate estimates, meteorological transport, and chemical transformation mechanisms to predict pollutant concentrations at the receptor locations (Glen *et al.*, 1996). These two types of models are complementary, with each type having strengths that compensate for the weaknesses of the other. Other models employed in source apportionment include the principal component analysis (Swietlicki *et al.*, 1996), positive matrix factorization models (Paterson *et al.*, 1999; Ramadan *et al.*, 2000), factor analysis (Hopke *et al.*, 1976; Henry and Hidy, 1979; Alpert and Hopke, 1980; Thurston and Spengler, 1985; Koutrakis and Spengler, 1987; Kavouras *et al.*, 2001; Park *et al.*, 2001;), and the artificial neural network model (Song and Hopke, 1996). The CMB air quality model is one of several receptor models, and is the type of model employed in this project. A more detailed description of its operation is given in Sections 2.11 and 2.12.

Chapter 2 Experimental Methods

$PM_{2.5}$, SVOCs, and VOCs were collected every 12 days at two locations in the Missoula Valley for an entire year. Chapter 2 discusses the methodologies for collecting samples, conducting analyses, and the Quality Assurance / Quality Compliance (QA/QC) procedures used in quantifying ambient levels of $PM_{2.5}$, SVOCs, and VOCs in the Missoula Valley airshed. A description of the CMB Model 8.0 is also given in Chapter 2. Table 2-1 summarizes these methodologies.

Table 2-1: CMB sampling, analysis, QA/QC, and computer modeling methodologies.

Sampling	
$PM_{2.5}$	40 CFR Part 50, Appendix L (EPA[1], 1997), 40 CFR Part 53, Subpart E, and 40 CFR part 58, Appendix A (EPA[2], 1997; EPA[3], 1997).
PUF (SVOCs)	Compendium Method TO-13A, Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography / Mass Spectrometry (GC/MS). January, 1999 (TO-13A, 1999).
VOCs	Modified Method TO-2, Method for the Determination of Volatile Organic Compounds in Ambient Air by Carbon Molecular Sieve Adsorption and Gas Chromatography / Mass Spectrometry (GC/MS). Revision 1.0, April, 1984 (TO-2, 1984).
Analyses	
$PM_{2.5}$ Gravimetric	EPA 40 CFR 50, Appendix L.
$PM_{2.5}$ Elemental	XRF Protocol Number 5.
$PM_{2.5}$ OC, EC, and TC	Thermal Optical Reflectance (TOR) Method.
$PM_{2.5}$ Anion and Cations	US EPA Method 300.0 and 200.7.
PUF (SVOCs)	Compendium Method TO-13A.
VOCs	Modified Method TO-2.
QA/QC – Sampling and Analyses	
$PM_{2.5}$	EPA QA Guidance Document "Field SOPs for the $PM_{2.5}$ Performance Evaluation Program," section 10 (EPA[1], 1998), EPA's QA Guidance Document 2.12 sections 7 and 10 (EPA[2], 1998), EPA "Guideline on Speciated Particulate Monitoring," section 6.0 and 7.0 (EPA[4], 1998)
PUF (SVOCs)	Compendium Method TO-13A.
VOCs	Modified Method TO-2.
Computer Modeling	
CMB	Chemical Mass Balance Receptor Model Version 8 (CMB8) User's Manual (Watson *et al.*, 1997).

2.1 Sampling Locations

Two sampling locations were used to collect data for the Missoula Valley Sampling Program (Figure 2-1), with one site located on the east side of the Missoula Valley (Boyd Park) and the other site on the west side (Frenchtown). Boyd Park is located at 3100 Washburn Street, a residential area on Missoula's south end only 6 blocks south of "Malfunction Junction," one of the busiest intersections in Missoula (see Figure 2-2). This site was an established sampling site used by the Montana Department of Environmental Quality (DEQ) for $PM_{2.5}$ compliance monitoring. The second sampling site was located in Frenchtown at the Frenchtown Fire Department parking lot on the corner of Marion and Ducharme (See Figure 2-3). Unlike the already established Boyd Park sampling location, the Frenchtown site had to be installed. Scaffolding was purchased to serve as the sampling platform, and electricity was wired to the sampling platform before sampling could begin. Both the Boyd Park and Frenchtown sampling sites met the spatial criteria between samplers as specified in the EPA's Network Design and Optimum Site Exposure Criteria for Particulate Matter (EPA[2], 1987) and 40 CFR Part 58, Appendix D (EPA[3], 1997).

Figure 2-1: Missoula Valley sampling locations.

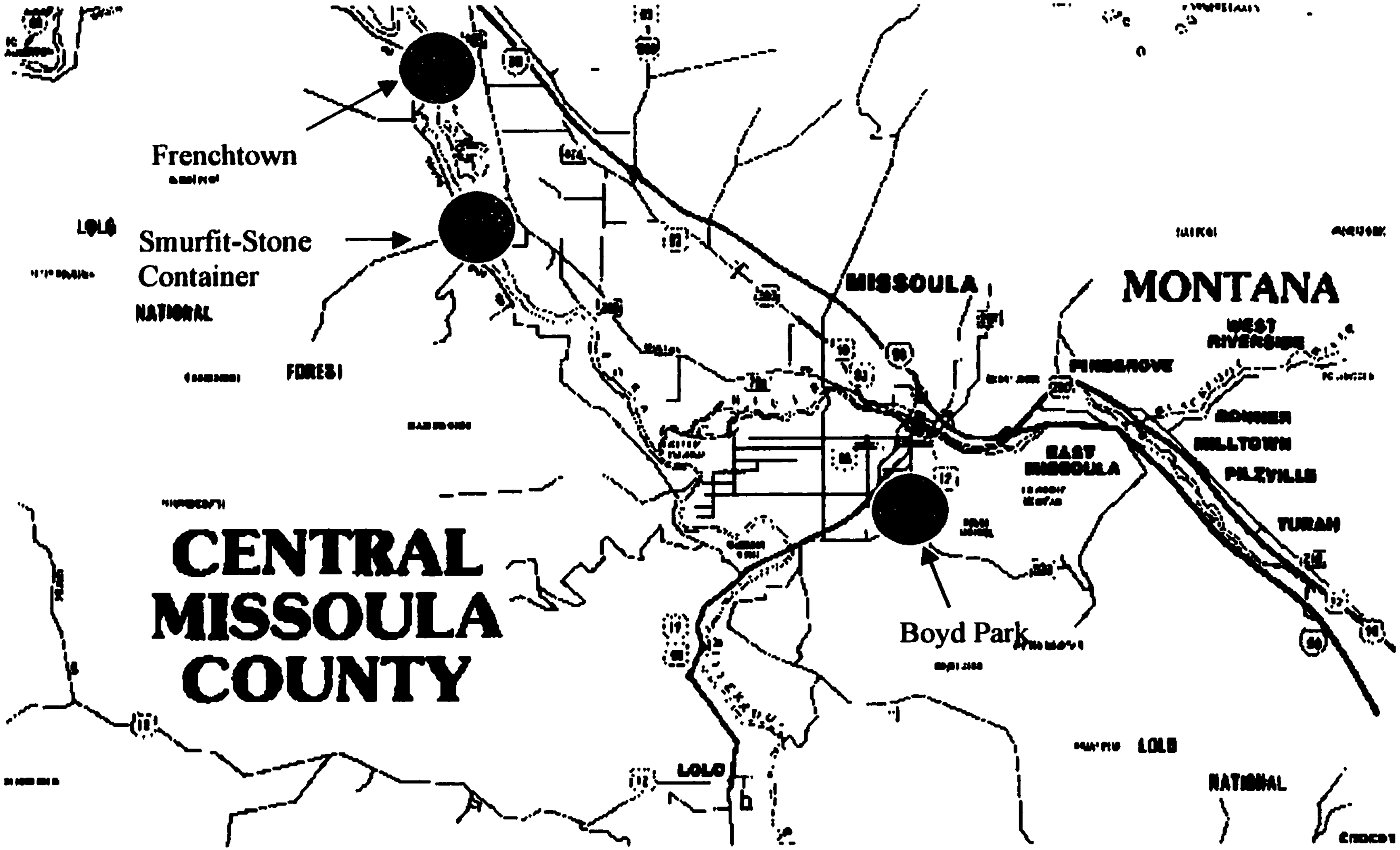


Figure 2-2: Boyd Park sampling site.

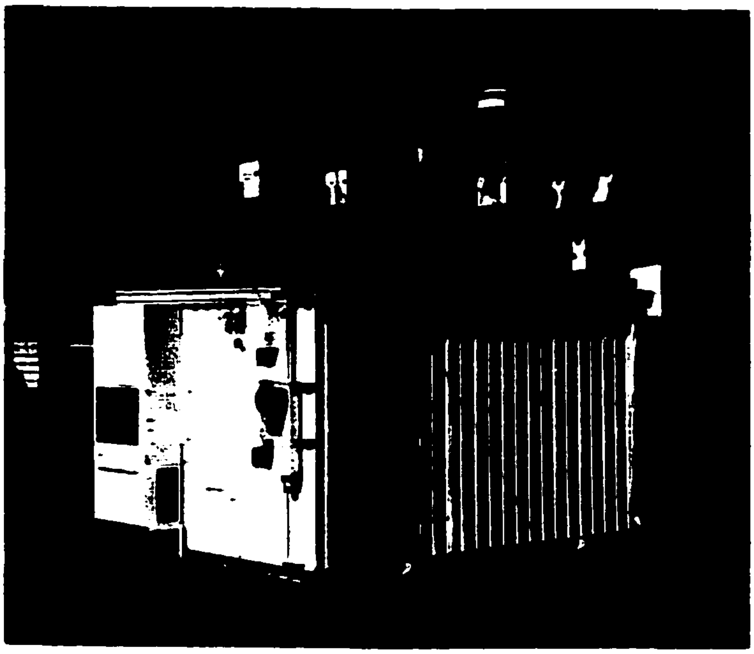
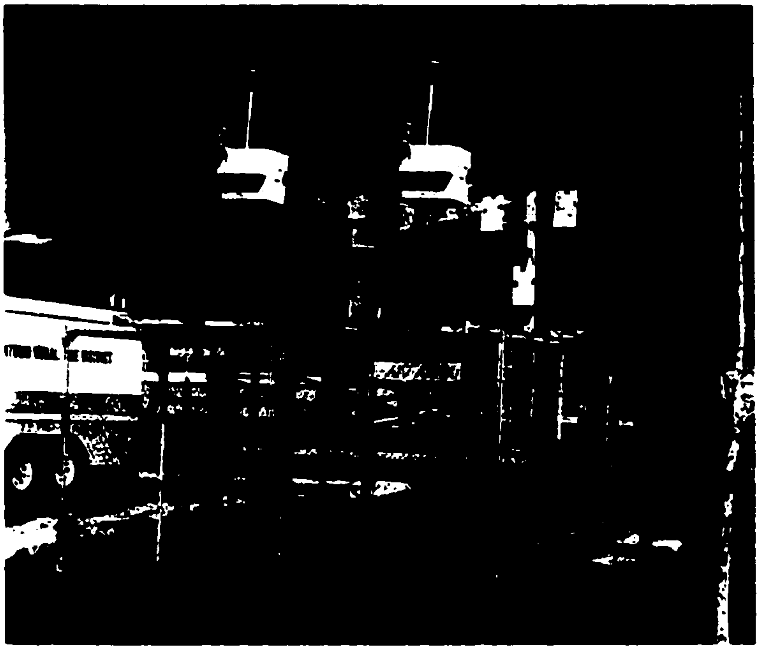


Figure 2-3: Frenchtown sampling site.



2.2 *$PM_{2.5}$ Sampling - CMB*

2.2.1 Summary

$PM_{2.5}$ sampling was conducted every 12 days during the yearlong sampling program (see Figure 2-4). During each CMB sampling event at Boyd Park and Frenchtown, two $PM_{2.5}$ samplers ran simultaneously over a 24 hour time period starting at midnight and ending at midnight the next day. Using a 47 mm filter media, air was drawn at a controlled flow rate of 16.67 Liters Per Minute (LPM) through a specially designed particle-size discriminating WINS (Well Impactor Ninety-Six) $PM_{2.5}$ inlet. Approximately 24,000 liters of sample was collected during each sample run. Because all analyses cannot be conducted on a singular type of filter media, one $PM_{2.5}$ sampler employed a quartz glass filter and the other $PM_{2.5}$ sampler used a Teflon filter. Data generated by the CMB sampling was used in the EPA Version 8.0 CMB Model to determine the sources of $PM_{2.5}$ in the Missoula Valley.

2.2.2 $PM_{2.5}$ Sampler and Media Description

There are several types of $PM_{2.5}$ samplers, however, the model used in the Missoula Valley Sampling Program was the BGI PQ200 Ambient $PM_{2.5}$ Federal Reference Method (FRM) Sampling System (see Figure 2-5). The PQ200 employs a WINS (Well Impactor-Ninety Six) based on the principle of direct impaction. During sampling, both 47 mm quartz glass and Teflon filters were used. All $PM_{2.5}$ filters (both quartz glass and Teflon) were purchased from Chester LabNet, an environmental laboratory in Tigard, Oregon. Before receipt of each batch of new and cleaned filters, the quartz glass filters (47 mm Whatman QMA) were prefired (baked for 6 hours at 800

°C) to eliminate existing organics. Teflon filters were stored for one month in a controlled environment, followed by one week of equilibration in the weighing environment, and then weighed in a temperature and humidity controlled environment before initial weights were taken to decrease the variability in the masses. All filters from Chester LabNet were subjected to their in-house QA/QC standards before being certified.

In handling all $PM_{2.5}$ filters, clean Teflon forceps were used. These forceps were cleaned using the following procedure: 1) initial wash with soap and hot water 2) rinse with hot water 3) rinse with deionized water 4) solvent rinse with 10% diethyl ether in hexane 5) solvent rinse with acetone 6) final solvent rinse with hexane. Clean quartz filters were stored in a freezer, while Teflon filters were stored at room temperature in labeled, individual containers before use. All quartz and Teflon $PM_{2.5}$ filters were examined for discoloration, pinholes, tears, and other abnormalities before being loaded into $PM_{2.5}$ cassettes at The University of Montana laboratory prior to sampling. All $PM_{2.5}$ samples were transported to and from the field in an ice chest, with filters kept cold during transport at all times. After the samples were brought back to The University of Montana laboratory, all filter samples were stored in a freezer until shipment to the contracted laboratories for analysis.

Figure 2-4: Missoula Valley Sampling Program schedule.

March 2000

Sun.	Mon.	Tues.	Wed.	Thurs.	Fri.	Sat.
			1	2	3	4
5	6	7	8	9	10	11
12	13	14	15	16	17	18
19	20	21	22	23	24	25
26	27	■	29	30	31	

April 2000

Sun.	Mon.	Tues.	Wed.	Thurs.	Fri.	Sat.
						1
2	3	4	5	6	7	8
■	10	11	12	13	14	15
16	17	18	19	20	■	22
23	24	25	26	27	28	29
30						

May 2000

Sun.	Mon.	Tues.	Wed.	Thurs.	Fri.	Sat.
	1	2	■	4	5	6
7	8	9	10	11	12	13
14	■	16	17	18	19	20
21	22	23	24	25	26	■
28	29	30	31			

June 2000

Sun.	Mon.	Tues.	Wed.	Thurs.	Fri.	Sat.
				1	2	3
4	5	6	7	■	9	10
11	12	13	14	15	16	17
18	19	■	21	22	23	24
25	26	27	28	29	30	

July 2000

Sun.	Mon.	Tues.	Wed.	Thurs.	Fri.	Sat.
						1
■	3	4	5	6	7	8
9	10	11	12	13	■	15
16	17	18	19	20	21	22
23	24	25	■	27	28	29
30	31					

August 2000

Sun.	Mon.	Tues.	Wed.	Thurs.	Fri.	Sat.
		1	2	3	4	5
6	■	8	9	10	11	12
13	14	15	16	17	18	■
20	21	22	23	24	25	26
27	28	29	30	■		

September 2000

Sun.	Mon.	Tues.	Wed.	Thurs.	Fri.	Sat.
					1	2
3	4	5	6	7	8	9
10	11	■	13	14	15	16
17	18	19	20	21	22	23
■	25	26	27	28	29	30

October 2000

Sun.	Mon.	Tues.	Wed.	Thurs.	Fri.	Sat.
1	2	3	4	5	■	7
8	9	10	11	12	13	14
15	16	17	■	19	20	21
22	23	24	25	26	27	28
29	■	31				

November 2000

Sun.	Mon.	Tues.	Wed.	Thurs.	Fri.	Sat.
			1	2	3	4
5	6	7	8	9	10	■
12	13	14	15	16	17	18
19	20	21	22	■	24	25
26	27	28	29	30		

December 2000

Sun.	Mon.	Tues.	Wed.	Thurs.	Fri.	Sat.
					1	
3	4	■	6	7	8	9
10	11	12	13	14	15	16
■	18	19	20	21	22	23
24	25	26	27	28	■	30
31						

January 2001

Sun.	Mon.	Tues.	Wed.	Thurs.	Fri.	Sat.
	1	2	3	4	5	6
7	8	9	■	11	12	13
14	15	16	17	18	19	20
21	■	23	24	25	26	27
28	29	30	31			

February 2001

Sun.	Mon.	Tues.	Wed.	Thurs.	Fri.	Sat.
				1	2	■
4	5	6	7	8	9	10
11	12	13	14	■	16	17
18	19	20	21	22	23	24
25	26	■	28			

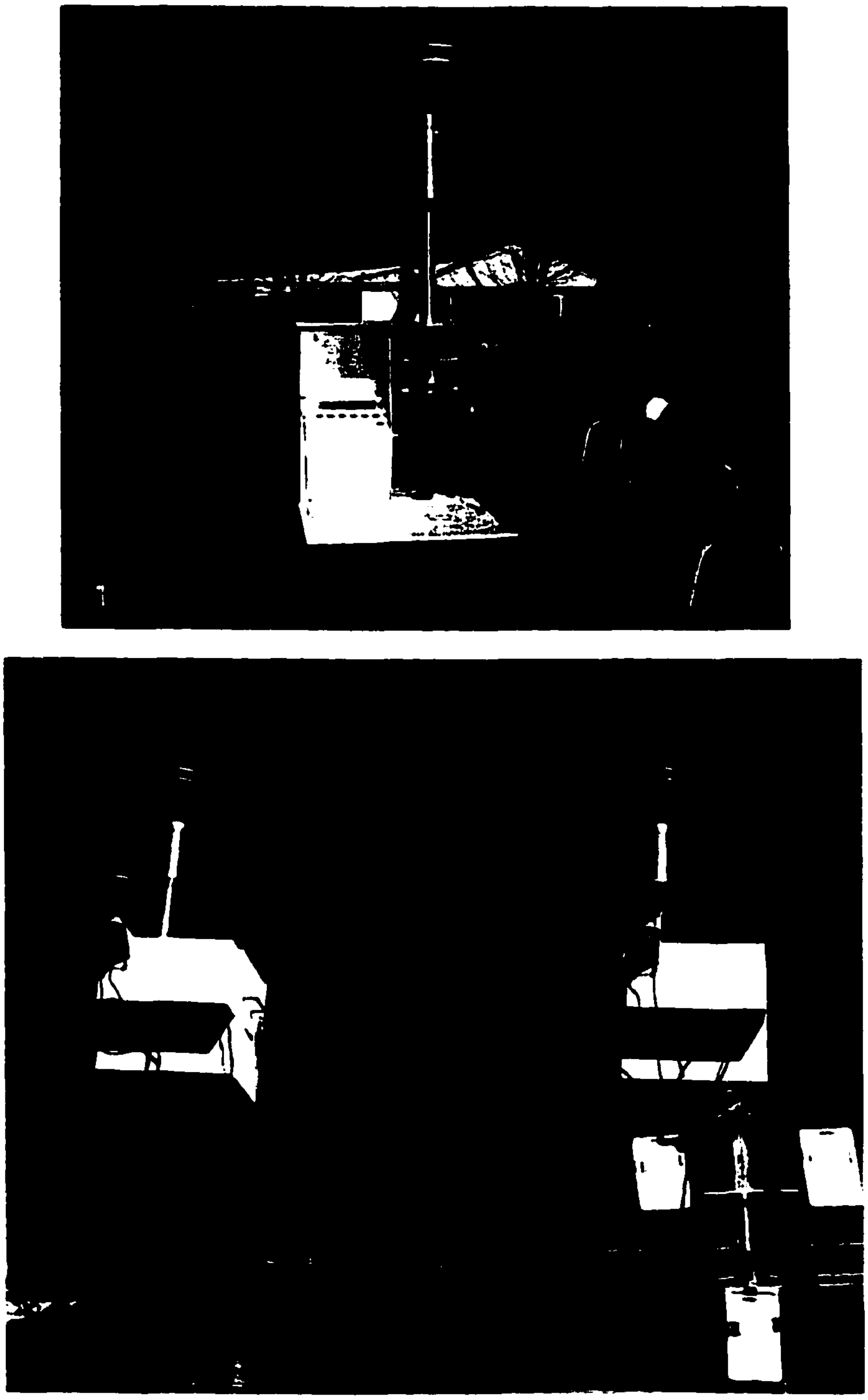
March 2001

Sun.	Mon.	Tues.	Wed.	Thurs.	Fri.	Sat.
				1	2	3
4	5	6	7	8	9	10
■	12	13	14	15	16	17
18	19	20	21	22	■	24
25	26	27	28	29	30	31

CMB Sampling - Boyd Park and Frenchtown

■ **Research Sampling - Frenchtown**

Figure 2-5: PM$_{2.5}$ samplers.



2.2.3 Conducting a Sample Run

Before collection of sample, the PQ200 $PM_{2.5}$ samplers had to successfully pass the leak check, barometric pressure, temperature (ambient and filter), and flow rate verifications. $PM_{2.5}$ data sheets were filled out documenting date, time, weather conditions, etc., for each sampling event. On the day of sampling, each PQ200 was visually checked to verify that they were functioning properly and to document any unusual conditions that might bias the samples (ex. weather conditions, sampler malfunction, etc.). The filters were retrieved on the day following the sampling event, and the run data parameters (pressure, temperature, and flows) were downloaded from the memory of the PQ200 using a BGI Datatrans downloader.

2.2.4 $PM_{2.5}$ Batch Shipment to Contracted Laboratory

$PM_{2.5}$ samples were held for three CMB sample runs before being shipped as a batch to the contracted laboratory. Each "batch" of samples was shipped within 30 days of the oldest sampling run. $PM_{2.5}$ samples were packaged in plastic Millipore containers during shipment and padded with bubble wrap to avoid vibrations which could have dislodged particles on the filters. Filter surfaces did not touch the interior surfaces of the protective container. The filter samples were shipped in an ice chest provided by the contracted laboratory and kept cool by placing leak-proof ice substitutes inside the cooler. Chain-of-custody sheets were also sent with each sample shipment.

2.3 $PM_{2.5}$ Analyses - CMB

2.3.1 Summary

All $PM_{2.5}$ filter samples collected during CMB sampling were sent to Chester LabNet in Tigard, Oregon for analyses. From the Teflon filter samples, gravimetric and elemental analyses were performed. From the quartz glass filter samples, OC, EC, TC, and ion analyses were conducted.

2.3.2 Gravimetric Analysis

Particulate mass concentration is the most commonly made measurement on $PM_{2.5}$ samples, and is used to determine compliance with $PM_{2.5}$ standards. Gravimetry measures the net mass on a Teflon filter by weighing the filter before and after sampling with a microbalance in a temperature and relative humidity controlled laboratory environment. $PM_{2.5}$ reference methods require that filters be equilibrated for 24 hours at a constant (within ±5%) relative humidity between 30% and 40% and at a constant (within ±2 °C) temperature between 20 °C and 23 °C to minimize particle volatilization and aerosol liquid water bias (EPA[3], 1998).

2.3.3 Elemental Analysis

Photon-induced X-Ray Fluorescence (XRF) of $PM_{2.5}$ Teflon filter samples was used to determine concentrations of elements ranging from atomic number 11 (sodium) through 92 (uranium). The following 36 trace elements were analyzed for:

aluminum
silicon
phosphorus
sulfur
chlorine
potassium
calcium
germanium
titanium
vanadium
chromium
manganese
iron
nickel
cobalt
copper
zinc
gallium
arsenic
selenium
bromine
rubidium
strontium
yttrium
zirconium
molybdenum
palladium
silver
cadmium
indium
tin
antimony
barium
lanthanum
mercury
lead

In XRF, the filter deposit is irradiated by high energy X-rays (XRF) which then eject inner shell electrons from the atoms of each element in the sample. A fluorescent X-Ray photon is released when a higher energy electron drops back down into the vacant lower energy orbital. The energy of this photon is unique to each element, and the number of photons is proportional to the concentration of the element. Concentrations are quantified by comparing photon counts for a sample with those obtained from thin-film standards of a known concentration.

2.3.4 Anions / Cations Analysis

The $PM_{2.5}$ quartz glass filters were analyzed by Ion Chromatography (IC) for anions (fluoride, chloride, nitrate, and sulfate) and cations (ammonium, magnesium, calcium, potassium, and sodium). This analysis was originally performed by Edglo Laboratories of Fort Wayne, Indiana. After getting high concentrations of chlorides and sulfates on our blank samples, we discovered that Edglo Laboratories was contaminating the $PM_{2.5}$ samples through their method of extracting the $PM_{2.5}$ filter during the analysis. Consequently, we began using Chester LabNet for the ion analyses about half way through the sampling program. In conducting the ion analyses, samples were extracted in deionized water, which were filtered to remove suspended insoluble residues or particulate matter prior to analysis. The extract was then analyzed by Ion Chromatography (IC).

2.3.5 OC, EC, and TC Analyses

In the Thermal Optical Reflectance (TOR) analysis, the quartz filter sample is first heated gradually from ambient temperature to 500 °C in a pure helium atmosphere causing organic compounds in the sample to volatize. The filter is then exposed to an oxidizing atmosphere (2% oxygen, 98% helium) and the temperature is ramped from 550 to 800 °C. The carbon that evolves at each temperature in both steps is subsequently converted to methane and measured by a flame ionization detector (FID). Throughout the analysis, the filter sample reflectance is monitored. During volatilization, this reflectance usually decreases in the helium atmosphere due to the pyrolysis of the organic material, then increases when the oxygen is added and the light-absorbing EC is oxidized and removed from the sample. The material that evolves from the beginning of the process until the sample reflectance, after passing through its minimum, returns to its original value is the OC. The organic material that evolves after this point is defined as the EC (light absorbing carbon).

2.4 QA/QC Program – $PM_{2.5}$ Sampling and Analyses

2.4.1 Summary

QA/QC integrates quality control, quality auditing, measurement method validation, and sample validation into the measurement process. The results of quality assurance are data values with specified precisions, accuracies, and validities.

2.4.2 $PM_{2.5}$ Filter Blanks

Field blanks are conditioned, unsampled filters used to determine whether contamination occurs during sampling. Field blanks were transported to the sampling site, momentarily installed in the $PM_{2.5}$ sampler, removed, and then taken back to The University of Montana laboratory to monitor for sampling artifacts. Two field blanks (one $PM_{2.5}$ Teflon filter and one $PM_{2.5}$ quartz glass filter) were collected for every batch of samples shipped to the contracted laboratory (every 3 CMB sampling events).

Trip blanks were used during shipment of the samples to the contracted laboratory to monitor for artifacts during the shipping process. These samples were not sent to the field. Trip blanks (one $PM_{2.5}$ Teflon and one $PM_{2.5}$ quartz glass per batch shipment) were used in the beginning of the sampling period. However, after no significant levels of contaminants were found in the method of sample shipment to the contracted laboratory, the use of trip blanks was suspended.

2.4.3 $PM_{2.5}$ Sampler Verification and Calibration

In conducting $PM_{2.5}$ sampling, the barometric pressure, ambient and filter temperatures, and flows were all initially calibrated and later verified with National Institute of Standards and Technology (NIST) traceable standards. For the Frenchtown $PM_{2.5}$ samplers, barometric pressure, ambient temperature, and filter temperatures were initially calibrated in the laboratory, with a full multipoint flow calibration conducted at Frenchtown upon installation. The Boyd Park samplers were maintained (calibrated and verified) by the Montana DEQ. Field performance checks (verifications) were conducted for pressure, ambient temperature, filter temperature, and flows to verify that the sensor calibrations had not drifted since the initial calibration. Also, a leak check had to be passed prior to each sampling event at Frenchtown. Only if the sampler sensor reading was not acceptable would a multipoint calibration be conducted. During the yearlong sampling program at Frenchtown, only the flows had to be recalibrated due to ambient temperature fluctuations throughout the year. All data and calculations were recorded in calibration logbooks, with separate logbooks kept for each of the $PM_{2.5}$ samplers at Frenchtown. The Montana DEQ maintains the Boyd Park calibration and verification data sheets.

2.4.4 $PM_{2.5}$ Sampler Performance Evaluations – Quarterly Audits

40 CFR Part 58, Appendix A requires that reporting organizations assess, on a calendar quarterly basis, the flow rate accuracy of each primary (data-reporting) $PM_{2.5}$ sampler used in their monitoring networks by conducting an audit of each sampler's operational flow rate. Auditing is performed by a quality assurance officer who is

independent of the normal sampling activities at the site. For the Missoula Valley Sampling Program, quarterly audits were conducted by the Montana DEQ. During these audits, a leak check was conducted, and the sampler flow rate, temperature (both filter and ambient), and barometric pressure were all verified.

The audits of the $PM_{2.5}$ sampler's flow rate consisted of one measurement made at the sampler's operational flow rate (16.67 LPM). The flow rate transfer standard used in the audit was not the same one used to verify or calibrate the samplers during the sampling program, however it was traceable to a primary standard. The barometric pressure and temperature verification devices used by the DEQ were traceable to standards as well.

2.4.5 Contracted Laboratory QA/QC Plan

Prior to the startup of this program, Chester LabNet submitted their laboratory QA/QC procedures to The University of Montana. The QA/QC plan was incorporated into the document "Study Design for the Sampling and Analysis of $PM_{2.5}$, Volatile Organic Compounds (VOCs), and Semi-Volatile Organic Compounds (SVOCs) in the Missoula Valley" (Ward, 1999). These QA/QC procedures were followed in conducting the $PM_{2.5}$ analyses.

2.5 PUF Sampling - CMB

2.5.1 Summary

In addition to the two $PM_{2.5}$ samplers installed at Boyd Park and Frenchtown, Polyurethane Foam (PUF) samplers were used to collect Total Suspended Particulates (TSPs) and Semi - Volatile Organic Compounds (SVOCs). The main objective of the PUF sampling program was to determine the concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) in the Missoula Valley airshed. Sampling was conducted over the same 24 hour time period as $PM_{2.5}$ sampling (midnight to midnight) to obtain average daily levels of SVOCs. PUF sampling at Boyd Park and Frenchtown was conducted every 12 days for CMB sampling, with approximately 300 m^3 of air drawn through the filter and PUF plug during the 24-hour sampling period at a controlled flow rate of approximately 0.225 m^3/min.

2.5.2 PUF Sampler and Media Description

The Andersen Model GPS1-1 PUF Hi-vol Sampling System (See Figure 2-6) is designed to simultaneously collect airborne organic vapors as well as suspended airborne particulates. The PUF sampler uses a dual chambered aluminum sampling module which contains a circular quartz filter followed downstream by a PUF plug. In this module, the upper chamber contains the 102 mm quartz glass filter in a circular filter holder, with the lower chamber holding a 65-mm O.D. (60-mm I.D.) x 125-mm borosilicate glass sorbent cartridge which contains the PUF plug for vapor entrapment. The PUF plug traps gaseous SVOCs. which otherwise would revolatize from the quartz filter before they could be analyzed in the lab. Two PUF samplers were rented from Envirocon of Missoula, Montana for this sampling program.

PUF filters and plugs were loaded into the modules at The University of Montana laboratory, and shipped to and from the sampling sites in an ice chest. All clean filters and PUF plugs were kept in a freezer before loading. In the handling of the quartz filters, Teflon forceps were cleaned using the following procedure: 1) initial wash with soap and hot water 2) rinse with hot water 3) rinse with deionized water 4) solvent rinse with 10% diethyl ether in hexane 5) solvent rinse with acetone 6) final solvent rinse with hexane. A pair of clean tongs were used to insert the PUF plugs into the glass cartridge. The PUF modules were always rinsed with hexane before being loaded with the sample media.

2.5.3 Conducting a Sample Run

Just prior to taking the PUF sample modules into the field for sampling, surrogate compounds (field surrogates) were added to the center of the PUF plug. Surrogate compounds are chemically inert compounds which are not expected to be found in the sample. Using a microsyringe, 20 µl of a 50 µg/ml surrogate solution was spiked onto the PUF plug to yield a final concentration of 1 µg. The field surrogates added were d_{10} -fluoranthene and d_{12} –benzo(a)pyrene.

Figure 2-6: PUF samplers.

Before collection of the sample, the PUF samplers had to successfully pass a leak check. Next, the PUF sampler motor was allowed to warm up by installing a dummy module which contained the same type of filter and PUF plug and turning the sampler on.

After ten minutes, the flow was then adjusted (as read by a magnehelic gauge) to the desired flow setting as determined from the calibration curve generated during the multipoint calibration. The dummy module was then replaced with the sample module, and the PUF sampler was turned on again to verify that the flow was still at the desired setting. The sampler was then turned off, and a time wheel was set to have the sampler turn on at midnight and turn off at midnight. The initial time (as read from a counter on the PUF sampler) was then recorded before sampling began.

Mid sampling flow checks were recorded on the day of sampling. Also, weather conditions and any visible sources of air pollution were recorded. In recovering the samples, the PUF sampler was turned on for approximately 5 minutes to obtain a final flow reading and the final time as read from the PUF sampler was recorded. The beginning, mid, and final flows were averaged to calculate the actual flow rate during sampling.

Samples were then transported back to The University of Montana laboratory in a cooler. A cover was kept on the top of the PUF module to protect the filter while hexane rinsed aluminum foil covered the bottom of the PUF module during transport to eliminate loss of sample. The PUF plug samples were stored in a glass container with Teflon lid, with the quartz glass filter samples kept in clean large glass petri dishes. All samples were kept in the freezer until analysis.

2.6 PUF Analyses - CMB

2.6.1 Summary

All PUF analyses were conducted at The University of Montana laboratory. The PUF filter and plug were extracted together in a Soxhlet apparatus using a solvent combination of diethyl ether and hexane. The extract was concentrated using a Kuderna-Danish (K-D) evaporator prior to analysis by Gas Chromatography / Mass Spectrometry (GC/MS). Samples were extracted within 10 days of sampling, with extracts analyzed by GC/MS within approximately 60 days of extraction. A suite of 61 SVOCs were originally quantified, but this list was later refined to the 19 highlighted compounds:

Phenol
Bis (2-chloroethyl) ether
2-Chlorophenol
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,2-Dichlorobenzene
2-Methylphenol
Bis (2-chloroisopropyl) ether
4-Methylphenol
N-Nitrosodi-n-propylamine
Hexachloroethane
Nitrobenzene
Isophorone
2-Nitrophenol
2,4-Dimethylphenol
Bis (2-chloroethoxy) methane
2,4-Dichlorophenol
1,2,4-Trichlorobenzene
Naphthalene
4-Chloroaniline
Hexachlorobutadiene
4-Chloro-3-methylphenol
2-Methylnaphthalene
Hexachlorocyclopentadiene
2,4,6-Trichlorophenol
2,4,5-Trichlorophenol
2-Chloronaphthalene
2-Nitroaniline
Dimethyl phthalate
Acenaphthylene
3-Nitroaniline
Acenaphthene
4-Nitrophenol
Dibenzofuran
2,4-Dinitrotoluene
Diethyl phthalate
4-Chlorophenyl phenyl ether
Fluorene
4-Nitroaniline
2-Methyl-4,6-dinitrophenol
Azobenzene
4-Bromophenyl phenyl ether
Hexachlorobenzene
Pentachlorophenol
Phenanthrene
Anthracene
Carbazole
Di-n-butyl phthalate
Fluoranthene
Pyrene
Butyl benzyl phthalate
Benzo(a)anthracene
Bis (2-ethylhexyl) phthalate
Chrysene
Di-n-octyl phthalate
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Indeno(1,2,3-cd)pyrene
Dibenzo(a,h)anthracene
Benzo(ghi)perylene

2.6.2 Cleaning of PUF Sampling Media

102 mm quartz glass PUF filters and PUF plugs were purchased from Tisch Environmental (Village of Cleaves, Ohio) and had to be cleaned at The University of

Montana laboratory. Before sampling, filters were baked in a muffle furnace at 400 °C for 5 hours and then placed in large glass petri dishes. The PUF plugs were Soxhlet extracted overnight with acetone for 16 hours at approximately 4 cycles per hour for initial cleanup. The cleaned PUF plugs were kept in glass containers with Teflon lids. Both filters and PUF plugs were stored in a freezer until use. Towards the end of the sampling program, PUF plugs were reused. These plugs were cleaned by Soxhlet extraction overnight with 700 ml of a 10 percent diethyl ether in hexane solution for 18 hours at approximately 4 cycles per hour.

2.6.3 Sample Extraction and Concentration

The PUF filter and plug samples were extracted together in the Soxhlet apparatus in order to reach detection limits, avoid questionable interpretation of the data, and minimize costs. Before the extraction began, 20 µl of a 50 µg/ml laboratory surrogate standard solution was spiked onto the sample to yield a final concentration of 1 µg. The laboratory surrogate standards used were d_{10} -fluorene and d_{10}-pyrene.

Samples were extracted in 700 ml of a 10 percent diethyl ether in hexane solution. The Soxhlet apparatus refluxed overnight for 18 hours at a rate of at least 3 cycles per hour. After being cooled, the extract was dried by passing it though a drying column containing about 10 grams of anhydrous sodium sulfate. 100 ml of the 10 percent diethyl ether / hexane solution was used as a wash to complete the quantitative transfer into a K-D concentrator with 10 ml concentrator tube. When the liquid was evaporated to an approximate volume of 5 ml, the K-D apparatus was removed from the water bath and the solvent was allowed to drain for at least 5 minutes while cooling.

The K-D flask was then washed with 5 ml of cyclohexane, and further concentrated to 1.0 ml by nitrogen blowdown. The internal wall of the concentrator was rinsed down several times with hexane during the nitrogen blowdown. The final extract was then transferred to an amber vial with Teflon septa and stored in a refrigerator until analysis.

2.6.4 Standard Preparation

In the beginning of the SVOC analysis program, a PAH standard mix containing 19 compounds was used for quantitation of compounds in the sample extracts. Later, the analysis was improved by using a different SVOC standard mix that contained 61 compounds, including the initial 19 PAHs. Using these SVOC stock mixes, a series of calibration standards were generated. The concentrations of these standards were 2.50 ng/µl, 1.25 ng/µl, 0.50 ng/µl, 0.25 ng/µl, and 0.10 ng/µl. The stock standard solutions and standards were kept in amber vials with Teflon septa and stored in a refrigerator. New standards were prepared before each set of sample extracts were analyzed by GC/MS.

2.6.5 Internal Standards

Before the GC/MS analysis, each 1 ml aliquot of the five calibration standards and sample extracts were spiked with deuterated internal standards to yield a final concentration of 0.5 ng/µl. The following internal standards were used for this procedure: d_8 –naphthalene, d_{10} –acenaphthene, d_{10} –phenanthrene, d_{12} –chrysene, and

d_{12} –perylene. These compounds were selected because they were similar in analytical behavior to the compounds of interest in the samples:

d_{12} -perylene
Benzo(e)pyrene
Benzo(a)pyrene
Benzo(k)fluoranthene

d_{12} -chrysene
Benz(a)anthracene
Chrysene
Pyrene

d_8 -naphthalene
Naphthalene

d_{10} -acenaphthene
Acenaphthene
Acenaphthylene
Fluorene
Benzo(g,h,i)perylene
Dibenz(a,h)anthracene
Indeno(1,2,3-cd)pyrene
Perylene
Benzo(b)fluoranthene
Coronene

d_{10} -phenanthrene
Anthracene
Fluoranthene
Phenenthrene

In making up the original internal standard mix, d_8 –naphthalene, d_{10} –acenaphthene, d_{12} –chrysene, and d_{12} –perylene were used. However, d_{12} –perylene had a poor response in the mass spectrum because it came out so late in the run and interfered with the rising baseline due to increasing temperatures. Therefore it was replaced with d_{10} –phenanthrene which had an earlier retention time and came out before the rise in baseline. The response from the internal standards were used in the quantitation of the target analytes by using the target response relative to the calibration curve.

2.6.6 Instrument Description

All SVOC analyses were conducted at The University of Montana laboratory. Two different kinds of GC/MSs were used for this analysis. The first was a Hewlett Packard GCD 5890 series II Gas Chromatograph with 5973 Mass Spectrometer. The second GC/MS was a Hewlett Packard 6890 series Gas Chromatograph with a 5973 Mass Spectrum Detector (MSD). Analyte separations were accomplished on a 0.32 mm ID X 30.0 meter Restek XTI-5 column. Sample extracts were analyzed using the instrument conditions and temperature program in Table 2-2.

Table 2-2: GC/MS instrument operating conditions – SVOC analysis.

Inlet Temperature	220 °C
Detector Temperature	270 °C
Injection Mode	Splitless
Initial Oven Temperature	40 °C
Initial Oven Hold	4.0 minutes
Oven Ramp Rate 1	10 °C / minute
Oven Ramp Final Temp 1	300 °C
Oven Ramp Rate 1 Final Time	5.0 minutes
Oven Ramp Rate 2	10 °C / minute
Oven Ramp Final Temp 2	330 °C
Oven Ramp Rate 2 Final Time	2.0 minutes
Total Run Time	40.0 minutes
Carrier Gas	Helium
Flow	1.0 ml / minute

2.7 QA/QC Program – PUF Sampling and Analyses

2.7.1 Field Surrogates

Immediately before field deployment, 20 μl of a 50 μg/ml field surrogate solution was spiked onto the PUF plug to yield a final concentration of 1 μg. The recovery of the field surrogate standard was used to monitor for matrix effects, breakthrough, sampling errors, etc. The field surrogates used were d_{10} -fluoranthene and d_{12} –benzo(a)pyrene. After the sample analysis, the field surrogate recovery was determined, with acceptable limits between 60-120%.

2.7.2 Field Blanks

During each CMB sampling episode, at least one PUF cartridge and filter were shipped to the field and returned to the laboratory. This sample served as the field blank.

2.7.3 PUF Sampler Flow Verification and Calibration

Calibration of the PUF sampler flow rates were performed without a PUF plug or filter in the sampling module. A multipoint calibration was conducted after initial placement in the field, after major repairs or maintenance, and whenever any audit point deviated from the calibration curve by more than 7 percent. For the PUF sampler calibrations, an orifice transfer standard with calibration traceable to NIST was used. Initially, the orifice transfer standard was certified against a positive displacement rootsmeter by Tisch Environmental on 12/22/99, and later recertified on 12/11/00.

Using this certified orifice transfer standard, the PUF samplers at both Boyd Park and Frenchtown were calibrated. The flow rate through the orifice was determined by the pressure drop caused by the orifice as measured by a "U" tube water manometer. A single point flow verification was conducted before and after each sampling event to track the sampler's calibration stability. A control chart for both the Frenchtown (Scooter) and the Boyd Park (Archie) samplers was kept to track the percentage difference between the sampler's indicated and measured flow rates. This chart provided a quick reference of sampler flow-rate drift problems and was useful for tracking the performance of the sampler.

2.7.4 PUF Sampler Performance Evaluations – Quarterly Audits

A quality assurance officer independent of the normal sampling activities performed the PUF quarterly audits. For the Missoula Valley Sampling Program, quarterly audits were conducted by the Montana DEQ. During these audits, the PUF sampler flow rates were verified at both Boyd Park and Frenchtown by conducting a single point audit without a PUF plug or filter in the sampling module. If any audit point deviated from the calibration curve by more than 10 percent, the PUF sampler failed the audit. For the PUF audits, the Missoula Valley Sampling Program orifice transfer standard was used because the DEQ did not have access to one. This orifice transfer standard was NIST traceable, with initial calibration by Tisch Environmental on 12/22/99 and recertification on 12/11/00.

2.7.5 Lab Surrogates

Just before the extraction of the PUF sample filter and plug, 20 µl of a 50 µg/ml laboratory surrogate standard solution was spiked into the sample to yield a final concentration of 1 µg in order to monitor for unusual matrix effects, gross sample processing errors, etc. The lab surrogates used were d_{10} -fluorene and d_{10} -pyrene. Surrogate recovery was evaluated for acceptance by determining if the measured concentration fell within the acceptance limits of 60-120% recovery.

2.7.6 PUF Batches

To determine how many cleaned PUF plugs would be needed during the sampling program, the analyses were divided into batches, with each batch consisting of 20 cleaned

PUF plugs. For each batch, a PUF batch certification, solvent blank, lab method blank, and laboratory control spike were analyzed. The remainder of the cleaned PUF plugs were used in sampling.

2.7.7 PUF Batch Certification

To verify that each batch of clean PUF cartridges was free of background contaminants prior to sampling, each batch had to be certified. For this certification, one PUF plug and quartz glass filter were Soxhlet extracted, concentrated, and then analyzed by GC/MS. For the batch to be acceptable, each target PAH analyte had to be less than the detection limit requirements. In general, the following guidelines were used in determining whether a PUF plug batch was acceptable for sampling:

• Naphthalene	<500 ng/cartridge
• Other PAHs	<200 ng total/cartridge

Cartridges were considered clean for up to 30 days from date of certification when sealed in their containers.

2.7.8 Solvent Blanks

Solvent blanks were used to monitor for laboratory and solvent contamination. For each solvent blank analysis, a Soxhlet extraction and evaporation procedure was conducted without a PUF plug or filter. No contaminants were discovered in the solvent after the first few solvent blank analyses, so the use of solvent blanks was suspended after the first few batches.

2.7.9 Laboratory Method Blanks (LMB)

Lab method blanks were used to monitor for laboratory contamination. For each lab method blank analysis, an unused, certified PUF filter / plug assembly was carried though the same extraction and evaporation procedures as the samples. The LMB also contained the same amount of surrogate compounds and internal standards that were added to each sample. One LMB was analyzed for each batch of 20 samples.

2.7.10 Laboratory Control Spikes (LCS)

Lab Control Spikes were used to monitor the extraction efficiency of the SVOC target analytes. For each LCS, a certified PUF filter and plug was spiked with the target SVOC analytes (1 μg) and carried through the same extraction and evaporation procedures as the samples. The LCS also contained the same amount of surrogate compounds and internal standards that were added to each sample. All target analytes spiked on the certified PUF cartridge had to have between a 60% and 120% recovery efficiency for acceptance. One LCS was analyzed for each batch of 20 samples.

2.7.11 GC/MS Continuing Calibration

To document that the GC/MS met tuning and standard mass spectral abundance criteria prior to SVOC sample analyses, 1μl of a 50 ng/μl solution of decafluorotriphenylphosphine (DFTPP) was analyzed at the start of each day. For acceptance, the GC/MS had to meet the mass spectral ion abundance criteria established for DFTPP. For each day that SVOC samples were analyzed, a continuing calibration standard was also analyzed to verify the initial calibration. SVOC standard number 3

(0.5 ng/μl) was used for the daily continuing calibration. For an acceptable continuing calibration, the percent difference between the measured concentration for each target/surrogate compound in SVOC standard number 3 and the mean value calculated during initial calibration had to be within ±30%.

2.8 VOC Sampling - CMB

2.8.1 Summary

To capture Volatile Organic Compounds (VOCs) with molecular weights smaller than 250 g/mol, constant flow air sampling pumps with sorbent tubes were used at both the Boyd Park and Frenchtown sites. Low-flow air sampling pumps actively sampled ambient air through sorbent tubes at a flow rate of approximately 45 ml/min for 24 hours to collect a total volume of sample between 60-65 Liters. The VOC air sampling pumps ran in conjunction with the $PM_{2.5}$ and PUF samplers during each CMB midnight to midnight sampling episode.

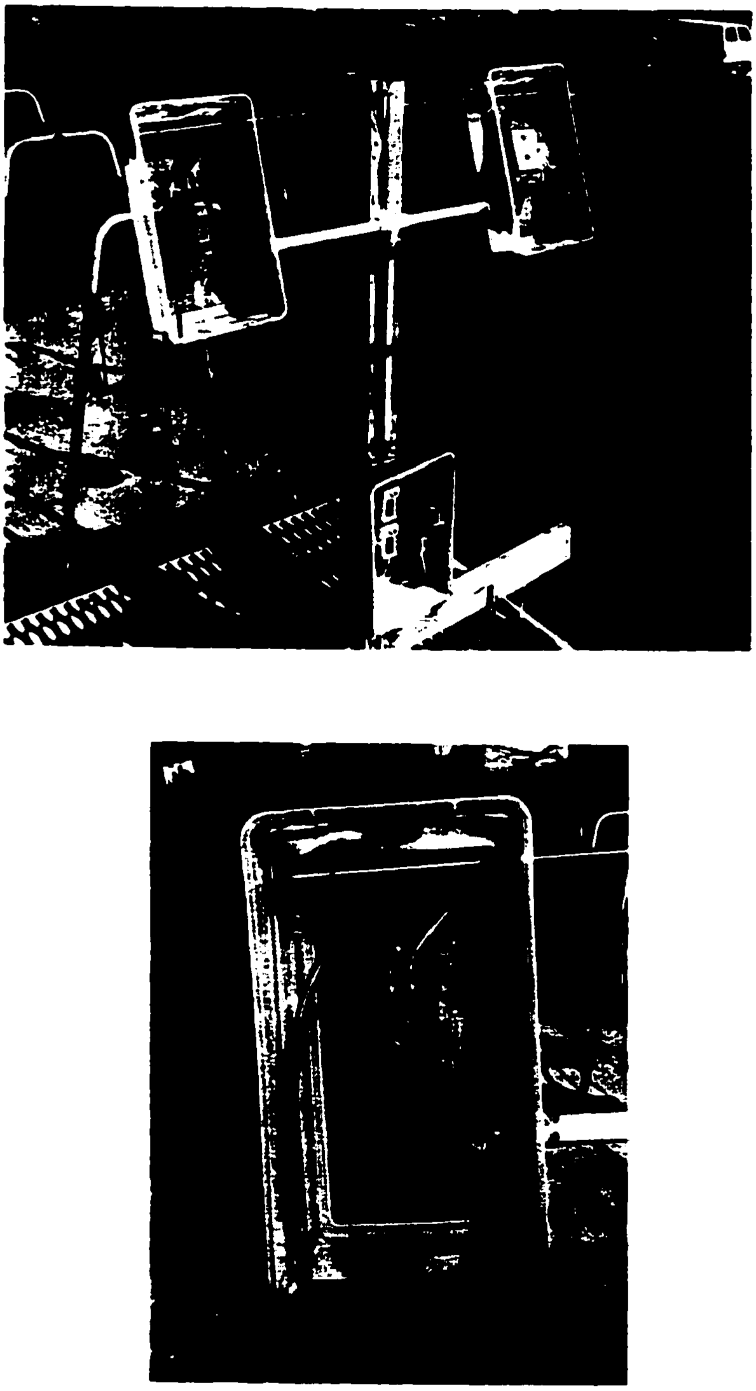
2.8.2 VOC Sampler and Media Description

SKC low flow air sampling pumps (Model Number 222-3) and Supelco Carbotrap™ 300 sorbent tubes were used for VOC sampling (See Figure 2-7). VOCs were captured in the adsorbent while major inorganic atmospheric constituents passed through (or were only partially retained). Separated by small plugs of silanized glass wool, each sample tube is composed of three different carbon sorbents. The first bed is 300 mg of 20 / 40 mesh Carbotrap™ C. This media is a graphitized carbon black with 10 m^2 / gram surface area for trapping and efficiently releasing the largest molecules (C_9 or more). The second contact layer is composed of 200 mg of 20 / 40 Carbotrap™ B - graphitized carbon black absorbent with 100 m^2 / gram surface area for trapping and releasing molecules starting at the C_4 to C_5 range through the C_{12}. The final sorbent layer contains 125 mg of 60 / 80 Carbosieve™ S-III, a spherical carbon molecular sieve with 820 m^2 / gram surface area with 15 to 40 angstrom pores to trap smaller organic molecules. For low level, low polarity, volatile contaminants, this combination of adsorbents/absorbents has been found to be extremely effective (Helmig and Greenberg, 1994).

Dr. Chris Wrobel's VOC study in the Missoula airshed (Wrobel, 2000) collected sample for only 8 hours per sample episode. For the Missoula Valley Sampling Program, 24-hour VOC sample collection periods were desired to be consistent with the PUF and $PM_{2.5}$ samplers which sampled for 24 hours. Through several experiments, it was determined that the battery in the SKC pump would not consistently last for 24 hours. With the help of Dr. Bruce King, the SKC pump was modified by attaching a capacitor which allowed the SKC pump to be powered by electricity instead of the unreliable battery. The pump modification also provided the capability to start the pumps at midnight and turn the pumps off at midnight the next night (24 hour sampling) by installing a timing device onto the pump.

The optimum flow rate then had to be determined for 24 hour VOC sampling. If the flow rate was too low, insufficient sample would be collected and the minimum detection limits of the GC/MS would not be met. If the flow rate was too high, breakthrough of the sample would occur. Breakthrough of the sample is when more than 5% of one or more of the target analytes is observed on any of the backup tubes. In choosing a practical safe sampling volume, a series of preliminary field experiments were conducted (Woolfenden, 1997). Through these experiments, a safe sampling volume of 45 ml/min was found acceptable for use in VOC sampling.

Figure 2-7: VOC samplers.



2.8.3 Sorbent Tube Preparation

Sorbent tubes used for sampling were cleaned and prepared in The University of Montana laboratory. Before sampling, each sorbent tube was conditioned for initial use by flushing the tube with approximately 60 ml/min of purified nitrogen gas and heating for 20 minutes at 350 °C to remove oxygen, moisture and organic contaminants. This process was conducted twice for each sorbent tube during the cleaning process. Each sample tube had its own individual storage vial with a clean glass jar with a Teflon-lined lid used to store the cleaned tubes together in a freezer until use.

2.8.4 Conducting a Sample Run

Clean sorbent tubes were transported to the field in a cooler. Prior to each sampling run, the pump's sampling flow rate was calibrated between 40-45 ml/min with a BIOS DryCal primary flow meter. After calibrating the initial flows, the system was leak checked by activating the sampling pump and observing that no flow occurred over a 1 minute period. The sampling pump was then shut off and the timer was set for sampling to begin at midnight and end at midnight the next day. On the actual day of sampling, a mid-point flow rate was taken, with a third and final flow measurement taken when samples were recovered. Samples were transported back to The University of Montana laboratory in a cooler and stored in a freezer until analysis.

2.9 VOC Analyses - CMB

2.9.1 Summary

Exposed sample tubes were brought back to The University of Montana laboratory for analysis by GC/MS using the thermal desorption method. The standard EPA suite of 54 VOCs were originally quantified, but was later refined to the 13 highlighted compounds:

Supelco Mix 1
Chlorobenzene
Isopropylbenzene
***n*-Propylbenzene**
1,2-Dimethylbenzene
1,4-Dimethylbenzene
sec-Butylbenzene
tert-Butylbenzene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
2-Chlorotoluene
4-Chlorotoluene

Supelco Mix 2
Benzene
Bromobenzene
Ethylbenzene
1,4-Dimethylbenzene
n-Butylbenzene
Naphthalene
Isopropyltoluene
Styrene
Toluene
1,2,3-Trichlorobenzene
1,2,4-Trichlorobenzene
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene

Supelco Mix 3
cis-1,3-Dichloropropene
Hexachlorobutadiene
trans-1,3-Dichloropropene
Trichloroethene
1,1-Dichloropropene
1,1,1,2-Tetrachloroethane
1,1,2-Trichloroethane
1,1,2,2-Tetrachloroethane
1,2-Dibromo-3-chloropropane
1,2-Dibromoethane
1,2-Dichloroethane
1,2-Dichloropropane
1,2,3-Trichloropropane
1,3-Dichloropropane

Supelco Mix 4
Bromochloromethane
Tribromomethane
Tetrachloromethane
Trichloromethane
Dibromomethane
Tetrachloroethene
1,1-Dichloroethene
1,1,1-Trichloroethane
2,2-Dichloropropane

Supelco Mix 5
Bromodichloromethane
cis-1,2-Dichloroethene
Dibromochloromethane
Dichloromethane
trans-1,2-Dichloroethene
1,1-Dichloroethane

2.9.2 Standard Preparation

A six-point VOC calibration curve was generated to quantify VOC analytes in the sorbent samples. Dr. Chris Wrobel designed and fabricated a new apparatus for putting standards on calibration sorbent tubes during his Ph.D. work. Using a deactivated quartz "tee", the standard compounds were flash volatized at 125 °C within the quartz tee. The compounds were then swept onto a sorbent tube at room temperature with purified nitrogen gas at a flow rate of 55 to 60 ml/min (Wrobel, 2000).

VOC calibration standards were made using this quartz tee apparatus. Five certified VOC mixes were purchased from Supelco and added together to make one stock standard solution. 1 µl of this mixture was injected onto the calibration sorbent tubes to prepare a calibration curve consisting of the following concentrations: 5 ng/µl, 25 ng/µl, 50 ng/µl, 100 ng/µl, 200 ng/µl, and 400 ng/µl. The sorbent tube was kept in the tee for five minutes after injection of the standard mix to ensure that a sufficient volume of nitrogen (275-300 ml) had completely flushed the analyte onto the sample tube. Standards were also made starting with the lowest concentration (5 ng/µl) and increasing through the largest concentration (400 ng/µl).

2.9.3 Internal Standards

Dr. Chris Wrobel's design of the quartz tee also created a method through which an internal standard could be added to each field sample, blank, and calibration standard prior to thermal desorption. In this procedure, the sorbent tubes were spiked with 1 µl of a 100 ng/µl internal standard solution. The internal standard solution contained the following compounds: fluorobenzene, 4-bromofluorobenzene, and 1,2-dichlorobenzene-d_4. The response from the internal standards were used in the quantitation of the target analytes by using the target response relative to the calibration curve.

2.9.4 Instrument Description

All VOC analyses were conducted in The University of Montana laboratory using the instrument conditions and temperature program in Table 2-3. Release of the sorbed chemicals was affected on a Dynatherm MTDU Model 910 thermal desorption unit. A model 900 ACEM sample concentrator was used to focus the samples prior to injection into the Hewlett Packard 6890 series Gas Chromatograph with Restek RTX502.2 capillary column (60 m, 0.32 mm ID). Quantitation was performed on a 5973 Mass Spectrum Detector (MSD).

Table 2-3: GC/MS instrument operating conditions – VOC analysis.

GC/MS Instrument Operating Conditions			
Inlet Temperature:	220 °C	Detector Temperature:	270 °C
Injection Mode:	Split	Split Flow:	9.9 ml/min
Split Ratio:	10:1	Total Flow:	13.0 ml/min
Initial Oven Temperature:	40 °C	Initial Oven Hold:	5.0 minutes
Oven Ramp Rate:	5 °C / minute	Oven Final Temperature:	220 °C
Oven Final Time:	9.0 minutes	Total Run Time:	50.0 minutes
Carrier Gas:	Helium	Flow:	1.0 ml/min
Dynatherm MTDU Model 910 Parameters			
Interface Temperature:	120 °C	Transfer Line Temperature:	120 °C
Interface Idle Temperature:	40 °C	Transfer Line Idle Temperature:	40 °C
Tube Desorb Temperature:	250 °C	Auxillary Temperature:	NA
Tube Purge Time:	4.0 minutes	Tube Heat Time:	10 minutes
Tube Cool Time:	6.0 minutes	Auxillary Time:	NA
Sample Flow:	100 ml/min	Sample Tube Purge / Desorb Flow:	25.0 ml/min
Gas:	Nitrogen		
ACEM Model 900 Parameters			
Valve Temperature:	150 °C	Transfer Line Temperature:	225 °C
Tube Desorb Temperature:	290 °C	Trap Desorb Temperature:	310 °C
Tube Idle Temperature:	40 °C	Trap Idle Temperature:	40 °C
Ext. Sample Time:	20.0 minutes	Tube Dry Time:	4.0 minutes
Tube Heat Time:	12.0 minutes	Tube Cool Time:	4.0 minutes
Trap Heat Time:	6.0 minutes	System Recycle Time:	10.0 minutes
Gas:	Nitrogen		

2.10 QA/QC Program – VOC Sampling and Analyses

2.10.1 Field Blanks

Field blanks were collected for each CMB sampling event. Clean sorbent tubes accompanied sample sorbent tubes to the field where they were exposed to the ambient air before being transported back to the laboratory.

2.10.2 Duplicate Samples

Duplicate samples were collected during each sampling episode at both Boyd Park and Frenchtown. This was achieved by having two pumps sampling side-by-side with the results from these samples averaged together and reported as a single measurement.

2.10.3 Backup Sorbent Tubes

Backup sorbent tubes were used in the beginning of the sampling program. These backup tubes were attached to the front sorbent tubes with a brass Swagelok fitting. Most of the backup tubes were found to be equivalent in concentrations to the field blanks, therefore, after the first few sampling episodes, the use of backup sorbent tubes was suspended.

2.10.4 Solvent Blanks

Solvent blanks were used to monitor for laboratory and instrument contamination. For each solvent blank, 1 μl of methanol was spiked onto a blank sorbent tube and then analyzed with a group of samples. Solvent blanks were analyzed approximately once a week during sample analysis.

2.10.5 System Blanks

System blanks (glass sorbent tubes without any media) were analyzed by the GC/MS to determine the amount of contamination in the system. At least one system blank was analyzed per day with other samples during the VOC analyses.

2.10.6 GC/MS Continuing Calibration / Spike

To document that the GC/MS met tuning and standard mass spectral abundance criteria prior to VOC sample analyses, 1 µl of a 25 ng/µl solution of bromofluorobenzene (BFB) was analyzed at the start of each day. For acceptance, the GC/MS had to meet the mass spectral ion abundance criteria established for BFB. For each day that VOC samples were analyzed, a continuing calibration standard was also analyzed to verify the initial calibration. Continuing VOC calibration standard number 4 (100 ng/µl) was used for the daily continuing calibration. For an acceptable continuing calibration, the percent difference between the measured concentration for each target/surrogate compound in the VOC standard number 4 and the mean value calculated during initial calibration had to be within ±30%. The VOC continuing calibrations were also used as spikes to monitor the analytical recovery efficiencies of the VOC target analytes.

2.11 CMB Modeling Program

2.11.1 Summary

An EPA Chemical Mass Balance (CMB) Model Version 8.0 was utilized to apportion the sources of air pollution in the Missoula Valley. CMB8 receptor model (Friedlander, 1973; Cooper and Watson, 1980; Gordon, 1980, 1988; Watson, 1984; Watson *et al.*, 1984, 1990, 1991; Hidy and Venkataraman, 1996) is a Windows 95 based version of CMB modeling software, and consists of a solution to linear equations that express each receptor chemical concentration as a linear sum of products of source profile abundances and source contributions. The source profile abundances (i.e., the mass fraction of a chemical or other property in the emissions from each source type) and measurements of the chemical compositions of suspended particles present in the areas of interest, with appropriate uncertainty estimates, serve as input data to the CMB model. The output consists of the amount contributed by each source type represented by a profile to the total mass and each chemical species. The CMB calculates values for the contributions from each source and the uncertainties of those values.

2.11.2 CMB Model Overview

The Chemical Mass Balance (CMB) receptor model was first applied by Winchester and Nifong (1971), Hidy and Friedlander (1972), and Kneip *et al.*, (1973), and 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. The CMB model can be written as:

$$C_i = \sum_{j=1}^{p} a_{ij} S_j, i = 1, n$$

where C_i is the ambient concentration of specie i, a_{ij} is the fractional concentration of specie i in the emissions from source j, S_j is the total mass concentration contributed by source j, p is the number of sources, and n is the number of species, with $n > p$. The C_i and a_{ij} are known and the S_j are found by a least squares solution of the overdetermined system of equations (Henry, 1982).

2.11.3 Application of the CMB Modeling Method

In a typical chemical mass balance application, the EPA's Version 8.0 CMB model is applied to selected ambient samples, and is performed according to the criteria set in EPA's *Protocol for Applying and Validating the CMB Model* (EPA[1], 1987). The CMB procedure begins with a set of linear equations which express the ambient concentrations of chemical species measured at an ambient receptor site as the sum of products of source compositions and source contributions, with source contributions the unknowns in these equations. A unique solution cannot be found for this set of equations because measurement uncertainty precludes determination of exact values for source and receptor data. When these uncertainties are estimated for both source and receptor measurements, additional physical constraints are applied which yield a most probable solution. This solution minimizes the difference between calculated and measured receptor concentrations by using an effective variance weighting scheme. The weighting has a physical significance in that it is derived from the measurement uncertainties of both source and receptor chemical species. Species with higher relative concentration uncertainties carry less weight in the regression than species with lower relative uncertainties.

After sources and chemical species have been selected for a particular sample day, a sample run is conducted by the model, and the results are given in an output file. The output file contains the contribution of each source to each measured species. Source contribution estimates (SCEs) and their standard errors (STD ERR) are presented in subsequent columns, identified by mnemonics in the first row of the source contribution display. The eligible space display and the species concentration display compose the remainder of the output file. Each of these three displays contains performance measures which are discussed in the CMB Model QA/QC portion of this document (section 2-12).

2.11.4 Source Profiles

Emissions of particulate matter from anthropogenic sources come primarily from four source categories: 1) fuel combustion, 2) industrial processes, 3) nonindustrial fugitive sources (roadway dust from paved and unpaved roads, wind erosion of cropland, construction, etc.), and 4) transportation sources. Transportation source emissions can further be defined by vehicle exhaust and vehicle-related particles from tires, clutches, and brake wear (Seinfeld and Pandis, 1998). In general, the same type of chemical species found in the fine fraction are found in direct emissions from various sources, although in different proportions. Source profiles are the fractional mass abundances of measured chemical species relative to primary $PM_{2.5}$ mass in source emissions. These profiles are used to create chemically speciated emission inventories and to apportion ambient concentrations of sources using the CMB model (Watson *et al.*, 2001).

In conducting the 2000/2001 CMB, source profiles were provided by the Missoula Health Department. These were developed using the following resources:

1) EPA SPECIATE 3.0 Source Profile Library (EPA, 1989).
2) Pacific Northwest Source Profile Library (Core, 1989).
3) A pulp and paper plant emissions library developed by Cooper *et al.* (1996).
4) Local sources based on road dust and sanding material collected during the 1995/1996 winter.
5) Previous Missoula CMB study (Carlson, 1990).

Source categories for which source profiles were specifically developed for Missoula include street sand, diesel exhaust, hog fuel boilers, secondary ammonium sulfate and nitrate sources, $MgCl_2$ deicer, residential wood combustion, and other sources common to the pulp, paper and wood products industry. Table 2-4 presents a listing of all of the sources used in the 2000/2001 CMB Model.

The CMB model is well suited for apportioning sources of primary aerosols (those emitted directly as particles). However, it is difficult to attribute secondary aerosols formed through gas-to-particle transformation in the atmosphere to specific sources because the CMB is based on the chemical composition of primary emissions measured at the source. Therefore, to account for secondary aerosol contributions to

$PM_{2.5}$ mass, sulfate (MSLA06), ammonium sulfate (MSLA07), and ammonium nitrate (MSLA08) were expressed as "pure" secondary source profiles.

Table 2-4: $PM_{2.5}$ source profiles used in the 2000/2001 CMB.

Source Code	Missoula Valley Source
MSLA01	CITY STREET SANDING PILE
MSLA02	INTERSECTION ERNEST AND RUSSEL ST
MSLA03	RUSSEL ST
MSLA04	DESPERADO PARKING LOT
MSLA05	STONE CONTAINER PRECIPITATOR #5 (SENT FROM MISSOULA)
MSLA06	SULFATE (SO4 IS ONLY SPECIE, THEREFORE IS ONLY NONZERO CONCENTRATION)
MSLA07	AMMONIUM SULFATE (INCLUDES NH4)
MSLA08	AMMONIUM NITRATE (INCLUDES NH4)
MSLA09	SPECIATE 31105 LIGHT DUTY VEHICLE-LEADED COMPOSITE
MSLA10	SPECIATE 31202 LIGHT DUTY VEHICLE-UNLEADED
MSLA11	SPECIATE 32102 LIGHT DUTY VEHICLE-DIESEL
MSLA12	SPECIATE 32103 LIGHT DUTY VEHICLE-DIESEL (2ND PROFILE OF THIS TYPE)
MSLA13	SPECIATE 32203 HEAVY DUTY VEHICLE-DIESEL
MSLA14	DIESEL TRAIN (SENT FROM MISSOULA)
MSLA15	DIESEL TRUCK (SENT FROM MISSOULA)
MSLA16	SPECIATE 34002 TIREWEAR
MSLA17	MAGNESIUM CHLORIDE DEICER (CHEMICAL ANALYSIS SENT FROM MISSOULA)
MSLA18	SPECIATE 12706 HOG FUEL BOILER/PLYWOOD MFG
MSLA19	SPECIATE 12708 HOG FUEL BOILER/PLYWOOD MFG (2ND PROFILE OF THIS TYPE)
MSLA20	SPECIATE 12707 HOG FUEL BOILER/DUTCH OVEN
MSLA21	HOG FUEL BOILER COMPOSITE (FROM STONE CONTAINER REPORT)
MSLA22	WHITE PINE HOG FUEL BOILER (SENT FROM MISSOULA)
MSLA23	SPECIATE 24101 SULFITE RECOVERY BOILER
MSLA24	KRAFT RECOVERY BOILER COMPOSITE (FROM STONE CONTAINER REPORT)
MSLA25	WASTE FUEL BOILER COMPOSITE (FROM STONE CONTAINER REPORT)
MSLA26	LIME KILN COMPOSITE (FROM STONE CONTAINER REPORT)
MSLA27	LP (LOUISIANA PACIFIC) CHIP DRYER (SENT FROM MISSOULA)
MSLA28	SPECIATE 42104 RESIDENTIAL WOOD SMOKE FROM MEDFORD, OR
MSLA29	SPECIATE 42105 RESIDENTIAL WOOD SMOKE FROM POCATELLO, ID
MSLA30	RESIDENTIAL WOOD COMBUSTION (SUPPLIED BY MISSOULA)
MSLA31	SPECIATE 42321 FOREST PRESCRIBED BURNING - BROADCAST CONIFER
MSLA32	SPECIATE 42301 SLASH BURNING PROFILE 1
MSLA33	SPECIATE 42302 SLASH BURNING PROFILE 2
MSLA34	SPECIATE 42305 SLASH BURNING (CONIFER-FLAMING PHASE)
MSLA35	SPECIATE 42306 SLASH BURNING (CONIFER-SMOLDERING PHASE)

2.12 QA/QC Program – CMB Model

The CMB model provides different performance measures that are used to evaluate the validity of source contribution estimates. The performance measures are given in three separate displays at the conclusion of each run: 1) the source contribution display; 2) the eligible space display; and 3) the species concentrations display. Note: The following description of the output displays is taken from the CMB8 User's Manual (Watson *et al.*, 1997).

2.12.1 Source Contribution Estimates Display

An example of a source contribution table display is shown below in Table 2-5. Source contribution estimates are the main output of the CMB model. The sum of these concentrations approximates the total mass concentration. When the absolute value of a positive or negative source contribution estimate is less than its standard error, the source contribution is undetectable. Two or three times the standard error may be taken as an upper limit of the source contribution in this case.

Table 2-5: Example of a source contribution table display.

```
SOURCE CONTRIBUTION ESTIMATES -  SITE: BOYDPARK    DATE: 01/28/01  CMB8 (97350)
SAMPLE DURATION          24       START HOUR         0          SIZE:    FINE
       R SQUARE        0.98     PERCENT MASS      105.0
     CHI SQUARE        0.28            DF          14
B and L: No    SRC ELIM: No
WEIGHTS:  CHISQR   1.000   R SQR   1.000  PCMASS   1.000  FRCEST   1.000

SOURCE
EST CODE   NAME     SCE(UG/M3)   STD ERR    TSTAT
-------------------------------------------------
YES MSLA08 NH4NO3F2    3.9397     0.5162     7.6327
YES MSLA12 LDV_DS2F    2.7360     0.4378     6.2488
YES MSLA24 KRB_CMPF    4.0149     0.8453     4.7495
YES MSLA30 RWC_F222    3.8125     0.6056     6.2955
-------------------------------------------------

MEASURED CONCENTRATION FOR SIZE: FINE
      13.8+-     0.4
```

The standard errors (STD ERR) reflect the precisions of the ambient data, the source profiles, and the amount of collinearity among different profiles. The standard error is a single standard deviation. There is about a 66% probability that the true source contribution is within one standard error and about a 95% probability that the true contribution is within two standard errors of the source contribution estimate. The T-statistic (TSTAT) is the ratio of the source contribution estimate to the standard error. A TSTAT value less than 2.0 indicates that the source contribution estimate is at or below a detection limit.

The reduced chi square, degrees of freedom, R square, and percent mass are other performance measures for the least squares calculation. The chi-square is the weighted sum of squares of the differences between the calculated and measured fitting species concentrations. The weighting is inversely proportional to the squares of the precisions in the source profiles and ambient data for each species. Ideally, there would be no difference between calculated and measured species concentrations and chi-square would equal zero. A value less than 1 indicates a very good fit to the data, while values between 1 and 2 are acceptable. The degrees of freedom equal the number of fitting species minus the number of fitting sources. The R-square is the fraction of the variance in the measured concentrations that is explained by the variance in the calculated species concentrations. It is determined by a linear regression of measured versus model-calculated values for the fitting species. R-square ranges from 0 to 1.0. The closer the value is to 1.0, the better the source contribution estimates explain the measured concentrations. Percent mass is the percent ratio of the sum of the model-calculated source contribution estimates to the measured mass concentration. This ratio should equal 100%, although values ranging from 80 to 120% are acceptable.

2.12.2 Eligible Space Display

The eligible space display identifies the potential for collinearity and the potential reductions in standard errors in the source contribution estimates when source profiles are combined. An example taken from the CMB Verison8 Manual is presented in Table 2-6.

Table 2-6: Example of an eligible space display.

```
ELIGIBLE SPACE DIM. =   7 FOR MAX. UNC. =  10.0687  (20.% OF TOTAL MEAS. MASS)

1 / SINGULAR VALUE
-----------------------------------------------------------------------------
   .1285     .1562     .3497     .5445     .7625    1.8313    2.1128
-----------------------------------------------------------------------------
NUMBER ESTIMABLE SOURCES =   7 FOR MIN. PROJ. =   .95
PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE   PROJ. SOURCE
-----------------------------------------------------------------------------
1.0000 SJV002  1.0000 SJV017  1.0000 SJV027  1.0000 SJV036  1.0000 SJV051
1.0000 SJV054  1.0000 SJV056
-----------------------------------------------------------------------------
ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES
OEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE  COEFF. SOURCE   SCE        STD ERR
-----------------------------------------------------------------------------
----------------------------------------------------------------------------
```

Henry's (1992) eligible space treatment uses the maximum source uncertainty, expressed as a percentage of the total measured mass, and the minimum source projection. The maximum source uncertainty defines a space, called the eligible space, to be that spanned by those eigenvectors with inverse singular values less than or equal to the maximum source uncertainty. The first part of this display gives the eligible space dimension and the uncertainty used in its calculation. This is followed by the inverse singular values. Source profiles lying within the eligible space may be estimated with an uncertainty less than the maximum source uncertainty. This strict criteria of inclusion is relaxed somewhat and estimable sources are defined to be those with projections into the eligible space of more than the specified minimum source projection.

The next part of the display gives the number of estimable sources, the minimum source projection used in the calculation, and the projections of each profile vector into the estimable space. These inestimable sources are caused by excessive similarity (collinearity) among the source profiles or by high uncertainties in the individual source profiles. The standard errors associated with the source contribution estimates of one or more inestimable sources are usually very large, often too large to allow an adequate separation of these source contributions to be made. Inestimable sources will not appear if the two above-stated criteria are not met. This absence of inestimable sources means that the source contributions can be resolved in the specific application.

If collinearity is the cause of these excessive standard errors, then certain linear combinations of inestimable sources may be estimable, and the final part of the display lists these, if any exist. This may be understood as removing uncertainty by combining collinear sources. This linear combination may be more useful than the individual source contribution estimates if the standard error of the linear combination is substantially lower than the standard errors of each source contribution estimate. The treatment does not allow differentiation among the contribution estimates of the sources contained in the linear combination, however.

2.12.3 Species Concentration Display

Table 2-7 gives an example of the species concentration display as taken from the CMB Manual.

Table 2-7: Example of the species concentration display.

```
SPECIES CONCENTRATIONS -  SITE: FRESNO       DATE: 02/27/89       CMB 8.0
SAMPLE DURATION         24       START HOUR         0         SIZE:    FINE
R SQUARE       .96     PERCENT MASS       83.2
    CHI SQUARE       1.06              DF        13

SPECIES-------I---MEAS-----------------CALC------------RATIO C/M----RATIO R/U
TMAC    TMAU      50.3433+-  2.5652  41.8809+-  2.7727     .83+-  .07     -2.2
N3IC    N3IU   *  19.2608+-   .9793  20.3104+-  1.9713    1.05+-  .12       .5
S4IC    S4IU   *   2.8779+-   .1653   2.9238+-   .3694    1.02+-  .14       .1
N4TC    N4TU   *   7.0496+-   .3636   6.6966+-   .5847     .95+-  .10      -.5
KPAC    KPAU   *    .1496+-   .0235    .1419+-   .0854     .95+-  .59      -.1
NAAC    NAAU   *    .1982+-   .0566    .1929+-   .0762     .97+-  .47      -.1
ECTC    ECTU   *   4.5527+-   .5979   4.5762+-  1.4756    1.01+-  .35       .0
OCTC    OCTU   *   5.9985+-   .8449   5.4261+-  1.8067     .90+-  .33      -.3
ALXC    ALXU   *    .0641+-   .0242    .1189+-   .0135    1.85+-  .73      2.0
SIXC    SIXU   *    .1869+-   .0392    .3353+-   .1071    1.79+-  .69      1.3
SUXC    SUXU       1.0952+-   .0565    .9798+-   .1232     .89+-  .12      -.9
CLXC    CLXU   *    .0641+-   .0080    .0704+-   .0221    1.10+-  .37       .3
KPXC    KPXU   *    .1695+-   .0107    .1624+-   .0429     .96+-  .26      -.2
CAXC    CAXU   *    .0450+-   .0071    .0484+-   .0077    1.07+-  .24       .3
TIXC    TIXU   *    .0006<    .0193    .0065<    .0010   10.80< *****       .3
VAXC    VAXU   *    .0016<    .0081    .0021<    .0004    1.32<  6.70       .1
CRXC    CRXU   *    .0020+-   .0017    .0004+-   .0002     .19+-  .18      -.9
MNXC    MNXU   *    .0049+-   .0009    .0036+-   .0018     .73+-  .39      -.7
FEXC    FEXU   *    .1125+-   .0129    .0759+-   .0086     .67+-  .11     -2.4
NIXC    NIXU   *    .0017+-   .0010    .0017+-   .0002    1.02+-  .62       .0
CUXC    CUXU        .0214<    .0679    .0006<    .0002     .03<   .09      -.3
ZNXC    ZNXU        .0295<    .0403    .0105<    .0025     .36<   .49      -.5
BRXC    BRXU   *    .0166+-   .0010    .0200+-   .0112    1.20+-  .68       .3
PBXC    PBXU   *    .0399+-   .0056    .0320+-   .0153     .80+-  .40      -.5
```

This display shows how well the individual ambient concentrations are reproduced by the source contribution estimates. This display offers clues concerning which sources might be missing or which ones do not belong in the calculation. Fitting species are marked with an asterisk in the column labeled 'I'. The column labeled RATIO R/U contains the ratio of the signed difference between the calculated and measured concentrations (the residual) divided by the uncertainty of that residual (square root of the sum of the squares of the uncertainty in the calculated and measured concentrations). The R/U ratio specifies the number of uncertainty intervals by which the calculated and measured concentrations differ. When the absolute value of the R/U ratio exceeds 2, the residual is significant. If it is positive, then one or more of the profiles is contributing too much to that species. If it is negative, then there is an insufficient contribution to that species and a source may be missing. The sum of the squared R/U for fitting species divided by the degrees of freedom yields the chi-square. The highest R/U values for fitting species are the cause of high chi square values. Table 2-8 gives a summary of the CMB model statistical criteria.

Table 2-8: Statistical criteria as recommended by the EPA in conducting a CMB analysis.

Output/Statistic	**Abbreviation**	**EPA Target**	**Explanation**
Std. Error	STD ERR	<SCE	The standard error of the SCE.
T-statistic	T-STAT	> 2.0	The ratio of the value of the SCE to the uncertainty in the SCE. A T-STAT greater than 2 means that the SCE has a relative uncertainty of less than 50%. **T-STAT = SCE/STD ERR**
R-square	R-SQUARE	0.80 to 1.00	A measure of the variance of the ambient concentration explained by the calculated concentration. The target range is 0.8 to 1.0, where an R-square of 1.0 is perfect.
Chi-square	CHI-SQUARE	0.0 to 4.0	A term that compares the difference between the calculated and measured ambient concentrations to the uncertainty of the difference. A perfect fit has a chi-square of 0.0, and a chi-square less than 2 usually indicates a good fit. The target range is 0.0 to 4.0.
Percent Mass Explained	% MASS	100% ± 20%	The ratio of the total calculated to measured mass. The target range is 80% to 120%. **% MASS = M_c/M_m * 100**
Degrees of Freedom	DF	> 5	The difference between the number of fitting species and the number of fitting sources. This value must exceed 1 and should be greater than 5.
Ratio of Calculated to Measured	RATIO C/M	0.5 to 2.0	The ratio of the calculated to measured concentration of an ambient species. Ideally, this value should be 1.0, but the target range is 0.5 to 2.0. **RATIO C/M = C_i/M_i for each species *i*.**
Ratio of Residual to Uncertainty	RATIO R/U	-2.0 to 2.0	The ratio of the residual (calculated minus measured) to the uncertainty of the residual (square root of the sum of squares of the uncertainties). Target range is -2.0 to 2.0.

Using the EPA statistical guidelines, the CMB modeling procedure will generally result in optimized source contributions. The resulting fit is only one of many possible solutions, but it should be the most probable solution. The existence of several different solutions with similar fitting parameters suggests similar probabilities of correctness for each set of source contributions. In such a case, the SCEs of the major sources will likely be quite similar.

2.13 Other Statistical Analyses

Two other statistical methods were applied to the different data sets in order to determine the significance of observed trends above the variation introduced by random error. First, the means for the Boyd Park and Frenchtown sampling locations were compared using the Student's *t* method to determine whether the two sets of replicate measurements were different at the 95% confidence interval. The following equation was used to calculate the t test:

$$t_{\text{calculated}} = ((X_1 - X_2)/s_{\text{pooled}}) * \text{SQRT}((n_1 * n_2)/(n_1+n_2))$$

where

$$s_{\text{pooled}} = \text{SQRT}((s_1^2(n_1-1)+s_2^2(n_2-1)/(n_1+n_2-2))$$

and

X_1 and X_2 are means,
s_1 and s_2 are standard deviations,
n_1 and n_2 are number of measurements.

In addition, regression analyses were performed between combinations of species pairs to measure the strength of the relationship between them.

Chapter 3 Results

The first parts of Chapter 3 (Sections 3.1 – 3.9) present the results of $PM_{2.5}$ (mass, OC, EC, TC, trace elements, ions), SVOC, and VOC sampling. Section 3.10 gives the results of the CMB modeling.

3.1 $PM_{2.5}$ Calculations

Raw data generated from the $PM_{2.5}$ analyses are reported in micrograms (μg) per filter. Using the volume collected per sample run in cubic meters (m^3), all final concentrations for $PM_{2.5}$ data (mass, elemental, ions, OC, EC, and TC) are presented in $\mu g/m^3$. Also, because all $PM_{2.5}$ field and trip blanks showed negligible levels of contamination, final concentrations are not blank corrected.

3.2 $PM_{2.5}$ Mass

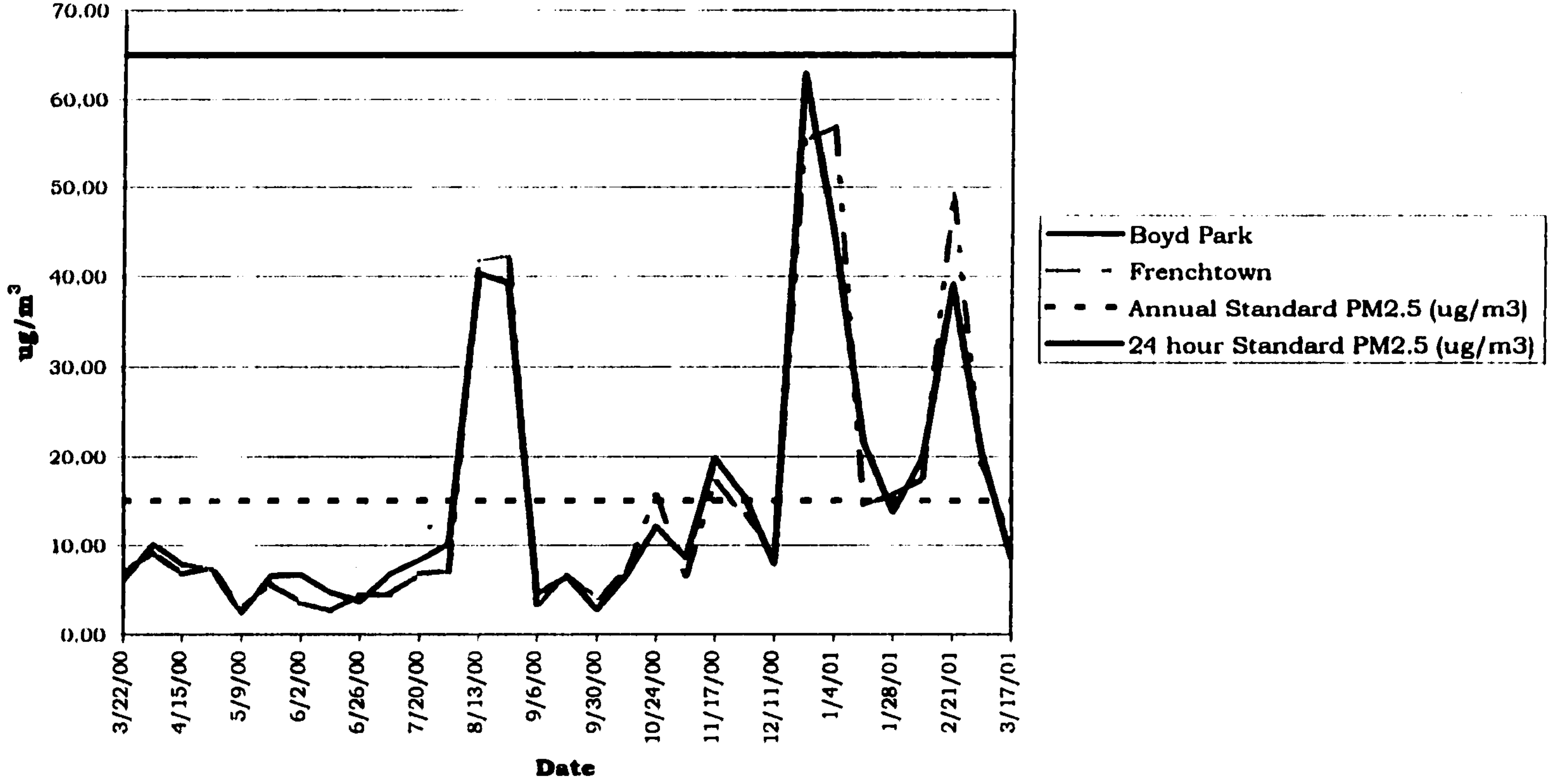
Table 3-1: $PM_{2.5}$ mass averages ($\mu g/m^3$) for Boyd Park and Frenchtown.

	Spring (3/22/00 – 6/14/00)	Summer (6/26/00 – 9/18/00)	2000 Fire Season (8/13/00, 8/25/00)	Summer (Excluding Fire Season)	Fall (9/30/00 – 12/11/00)	Winter (12/23/00 – 3/17/01)	Yearly Avg	Yearly Avg (Excluding Fire Season)
Boyd Park	6.5	15.0	39.9	6.7	10.6	29.0	15.4	13.7
Frenchtown	5.8	14.7	42.2	5.6	10.5	29.9	15.4	13.6

Excluding the fire season, spring and summer levels of $PM_{2.5}$ are low in the Missoula Valley, with levels increasing in the fall and peaking during the winter. Generally, both Boyd Park and Frenchtown have consistent concentrations of $PM_{2.5}$ between them, which verifies the findings in other studies that $PM_{2.5}$ concentrations in an airshed are uniform (Wilson and Suh, 1997; Chen *et al.*, 2001). In fact, when applying the student's *t* test to the yearly averages, there is no statistical difference between the measured masses at the two sites (t_{calc} = 0.010, 95% confidence interval). A correlation coefficient (R^2) of 0.971 also shows that the two sites have correlated concentrations throughout the year. The elevated winter $PM_{2.5}$ concentrations in the Missoula Valley are likely the result of temperature inversions. During an inversion, the temperature of the air in the lower troposphere increases with height, and the cooler air below does not mix with the warmer air above, thus trapping the pollution close to the ground. These inversions are characterized by cold weather, fog, and a lack of wind and dispersion which allows pollutant levels to build up. During this sampling program, the winter sample days which exhibited the highest $PM_{2.5}$ concentrations were 12/23/00, 1/4/01, and 2/21/01. Weather data collected during these days report low winds, cold temperatures, and fog – classic inversion conditions. Table 3-1 gives the $PM_{2.5}$ mass averages at both sites over the entire sampling program, with Figure 3-1 showing the mass traces. All weather data collected during the sampling program are presented in section 4.2, Table 4-1.

Elevated $PM_{2.5}$ levels were also measured during the fire season, particularly in August 2000. Yearly $PM_{2.5}$ averages including the fire season are above the 15 μg/m^3 annual standard, but without the fire season the averages are below the standard. At no time during the CMB sampling program did the $PM_{2.5}$ concentrations exceed the 24 hour standard of 65 μg/m^3. A more complete discussion of $PM_{2.5}$ levels found during the 2000 fire season is given in Part III of this document.

Figure 3-1: PM$_{2.5}$ - Boyd Park and Frenchtown Combined (3/22/00 - 3/17/01)



3.3 Organic Carbon (OC), Elemental Carbon (EC), and Total Carbon (TC)

Table 3-2: OC, EC, and TC averages (μg/m^3) for Boyd Park and Frenchtown.

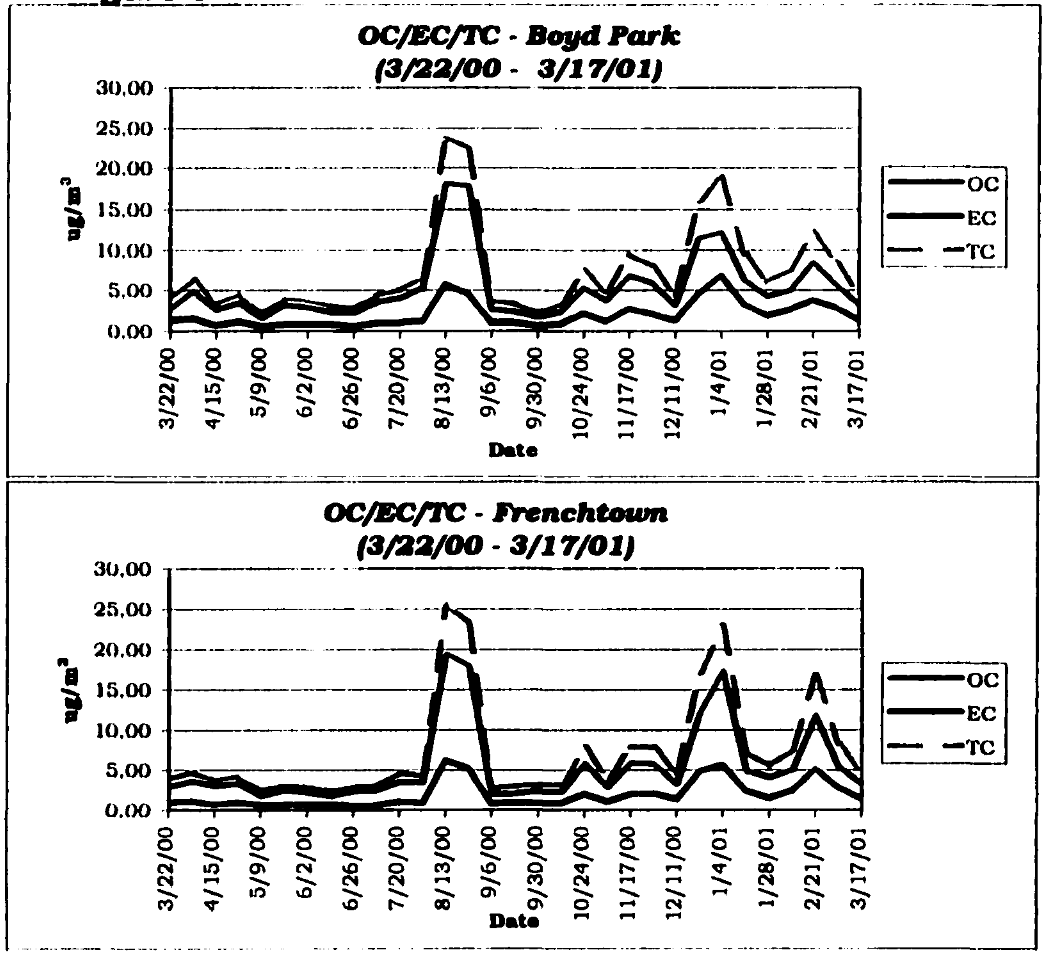
	Spring (3/22/00 – 6/14/00)	Summer (6/26/00 – 9/18/00)	2000 Fire Season (8/13/00, 8/25/00)	Summer (Excluding Fire Season)	Fall (9/30/00 – 12/11/00)	Winter (12/23/00 – 3/17/01)	Yearly Avg	Yearly Avg (Excluding Fire Season)
Boyd Park								
OC	2.95	7.04	18.02	3.38	4.17	7.12	5.36	4.48
EC	0.97	2.02	5.18	0.97	1.56	3.39	2.00	1.78
TC	3.93	9.06	23.19	4.35	5.74	10.51	7.36	6.27
Frenchtown								
OC	2.70	6.72	18.77	2.71	4.10	8.07	5.44	4.52
EC	0.81	2.03	5.72	0.81	1.46	3.30	1.92	1.65
TC	3.51	8.76	24.49	3.51	5.56	11.36	7.35	6.17

The average mass of $PM_{2.5}$ collected throughout the year at Boyd Park was composed of 35% organic carbon (OC) and 13% elemental carbon (EC), with Frenchtown $PM_{2.5}$ composed of 36% OC and 12% EC. Figure 3-2 presents a graphical representation of the concentrations throughout the year, while Figures 3-3 and 3-4 present pie charts for Boyd Park and Frenchtown displaying the percent compositions of $PM_{2.5}$ for each season. The volatile OC and non-volatile EC fractions at Boyd Park and Frenchtown showed similar trends with the $PM_{2.5}$ data, with lowest concentrations measured during the spring and summer (excluding the fire season) and highest levels during the winter. OC values were higher at Boyd Park during spring, summer, and fall, with Frenchtown levels higher during the winter. EC average concentrations were higher at Boyd Park compared to Frenchtown throughout each season. TC measurements were higher at Boyd Park during the spring, summer, and fall, but winter levels were lower than Frenchtown due to a higher average OC measurement. TC composed 48% of the average annual $PM_{2.5}$ during the 2000/2001 CMB at both Boyd Park and Frenchtown. TC was estimated to account for 37% of the total fine mass at eastern Canadian sites

(Winnipeg and east) and 48% of the total fine mass at sites in Alberta and British Columbia (Brook and Dann, 1999). In another study, the carbonaceous material (TC) of the $PM_{2.5}$ accounted for 27% of mass at Rubidoux and 38% in downtown Los Angeles (Kim *et al.*, 2000).

Both sites showed good consistency with one another throughout the year. The R^2 for OC, EC, and TC between the two sites are 0.971, 0.965, and 0.981, respectively. Like the $PM_{2.5}$, levels of OC, EC, and TC increased during the inversions on 12/23/00, 1/4/01, and 2/21/01, and during the wildfire season. A more complete discussion of the fire season is given in Part III.

Figure 3-2:



OC/EC/TC - Boyd Park (3/22/00 - 3/17/01)

OC/EC/TC - Frenchtown (3/22/00 - 3/17/01)

Figure 3-3; PM$_{2.5}$ Seasonal Average Compositions - Boyd Park

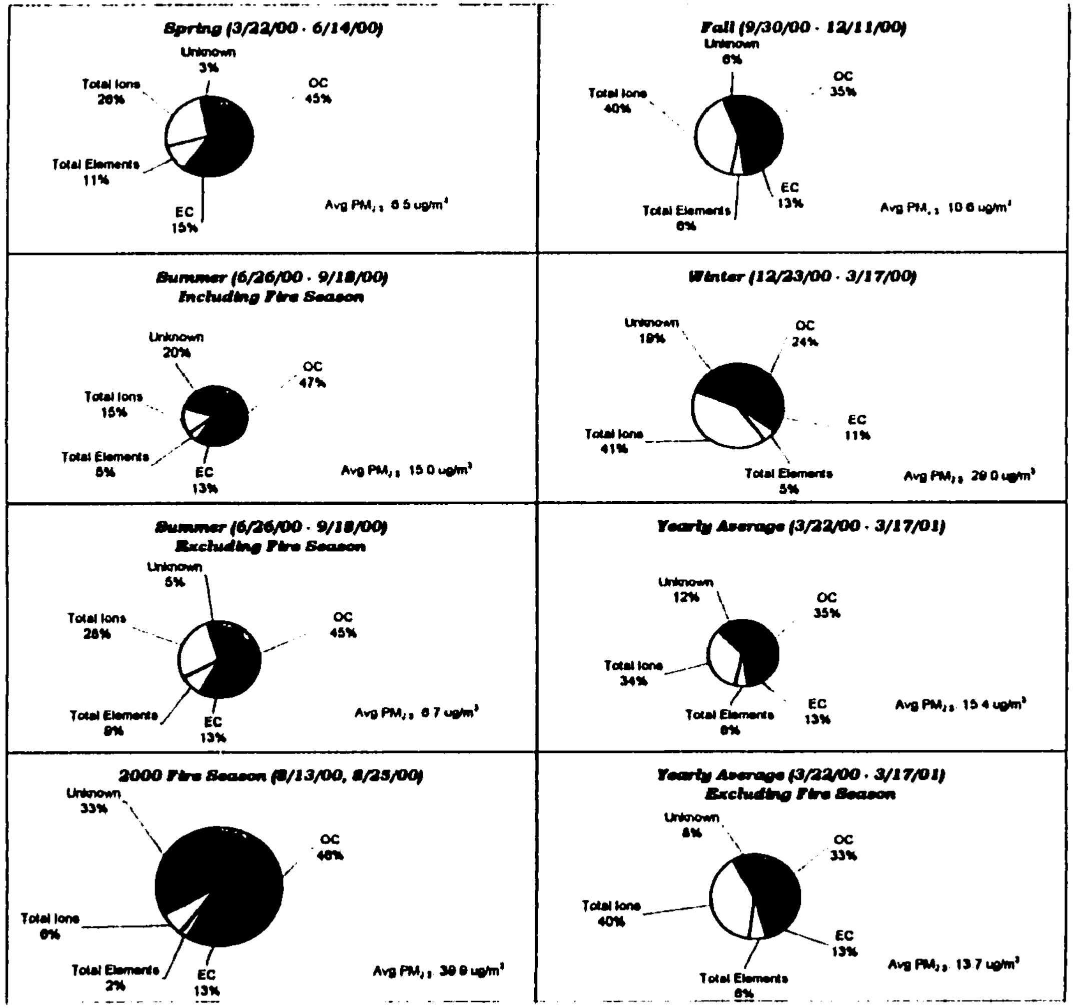
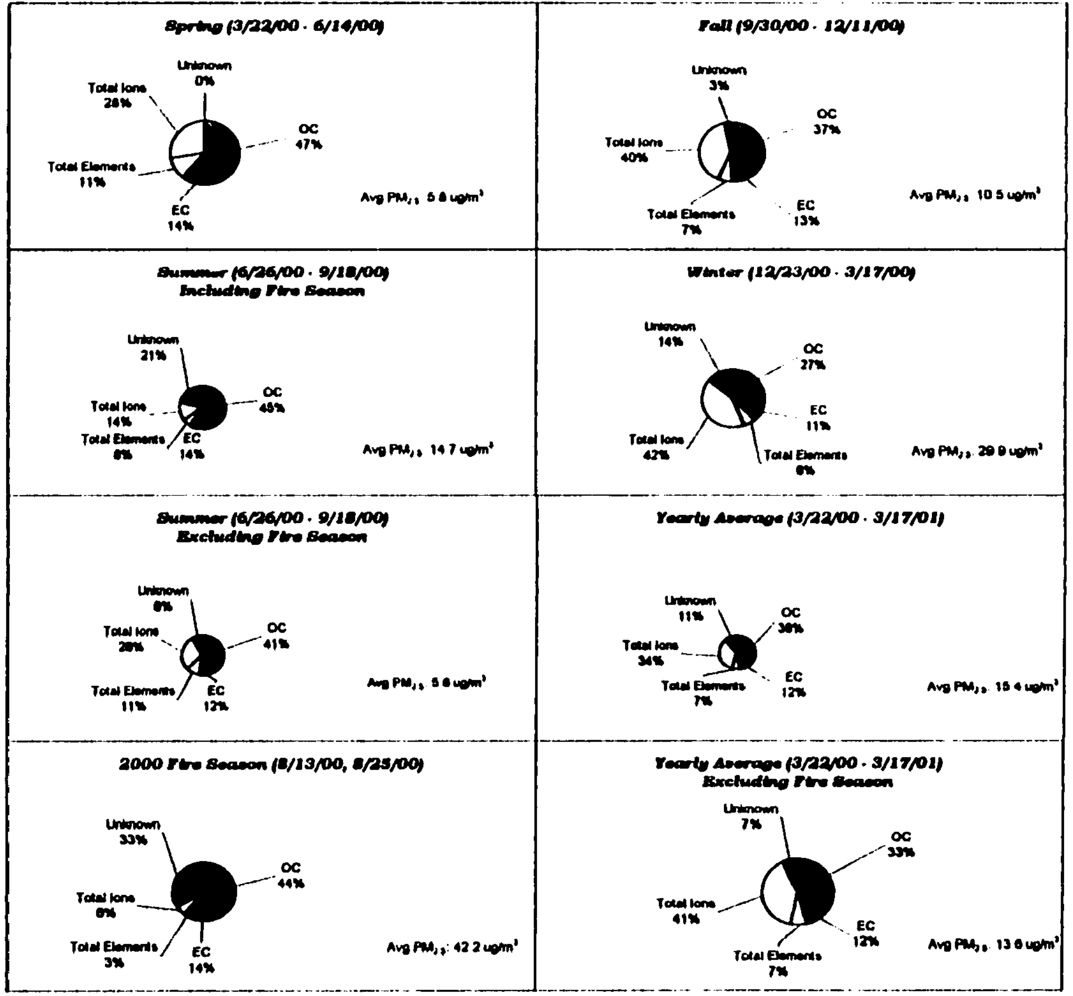


Figure 3-4: $PM_{2.5}$ Seasonal Average Compositions - Frenchtown



Spring (3/22/00 - 6/14/00)

Fall (9/30/00 - 12/11/00)

Summer (6/26/00 - 9/18/00) Including Fire Season

Winter (12/23/00 - 3/17/00)

Summer (6/26/00 - 9/18/00) Excluding Fire Season

Yearly Average (3/22/00 - 3/17/01)

2000 Fire Season (8/13/00, 8/25/00)

Yearly Average (3/22/00 - 3/17/01) Excluding Fire Season

3.4 Trace Elements

Tables 3-3 and 3-4 present the averages of all of the elements measured at Boyd Park and Frenchtown throughout the sampling program.

Table 3-3: Trace elemental averages (ug/m^{3}) for Boyd Park.

	Spring (3/22/00 – 6/14/00)	Summer (6/26/00 – 9/18/00)	2000 Fire Season (8/13/00, 8/25/00)	Summer (Excluding Fire Season)	Fall (9/30/00 – 12/11/00)	Winter (12/23/00 – 3/17/01)	Yearly Avg	Yearly Avg (Excluding Fire Season)
Aluminum, Al^{1}	0.052	0.022	0.019	0.023	0.007	0.028	0.028	0.029
Silicon, Si^{1}	0.192	0.111	0.118	0.109	0.072	0.108	0.123	0.123
Phosphorous, P	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sulfur, S^{2}	0.195	0.319	0.318	0.320	0.322	0.619	0.365	0.368
Chlorine, Cl^{3}	0.002	0.006	0.016	0.002	0.026	0.201	0.060	0.063
Potassium, K^{3}	0.088	0.141	0.322	0.080	0.114	0.256	0.151	0.139
Calcium, Ca^{1}	0.048	0.050	0.075	0.042	0.022	0.043	0.041	0.039
Titanium, Ti	0.004	0.003	0.003	0.003	0.003	0.003	0.003	0.003
Vanadium, V	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Chromium, Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Manganese, Mn	0.002	0.002	0.002	0.002	0.001	0.005	0.003	0.003
Iron, Fe^{1}	0.055	0.041	0.043	0.040	0.031	0.060	0.047	0.048
Cobalt, Co	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Nickel, Ni	0.000	0.001	0.002	0.000	0.000	0.000	0.000	0.000
Copper, Cu^{1}	0.013	0.004	0.003	0.004	0.007	0.010	0.008	0.009
Zinc, Zn^{3}	0.005	0.004	0.006	0.003	0.011	0.028	0.012	0.012
Gallium, Ga	0.001	0.001	0.001	0.001	0.001	0.000	0.001	0.001
Germanium, Ge	0.000	0.001	0.000	0.001	0.001	0.000	0.000	0.000
Arsenic, As	0.001	0.000	0.001	0.000	0.000	0.001	0.001	0.001
Selenium, Se	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Bromine, Br	0.001	0.002	0.004	0.001	0.001	0.002	0.002	0.000
Rubidium, Rb	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Strontium, Sr	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Yttrium, Y	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000
Zirconium, Zr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Molybdenum, Mo	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Palladium, Pd	0.001	0.002	0.004	0.001	0.002	0.001	0.001	0.001
Silver, Ag	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0.001
Cadmium, Cd	0.002	0.001	0.000	0.002	0.003	0.001	0.002	0.002
Indium, In	0.002	0.002	0.001	0.002	0.000	0.001	0.001	0.001
Tin, Sn	0.009	0.006	0.006	0.006	0.006	0.006	0.007	0.007
Antimony, Sb	0.002	0.001	0.000	0.002	0.001	0.002	0.001	0.002
Barium, Ba^{4}	0.020	0.023	0.025	0.023	0.027	0.020	0.023	0.022
Lanthanum, La	0.009	0.009	0.009	0.010	0.004	0.004	0.007	0.007
Mercury, Hg	0.000	0.000	0.001	0.000	0.001	0.000	0.000	0.000
Lead, Pb	0.002	0.003	0.004	0.003	0.003	0.004	0.003	0.003

1: Class 1 elements.
2: Class 2 Elements.
3: Class 3 Elements.
4: Other Notables.

Table 3-4: Trace elemental averages (ug/m^3) for Frenchtown.

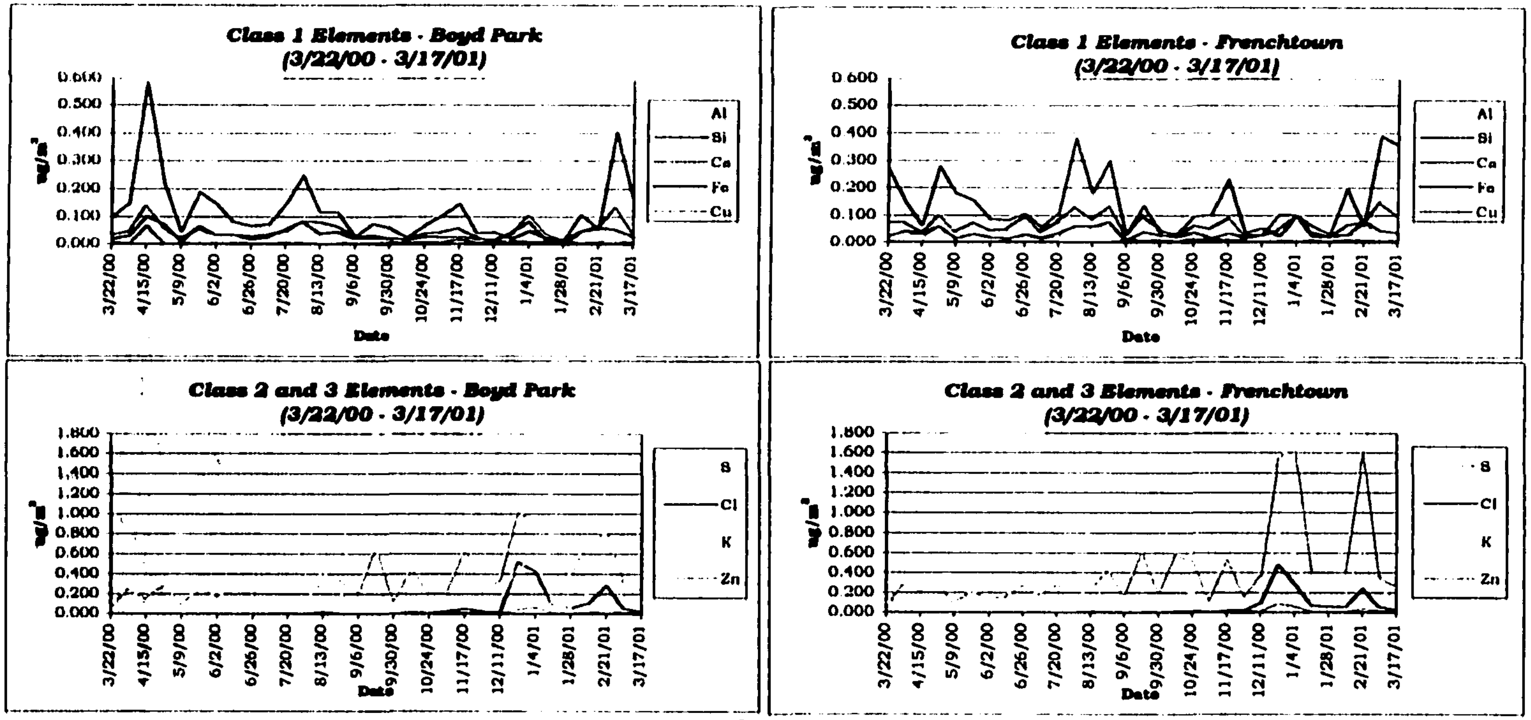
	Spring (3/22/00 — 6/14/00)	Summer (6/26/00 — 9/18/00)	2000 Fire Season (8/13/00, 8/25/00)	Summer (Excluding Fire Season)	Fall (9/30/00 — 12/11/00)	Winter (12/23/00 — 3/17/01)	Yearly Avg.	Yearly Avg. (Excluding Fire Season)
Aluminum, Al^1	0.045	0.043	0.061	0.037	0.017	0.046	0.038	0.037
Silicon, Si^1	0.161	0.165	0.243	0.139	0.087	0.154	0.144	0.137
Phosphorous, P	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sulfur, S^2	0.189	0.304	0.332	0.295	0.358	0.848	0.427	0.433
Chlorine, Cl^3	0.002	0.004	0.013	0.001	0.030	0.165	0.051	0.053
Potassium, K^3	0.085	0.120	0.291	0.062	0.124	0.354	0.172	0.164
Calcium, Ca^1	0.030	0.043	0.069	0.034	0.027	0.056	0.039	0.037
Titanium, Ti	0.003	0.004	0.006	0.003	0.002	0.004	0.003	0.003
Vanadium, V	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Chromium, Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Manganese, Mn	0.002	0.002	0.003	0.002	0.002	0.006	0.003	0.003
Iron, Fe^1	0.061	0.087	0.110	0.079	0.047	0.072	0.067	0.065
Cobalt, Co	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Nickel, Ni	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Copper, Cu^1	0.001	0.003	0.002	0.004	0.008	0.007	0.005	0.005
Zinc, Zn^3	0.005	0.003	0.007	0.002	0.010	0.032	0.013	0.013
Gallium, Ga	0.001	0.001	0.001	0.001	0.000	0.001	0.001	0.001
Germanium, Ge	0.001	0.000	0.000	0.000	0.001	0.001	0.001	0.001
Arsenic, As	0.001	0.000	0.000	0.000	0.001	0.001	0.001	0.001
Selenium, Se	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000
Bromine, Br	0.001	0.002	0.003	0.001	0.001	0.002	0.002	0.001
Rubidium, Rb	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000
Strontium, Sr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Yttrium, Y	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Zirconium, Zr	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Molybdenum, Mo	0.001	0.001	0.000	0.001	0.001	0.000	0.001	0.001
Palladium, Pd	0.001	0.002	0.004	0.001	0.000	0.001	0.001	0.001
Silver, Ag	0.001	0.003	0.004	0.003	0.001	0.000	0.001	0.001
Cadmium, Cd	0.001	0.001	0.000	0.002	0.001	0.001	0.001	0.001
Indium, In	0.002	0.001	0.000	0.001	0.000	0.001	0.001	0.001
Tin, Sn	0.007	0.008	0.009	0.007	0.006	0.005	0.006	0.006
Antimony, Sb	0.002	0.002	0.006	0.001	0.003	0.001	0.002	0.002
Barium, Ba^4	0.024	0.018	0.015	0.020	0.023	0.024	0.022	0.023
Lanthanum, La	0.007	0.005	0.002	0.005	0.008	0.004	0.006	0.006
Mercury, Hg	0.001	0.000	0.001	0.000	0.000	0.001	0.001	0.001
Lead, Pb	0.003	0.002	0.004	0.002	0.002	0.004	0.003	0.003

1: Class 1 Elements.
2: Class 2 Elements.
3: Class 3 Elements.
4: Other Notables.

Trace elements composed 6% of the annual $PM_{2.5}$ at Boyd Park, and 7% in Frenchtown. Out of the 36 elements quantified, only nine showed elevated concentrations, with the remainder at or below the analytical detection limits. These nine can be further broken down into three classes, and are displayed in Figure 3-5. The first class contains geological material: aluminum, silicon, calcium, iron, and copper. At Boyd Park, this class displayed highest concentrations during the spring and winter and lowest during the summer and fall. Elevated levels during winter could be due to the application of street sand to control icy roads, and then resuspended during the spring thaw. In other studies, aluminum, silicon, calcium, iron, and titanium have been used as tracers for soil (Kavouras *et al.*, 2001). Soil-based inorganics or crustal components were found to account from 5% to 15% of the fine mass across multiple Canadian locations (Brook *et al.*, 1997) and 3.4% to 8.3% of the $PM_{2.5}$ mass in a Southern California study (Kim *et al.*, 2000). Geological material has been found to contribute ~50% of PM_{10} while only contributing 5 to 15% of $PM_{2.5}$. Class 2 contains only one element, sulfur. Out of the 36 elements measured at both locations, sulfur showed the highest concentrations, with values lowest during the spring and highest during the winter. Both Class 1 and 2 elements at Boyd Park showed no significant concentration increases resulting from the fire season, with the exception of calcium. Class 3 contains chlorine, potassium, and zinc. All three of these elements are low during the spring, and then increased dramatically during the fire season, possibly the result of smoke. Summer averages of chlorine, potassium, and zinc minus the smoke season are consistent with spring values. Concentrations of the Class 3 compounds increased during the fall and peaked during the winter, most likely the result of residential wood combustion in the Missoula Valley and poor dispersion. Potassium and rubidium have been used as tracers for wood combustion (Kavouras, 2001).

Class 1 compounds at Frenchtown still have generally higher levels during the spring and winter, but also have higher concentrations of aluminum, silicon, and iron during the fire season compared to Boyd Park. This could be the result of the increased fire activity at the Frenchtown Fire Department parking lot during the 2000 fire season. Many out-of-state fire trucks, flat bed trailers, and personnel brought to Montana to fight the wildfires were stationed at Frenchtown. Some of the areas around the sampling station were not paved, and dust was kicked up with the increased activity. Frenchtown copper does not exhibit Class 1 properties because it shows its highest levels during the fall followed by winter, summer, and spring. Sulfur holds the same trend as Boyd Park, as does the Class 3 compounds. Figure 3-5 demonstrates that the Class 2 and 3 elements show the same overall trend as the $PM_{2.5}$ mass in Figure 3-1. These elements contribute to the high mass days of 12/23/00, 1/4/01, and 2/21/01. Sulfur has the highest levels during these days, particularly in Frenchtown. One element worth noting is barium, which hovers consistently around 0.02 $\mu g/m^3$ throughout the year at both sites. Finally, Class 3 elemental concentrations increased during the fire season. A more complete discussion of this is given in Part III of this document.

Figure 3-5:



Note: Class 1 and Class 2 / 3 Elements have different scales on y-axis (ug/m^3).

3.5 Anions and Cations

Table 3-5: Anion and cation averages (μg/m^3) for Boyd Park and Frenchtown.

	Spring (3/22/00 – 6/14/00)	Summer (6/26/00 – 9/18/00)	2000 Fire Season (8/13/00, 8/25/00)	Summer (Excluding Fire Season)	Fall (9/30/00 12/11/00)	Winter (12/23/00 3/17/01)	Yearly Avg	Yearly Avg (Excluding Fire Season)
Boyd Park								
Fluoride[1]	0.610	0.157	0.235	0.130	0.019	0.047	0.214	0.213
Chloride[2]	0.009	0.024	0.010	0.028	0.131	0.242	0.101	0.107
Nitrate[2]	0.117	0.214	0.468	0.129	1.285	6.608	2.081	2.192
Sulfate[2]	0.511	0.878	0.810	0.901	1.158	1.638	1.043	1.059
Sodium[2]	0.140	0.243	0.131	0.280	0.972	0.976	0.570	0.600
Magnesium[1]	0.010	0.017	0.000	0.022	0.000	0.000	0.007	0.007
Ammonium[2]	0.168	0.270	0.346	0.244	0.552	2.140	0.790	0.821
Potassium[2]	0.114	0.178	0.327	0.128	0.216	0.215	0.180	0.170
Calcium[2]	0.000	0.208	0.183	0.216	0.591	0.443	0.302	0.310
Frenchtown								
Fluoride[1]	0.538	0.188	0.373	0.126	0.007	0.047	0.201	0.189
Chloride[2]	0.011	0.033	0.010	0.040	0.076	0.265	0.097	0.103
Nitrate[2]	0.113	0.152	0.362	0.083	1.035	6.095	1.875	1.980
Sulfate[2]	0.497	0.846	0.803	0.860	1.160	2.221	1.181	1.208
Sodium[2]	0.153	0.208	0.110	0.241	1.050	1.317	0.670	0.709
Magnesium[1]	0.006	0.005	0.000	0.007	0.000	0.000	0.003	0.003
Ammonium[2]	0.153	0.270	0.333	0.249	0.464	2.036	0.739	0.767
Potassium[2]	0.116	0.152	0.285	0.108	0.191	0.342	0.201	0.195
Calcium[2]	0.029	0.170	0.171	0.170	0.564	0.403	0.283	0.290

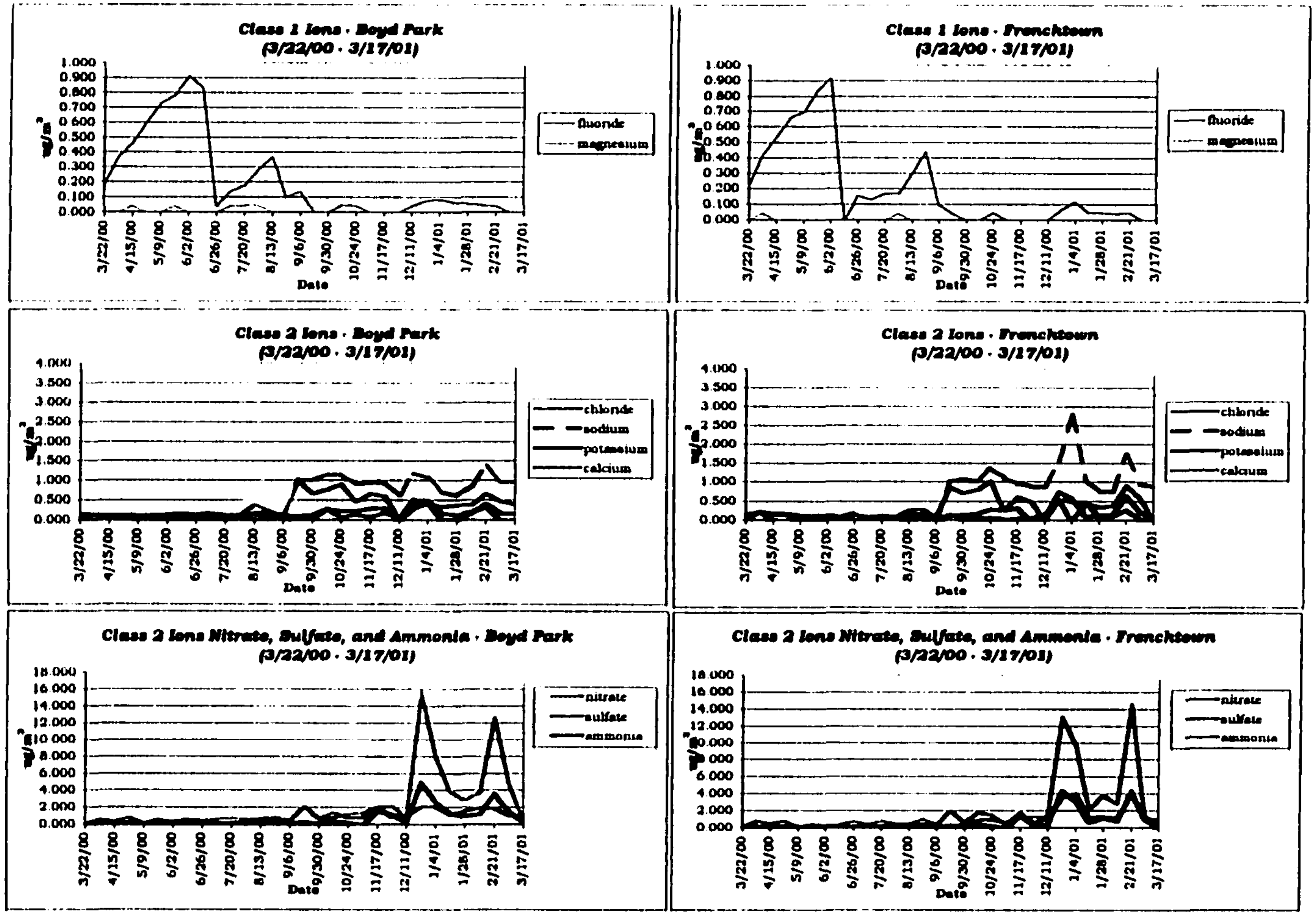
1: Class 1 Ions.
2: Class 2 Ions.

Anions and cations averaged 34% of the yearly PM$_{2.5}$ composition at both Boyd Park and Frenchtown. Nine anions and cations were quantified, and these can be further broken into two classes as displayed in Table 3-5. The first class contains fluoride and magnesium, characterized by higher levels during the spring and summer months. The second class contains the remaining seven ions which exhibit higher levels during the fall and winter and lower levels during the spring and summer. This group not only contains the most members, but also the three most abundant ions measured: nitrate, ammonium, and sulfate. The ion with the highest measured concentration at both sites is nitrate, with levels reaching an average of 6.608 μg/m^3 at Boyd Park and 6.095 μg/m^3 at Frenchtown during the winter season. The second most abundant ion measured during the year is sulfate, which is found in greater concentrations at Frenchtown. The third most abundant ion measured is ammonium, with higher levels at Boyd Park.

Figure 3-6 shows the trends for Class 1 ions, Class 2 ions, and another graph displaying nitrate (NO_3^-), sulfate (SO_4^{2-}), and ammonium (NH_4^+) throughout the year at both Boyd Park and Frenchtown. This figure demonstrates that during the winter months, NH_4^+ and NO_3^- show the same overall trend as the $PM_{2.5}$ mass in Figure 3-1. These two ions compose the secondary air pollutant ammonium nitrate (NH_4NO_3), which is formed from the atmospheric reaction of ammonia (NH_3) and nitric acid (HNO_3). These two ions are highly correlated, with correlation coefficients of 0.978 at Boyd Park and 0.975 at Frenchtown. SO_4^{2-} also follows the $PM_{2.5}$ trend during the winter months. The SO_4^{2-} measured is likely in the form of ammonium sulfate ($(NH_4)_2SO_4$), which is commonly emitted from the kraft pulping process at Smurfit-Stone Container. It can also be formed as a secondary pollutant from the atmospheric reaction of NH_3 and sulfuric acid (H_2SO_4). NH_4^+ and SO_4^{2-} show correlation coefficients of 0.718 at Boyd Park and 0.911 at Frenchtown. All three of these ions contribute to the high mass days of 12/23/00, 1/4/01, and 2/21/01. During the warmer sample days, NH_4NO_3 is still present, but not collected as $PM_{2.5}$ because it is in the gaseous phase.

SO_4^{2-} / NO_3^- / NH_4^+ contribute 25% to the annual fine fraction at both Boyd Park and Frenchtown. Brook *et al.* (1997) reported that the average SO_4^{2-} / NO_3^- / NH_4^+ component accounts for about 20% to 45% of the fine fraction at multiple Canadian locations. These values are within the range reported by Malm *et al.* (1994) for the IMPROVE (Interagency Monitoring of Protected Visual Environments) network across the United States. A study in the South Coast Air Basin of Southern California conducted by Kim *et al.* (2000) reported that the sum of secondary $PM_{2.5}$ species SO_4^{2-} / NO_3^- / NH_4^+ accounted for 55% of $PM_{2.5}$ at Fontana and 66% of $PM_{2.5}$ at Rubidoux. A discussion of the anions and cations measured during the 2000 fire season is given in Part III.

Figure 3-6:



Note: Class 1 and Class 2 Ions have different scales on y-axis (ug/m³).

3.6 SVOC Calculations

The temperatures and pressures used in calculating the concentrations of SVOCs were those logged by the BGI PQ200 during $PM_{2.5}$ sampling. After determining the flow rate for the PUF samplers during the 24 hour sample run, the concentrations of each analyte were calculated in parts per trillion by volume (pptv) using the following equation:

$$\text{Analyte (pptv)} = [A / ((1 \times 10^9 \text{ ng}) * X)] / [PV / RT] * (1 \times 10^{12})$$

where,

A = Mass of analyte from quantitation database (ng).
X = Molecular weight of analyte (g / mol).
P = Average atmospheric pressure during sampling (mm Hg).
V = Volume of air sampled (L).
R = Gas constant (62.4 L*mm Hg / K*mol).
T = Average temperature during sampling (K).

Results from the PUF field blank analyses showed that phenol was usually present at low background levels. Final concentrations for phenol were corrected by subtracting out the average mass of phenol (ng) detected in the field blanks from each sample before the concentration calculation. Other SVOC analytes did not have a consistent presence in the field blanks, and therefore did not have to be corrected for background levels.

3.7 SVOCs

Table 3-6: SVOC averages (pptv) for Boyd Park.

	Spring (3/22/00 – 6/14/00)	Summer (6/26/00 – 9/18/00)	2000 Fire Season (8/13/00 – 8/25/00)	Summer (Excluding Fire Season)	Fall (9/30/00 – 12/11/00)	Winter (12/23/00 – 3/17/01)	Yearly Avg	Yearly Avg (Excluding Fire Season)
Boyd Park								
Phenol[1]	0.52	0.75	1.50	0.50	3.29	6.81	3.07	3.20
2-methylphenol[1]	0.34	0.51	1.03	0.34	1.70	3.79	1.71	1.77
4-methylphenol[1]	0.44	0.97	2.35	0.51	3.31	8.06	3.49	3.57
2,4-dimethylphenol[1]	0.31	0.46	0.97	0.30	1.24	2.43	1.19	1.21
Napthalene[2]	0.17	0.26	0.33	0.23	1.91	2.95	1.30	1.37
2-methylnapthalene[2]	0.33	0.46	0.57	0.43	2.66	5.23	2.35	2.49
Aceanaphthylene[2]	0.09	0.13	0.14	0.12	0.61	1.75	0.64	0.68
Acenaphthene[2]	0.07	0.09	0.10	0.09	0.15	0.30	0.15	0.16
Dibenzofuran[2]	0.11	0.17	0.32	0.12	0.44	1.12	0.50	0.51
Fluorene[2]	0.20	0.22	0.27	0.21	0.50	1.12	0.51	0.53
Phenanthrene[2]	0.86	1.17	1.44	1.07	1.23	2.56	1.46	1.46
Anthracene[2]	0.15	0.17	0.17	0.17	0.17	0.33	0.21	0.21
Fluoranthene[2]	0.20	0.26	0.29	0.26	0.35	0.80	0.40	0.41
Pyrene[2]	0.17	0.21	0.22	0.21	0.35	0.74	0.37	0.38
Benzo(a)anthracene[3]	0.03	0.00	0.00	0.00	0.07	0.19	0.07	0.08
Chrysene[3]	0.02	0.00	0.00	0.00	0.05	0.19	0.07	0.07
Benzo(b)fluoranthene[3]	0.02	0.00	0.00	0.00	0.03	0.13	0.05	0.05
Benzo(k)fluoranthene[3]	0.01	0.00	0.00	0.00	0.03	0.12	0.04	0.04
Benzo(a)pyrene[3]	0.03	0.00	0.00	0.00	0.05	0.15	0.06	0.06

1: Class 1 SVOCs.
2: Class 2 SVOCs.
3: Class 3 SVOCs.

Table 3-7: SVOC averages (pptv) for Frenchtown.

	Spring (3/22/00 – 6/14/00)	Summer (6/26/00 – 9/18/00)	2000 Fire Season (8/13/00 – 8/25/00)	Summer (Excluding Fire Season)	Fall (9/30/00 – 12/11/00)	Winter (12/23/00 – 3/17/01)	Yearly Avg	Yearly Avg (Excluding Fire Season)
Frenchtown								
Phenol[1]	0.29	1.01	2.50	0.27	3.38	6.73	3.15	3.21
2-methylphenol[1]	0.25	0.72	1.66	0.25	2.05	4.32	2.02	2.06
4-methylphenol[1]	0.24	0.64	1.70	0.12	3.90	9.55	3.99	4.21
2,4-dimethylphenol[1]	0.21	0.58	1.45	0.15	1.74	3.19	1.57	1.58
Napthalene[2]	0.13	0.24	0.29	0.22	1.03	1.20	0.65	0.68
2-methylnapthalene[2]	0.24	0.28	0.32	0.26	1.44	1.83	1.03	1.09
Aceanaphthylene[2]	0.06	0.12	0.16	0.10	0.68	1.21	0.52	0.55
Acenaphthene[2]	0.19	0.36	0.37	0.35	0.23	0.40	0.29	0.29
Dibenzofuran[2]	0.33	0.51	0.65	0.44	0.65	1.22	0.72	0.72
Fluorene[2]	0.45	0.63	0.70	0.59	0.59	1.08	0.69	0.69
Phenanthrene[2]	1.70	3.33	3.36	3.31	1.49	2.67	2.29	2.20
Anthracene[2]	0.19	0.37	0.36	0.38	0.21	0.33	0.27	0.27
Fluoranthene[2]	0.32	0.70	0.60	0.74	0.38	0.67	0.52	0.51
Pyrene[2]	0.21	0.40	0.38	0.41	0.33	0.59	0.38	0.38
Benzo(a)anthracene[3]	0.03	0.02	0.05	0.00	0.09	0.17	0.08	0.08
Chrysene[3]	0.03	0.00	0.00	0.00	0.06	0.18	0.07	0.07
Benzo(b)fluoranthene[3]	0.02	0.00	0.01	0.00	0.04	0.10	0.04	0.04
Benzo(k)fluoranthene[3]	0.01	0.01	0.02	0.00	0.03	0.10	0.04	0.04
Benzo(a)pyrene[3]	0.02	0.00	0.00	0.00	0.04	0.12	0.05	0.05

1: Class 1 SVOCs.
2: Class 2 SVOCs.
3: Class 3 SVOCs.

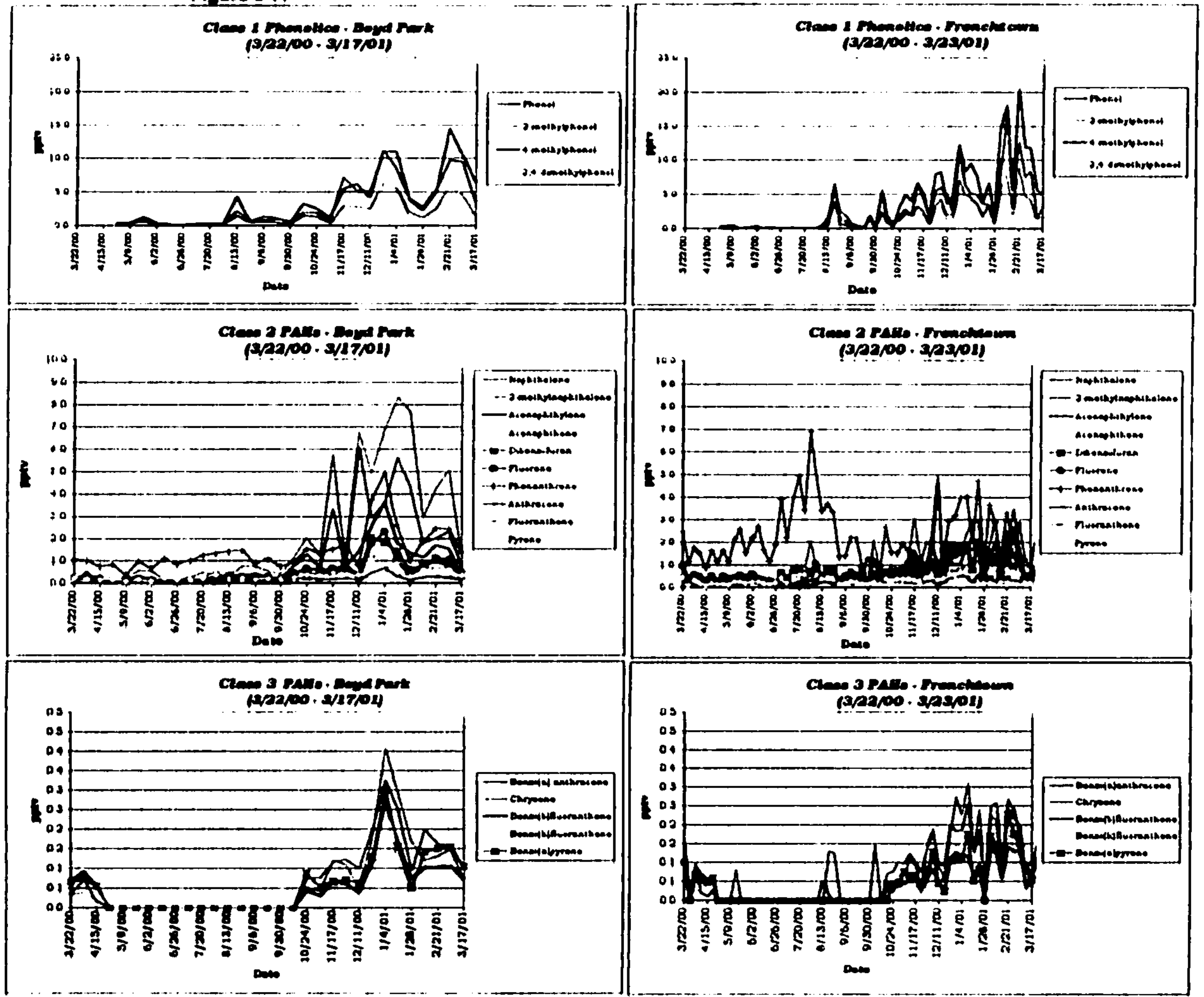
Out of the 61 SVOCs originally quantified, only 19 were tracked throughout the entire sampling program, with seasonal averages presented in Tables 3-6 and 3-7 and yearly trends presented in Figure 3-7. These 19 can be further broken down into three classes by molecular weights: 1) phenolics (94.12 – 122.17 g/mol) 2) lighter PAHs (128.18 – 202.26 g/mol), and 3) heavier PAHs (228.30 – 252.32 g/mol). More than 100 PAH compounds have been identified in both the gas and particle phases in urban air. As a rule of thumb, two- and three-ring PAHs (naphthalene, fluorene, phenanthrene, anthracene, etc.) are found predominantly in the gas phase, four-ring PAHs (pyrene) exist in both phases, while five- and six-ring PAHs exist primarily in the particulate phase (Seinfeld and Pandis, 1998). This partition between the gaseous and particulate phase is extremely complex, and depends on temperature, vapor pressures of individual species, the absolute and relative concentrations of all of the different species, and the amounts and types of adsorbing particle surfaces.

At Boyd Park, concentrations of Class 1 phenolics did not change a great deal from spring to summer (excluding forest fires). Their levels increased dramatically in fall before peaking during the winter. Class 2 PAHs had slightly higher levels during the summer (excluding the fire season) than spring. Their levels also increased during the fall and spiked during the winter. The heavier PAHs had low concentrations during the spring but were not detected during the summer months. They were detected again during the fall at slightly higher levels than spring, and like Class 1 and 2, spiked during the winter months.

Frenchtown phenolics show similar patterns with Boyd Park. Phenol and 2-methylphenol had nearly identical concentrations from spring to summer (excluding the fire season), while 4-methylphenol and 2,4-dimethylphenol had lower levels during the summer. All phenolics then increased through the fall before peaking during the winter. Class 2 Frenchtown PAHs behaved a little differently than Boyd Park. Like Boyd Park, all concentrations of Class 2 PAHs had higher levels during the summer (excluding the fire season) compared to spring. Naphthalene, 2-methylnapthalene, acenaphthylene, and dibenzofuran again increased through the fall before peaking during the winter months. Fluorene had the same levels from summer to fall, while acenaphthene and pyrene measured higher levels during the summer (excluding fire season) compared to fall. All three displayed their highest average concentrations during the winter. Phenanthrene, anthracene, and fluoranthene showed completely new trends with their highest concentrations of the year during the summer (excluding the fire season). The heavier PAHs at Frenchtown showed the same trends as Boyd Park, with low levels during the spring, absent during the summer (excluding fire season), and then reappearing during the fall before peaking during the winter months.

SVOC average concentrations are comparable between both sides of the Missoula Valley, with Class 1 phenolics the most abundant species at both sites. Naphthalene and 2-methylnaphthalene have higher average concentrations at Boyd Park, possibly the result of more automobiles in Missoula. Mobile sources have been shown to be the major PAH contributors in urban areas (Seinfeld and Pandis, 1998). Levels of PAHs measured in the Missoula Valley are either at or below the ranges reported in other studies. In PAH sampling (Yamasaki *et al.*, 1982) conducted in Tokyo in the early 1980's, phenanthrene concentrations were measured between 50.2 – 295.0 ng/m^3, while fluoranthene was measured from 13.3 – 80.0 ng/m^3. In a more recent study conducted by Subramanyam *et* *al.* (1994) in Baton Rouge, Louisiana, phenanthrene was measured between 7.0 – 71.7 ng/m^3, while fluoranthene was measured from 0.2 – 41.9 ng/m^3. On one of the highest PAH days in Missoula (1/4/01), phenanthrene and fluoranthene were measured at 35.8 ng/m^3 and 11.7 ng/m^3, respectively. The high pollution inversion days of 12/23/00, 1/4/01, and 2/21/01 are reflected in the Class 1 phenolics trend (Figure 3-7), but are harder to see in the Class 2 and 3 PAH graphs. Finally, a complete discussion of the fire season SVOCs is given in Part III.

Figure 3-7:



Note: Class 1, Class 2, and Class 3 SVOCs have different scales on y-axis (ppbv).

3.8 VOC Calculations

The temperatures and pressures used in calculating the concentrations of VOCs were those logged by the BGI PQ200 during $PM_{2.5}$ sampling. After determining the flow rate for the VOC pumps during the 24 hour sample run, the concentrations of each analyte were calculated in parts per trillion by volume (pptv) using the following equation:

$$\text{Analyte (pptv)} = [A / ((1 \times 10^{9}\ \text{ng})*X)] / [PV / RT] * (1 \times 10^{12})$$

where,

A = Mass of analyte from quantitation database (ng).
X = Molecular weight of analyte (g / mol).
P = Average atmospheric pressure during sampling (mm Hg).
V = Volume of air sampled (L).
R = Gas constant (62.4 L*mm Hg / K*mol).
T = Average temperature during sampling (K).

Results from the VOC field blank analyses showed that chloroform, benzene, toluene, ethylbenzene, 1,4-dimethylbenzene, 1,2-dimethylbenzene, *n*-propylbenzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, isopropylbenzene, and naphthalene showed low but consistent background levels in the blanks. Final concentrations for these compounds were corrected by subtracting out the average mass of each analyte (ng) detected in the field blanks from each sample analyte before the concentration calculation.

3.9 VOCs

Table 3-8: VOC averages (pptv) for Boyd Park.

	Spring (3/22/00 — 6/14/00)	Summer (6/26/00 — 9/18/00)	2000 Fire Season (8/13/00, 8/25/00)	Summer (Excluding Fire Season)	Fall (9/30/00 — 12/11/00)	Winter (12/23/00 — 3/17/01)	Yearly Avg	Yearly Avg (Excluding Fire Season)
Boyd Park								
Trichloromethane[2]	26.40	13.18	11.42	13.77	16.59	5.22	15.31	15.57
Tetrachloromethane[2]	92.38	60.17	68.71	57.32	62.32	72.58	72.17	72.41
Benzene[1]	310.03	387.32	581.72	322.52	580.94	1020.12	574.40	573.89
Toluene[1]	1062.80	1114.93	1590.44	956.42	1526.06	2068.34	1440.35	1430.00
Ethyl Benzene[1]	121.82	137.28	181.28	122.61	188.65	340.59	197.35	198.46
1,4-Dimethylbenzene[1]	224.54	238.51	301.76	217.42	347.93	644.51	364.38	368.70
1,2-Dimethylbenzene[1]	171.81	181.15	230.02	164.85	249.58	478.45	270.91	273.73
Isopropylbenzene[2]	41.98	30.65	29.68	30.97	45.66	45.65	40.84	41.61
n-Propylbenzene[2]	45.29	41.77	46.61	40.15	58.92	67.32	53.14	53.60
1,3,5-Trimethylbenzene[1]	70.59	68.69	77.53	65.74	86.57	132.98	89.81	90.65
1,2,4-Trimethylbenzene[1]	124.34	158.73	183.60	150.44	234.68	376.39	223.17	225.90
Isopropyl Toluene[2]	42.80	39.78	49.36	36.58	33.98	25.87	35.66	34.71
Naphthalene[1]	58.09	60.71	77.09	55.25	61.32	85.47	66.56	65.84

1: Class 1 Automobile Emission VOCs.
2: Class 2 Other VOCs.

Table 3-9: VOC averages (pptv) for Frenchtown.

	Spring (3/22/00 — 6/14/00)	Summer (6/26/00 — 9/18/00)	2000 Fire Season (8/13/00, 8/25/00)	Summer (Excluding Fire Season)	Fall (9/30/00 — 12/11/00)	Winter (12/23/00 — 3/17/01)	Yearly Avg	Yearly Avg (Excluding Fire Season)
Frenchtown								
Trichloromethane[2]	20.43	7.33	7.13	7.43	13.02	4.13	11.26	11.62
Tetrachloromethane[2]	83.56	57.70	58.14	57.48	53.73	71.15	66.88	67.65
Benzene[1]	215.80	259.83	428.15	175.67	338.74	486.33	326.01	317.05
Toluene[1]	422.97	639.32	781.78	568.09	687.89	804.54	641.40	628.86
Ethyl Benzene[1]	74.42	76.24	102.34	63.20	81.97	125.78	89.94	88.86
1,4-Dimethylbenzene[1]	140.85	122.88	155.65	106.50	139.16	214.65	155.14	155.10
1,2-Dimethylbenzene[1]	122.98	98.83	122.23	87.12	106.52	168.13	124.80	125.03
Isopropylbenzene[2]	40.21	28.28	25.03	29.90	41.60	35.87	36.54	37.55
n-Propylbenzene[2]	36.92	30.17	30.89	29.80	36.10	27.55	32.67	32.83
1,3,5-Trimethylbenzene[1]	55.74	49.26	53.56	47.12	43.36	55.40	51.09	50.87
1,2,4-Trimethylbenzene[1]	79.78	96.50	114.15	87.67	104.25	101.95	95.47	93.83
Isopropyl Toluene[2]	45.42	39.74	47.12	36.05	39.00	51.54	44.07	43.80
Naphthalene[1]	49.98	60.99	75.38	53.80	39.28	40.64	47.64	45.21

1: Class 1 Automobile Emission VOCs.
2: Class 2 Other VOCs.

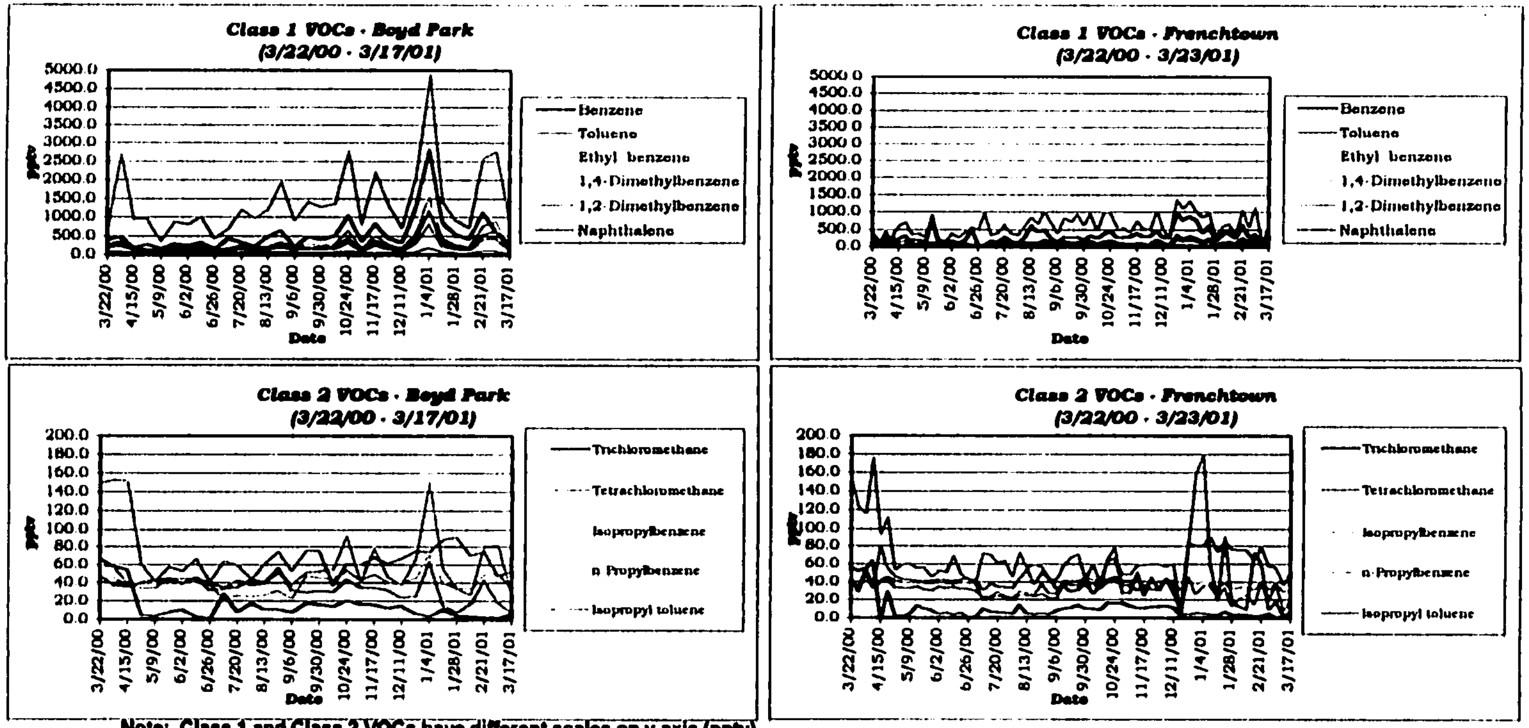
54 VOCs were originally quantified, but later focused to the 13 most abundant VOCs presented in Tables 3-8 and 3-9 and Figure 3-8. These can be further broken down into two classes: automobile emission compounds (Class 1) and others (Class 2). At Boyd Park, Class 1 VOCs had approximately the same levels in comparing spring to

summer (excluding fire season) before levels increased through fall and peaked during the winter. Class 2 VOCs were fairly stable throughout the year, with chloroform and isopropyltoluene having their lowest measured concentrations during the winter. Isopropyltoluene, or *p*-cymene, is a terpene commonly found in the tissues of coniferous plants (Fengel and Wegener, 1984). Terpene emissions have been found to increase exponentially with temperature (Lamb *et al.*, 1985; Juuti *et al.*, 1990; Fehsenfeld *et al.*, 1992), and have been shown to peak during the warmer months and be at their lowest during the winter (Yatagai *et al.*, 1995; Staudt *et al.*, 1997). These findings are consistent with Boyd Park isopropyltoluene. The most abundant VOC measured at Boyd Park was toluene, with a yearly average of 1440.35 pptv. This was followed by benzene (574.40 pptv) and 1,4-dimethylbenzene (364.38 pptv), which are all associated with gasoline powered automobile emissions (Class 1). Chloroform (15.31 pptv) was the least abundant VOC measured at Boyd Park.

At Frenchtown, Class 1 VOC averages generally either decreased or stayed the same from spring to summer (excluding fire season), with the exception of toluene. The original toluene data reported in the 4/3/00 sample measured 6239.2 pptv, nearly 15 times the toluene average for spring. Boyd Park toluene levels were slightly elevated on that day as well, but it did not have the huge increase in levels that Frenchtown did. Therefore, 4/3/00 Frenchtown toluene was deleted from the spring average. This could explain why spring levels of toluene were lower than summer levels (excluding fire season) at Frenchtown. Class 1 automobile emission VOCs again increased from summer to fall before peaking in winter, with the exception of naphthalene, which had slightly higher measured concentrations during the summer compared to the fall and winter months. Class 2 VOC levels, like Boyd Park, were fairly stable throughout the year. Toluene (641.40 pptv), benzene (326.01 pptv), and 1,4-Dimethylbenzene (155.14 pptv) were the most abundant measured compounds at Frenchtown, with chloroform (11.26 pptv) the least abundant.

On average, there were more VOCs at Boyd Park compared to Frenchtown, with nearly double the amount of measured Class 1 automobile emission VOCs in Missoula. This can be explained by the greater number of automobiles on the east side of the Valley compared to the amount on the more rural west side. Car exhaust contains both unburned fuel and volatile chemicals formed during combustion (Kirchstetter *et al.*, 1999) making automobiles the largest contributor of alkane and aromatic chemicals to the atmosphere (Seinfeld and Pandis, 1998). These VOCs can be emitted from the exhaust, evaporative emissions, and in the process of refueling. Trace quantities of chloroform have also been detected in automobile exhaust and in other combustion gases (Aucott *et al.*, 1999). The only VOC measured that did not show a greater annual average concentration at Boyd Park was isopropyltoluene (*p*-cymene), which was found to be a tracer molecule for Smurfit-Stone Container mill emissions in an earlier study (Wrobel, 2000). In Wrobel's study, isopropyltoluene was found in large concentrations at all of the mill locations sampled, and in lower concentrations at sites farther from the mill. Finally, 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene behaved differently at each site. At Boyd Park, these two compounds acted like a Class 1 compound, while at Frenchtown they behaved more like a Class 2 compound. For consistency, they were called Class 2 at both sites, but were not put in either graph. A complete discussion of the smoke season VOCs is given is Part III of this document.

Figure 3-8:



Note: Class 1 and Class 2 VOCs have different scales on y-axis (pptv).

3.10 $PM_{2.5}$ CMB Source Apportionment Model

Average source contribution estimates (SCEs) for each season are presented in pie charts (% SCEs) and graphs ($\mu g/m^3$) in Figures 3-9 through 3-15, while Table 3-10 gives a summary of the SCE information. The following is a description of each of the figures:

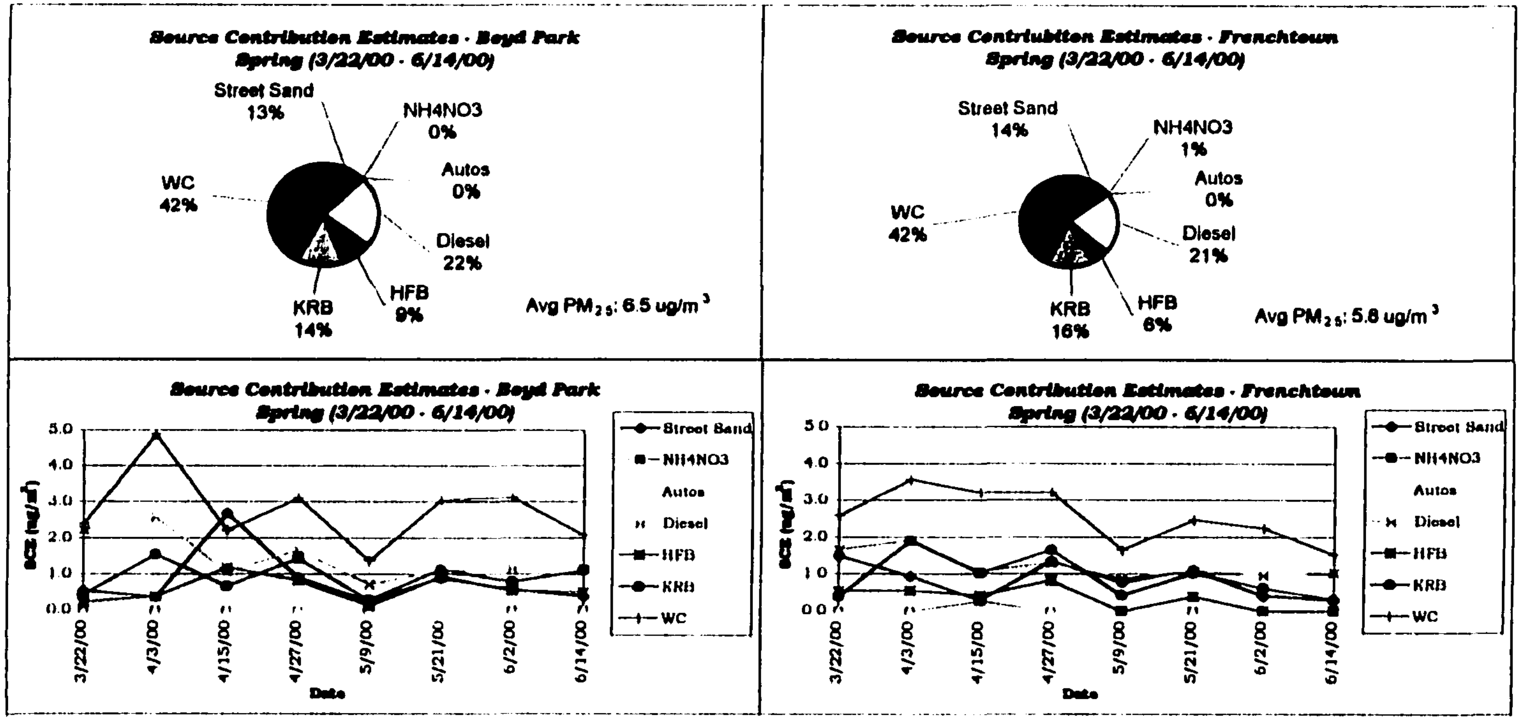
Figure 3-9:	Spring 2000 source contribution estimates for Boyd Park and Frenchtown.
Figure 3-10:	Summer 2000 (including fire season) source contribution estimates for Boyd Park and Frenchtown.
Figure 3-11:	Summer 2000 (excluding fire season) source contribution estimates for Boyd Park and Frenchtown.
Figure 3-12:	Fall 2000 source contribution estimates for Boyd Park and Frenchtown.
Figure 3-13:	Winter 2000/2001 source contribution estimates for Boyd Park and Frenchtown.
Figure 3-14:	2000/2001 Yearly Average (including fire season) source contribution estimates for Boyd Park and Frenchtown.
Figure 3-15:	2000/2001 Yearly Average (excluding fire season) source contribution estimates for Boyd Park and Frenchtown.

Table 3-10: Summary of the source contribution estimates (% and μg/m^3) for Boyd Park and Frenchtown throughout the 2000/2001 CMB Sampling Program.

Boyd Park	Spring (3/22/00 – 6/14/00)	Summer (6/26/00 – 9/18/00)	2000 Fire Season (8/13/00, 8/25/00)	Summer (Excluding Fire Season)	Fall (9/30/00 – 12/11/00)	Winter (12/23/00 – 3/17/01)	Yearly Avg	Yearly Avg (Excluding Fire Season)
Wood Combustion (WC)	42% 2.8 μg/m^3	72% 10.7 μg/m^3	83% 32.5 μg/m^3	50% 3.4 μg/m^3	38% 4.1 μg/m^3	23% 6.0 μg/m^3	40% 5.9 μg/m^3	32% 4.1 μg/m^3
Diesel	22% 1.5 μg/m^3	13% 2.0 μg/m^3	10% 3.9 μg/m^3	19% 1.3 μg/m^3	19% 2.1 μg/m^3	22% 5.6 μg/m^3	19% 2.8 μg/m^3	21% 2.6 μg/m^3
Ammonium Nitrate (NH4NO3)	0% 0.0 μg/m^3	0% 0.0 μg/m^3	0% 0.0 μg/m^3	1% 0.1 μg/m^3	15% 1.7 μg/m^3	33% 8.7 μg/m^3	18% 2.6 μg/m^3	21% 2.6 μg/m^3
Kraft Recovery Boilers (KRB)	14% 0.9 μg/m^r	8% 1.3 μg/m^3	3% 1.2 μg/m^3	18% 1.3 μg/m^3	19% 2.1 μg/m^3	13% 3.3 μg/m^3	13% 1.9 μg/m^3	15% 1.9 μg/m^3
Hog Fuel Boilers (HFB)	9% 0.6 μg/m^3	4% 0.6 μg/m^3	3% 1.4 μg/m^3	5% 0.3 μg/m^3	4% 0.4 μg/m^3	7% 1.9 μg/m^3	6% 0.9 μg/m^3	7% 0.8 μg/m^3
Street Sand	13% 0.8 μg/m^3	3% 0.5 μg/m^3	1% 0.4 μg/m^3	7% 0.5 μg/m^3	3% 0.3 μg/m^3	2% 0.5 μg/m^3	4% 0.5 μg/m^3	4% 0.5 μg/m^3
Autos	0% 0.0 μg/m^3	0% 0.0 μg/m^3	0% 0.0 μg/m^3	0% 0.0 μg/m^3	2% 0.2 μg/m^3	0% 0.0 μg/m^3	0% 0.1 μg/m^3	0% 0.1 μg/m^3
Avg $PM_{2.5}$ Mass	6.5 μg/m^3	15.0 μg/m^3	39.9 μg/m^3	6.7 μg/m^3	10.6 μg/m^3	29.0 μg/m^3	15.4 μg/m^3	13.7μg/m^3
Frenchtown								
Wood Combustion (WC)	42% 2.6 μg/m^3	70% 10.4 μg/m^3	79% 33.6 μg/m^3	46% 2.6 μg/m^3	39% 4.1 μg/m^3	26% 7.1 μg/m^3	41% 6.0 μg/m^3	33% 4.1 μg/m^3
Diesel	21% 1.3 μg/m^3	13% 2.0 μg/m^3	11% 4.7 μg/m^3	19% 1.1 μg/m^3	21% 2.2 μg/m^3	20% 5.4 μg/m^3	18% 2.7 μg/m^3	20% 2.5 μg/m^3
Ammonium Nitrate (NH4NO3)	1% 0.0 μg/m^3	0% 0.0 μg/m^3	0% 0.0 μg/m^3	1% 0.1 μg/m^3	12% 1.3 μg/m^3	29% 8.0 μg/m^3	16% 2.4 μg/m^3	19% 2.4 μg/m^3
Kraft Recovery Boilers (KRB)	16% 0.9 μg/m^3	9% 1.3 μg/m^3	4% 1.7 μg/m^3	21% 1.2 μg/m^3	20% 2.1 μg/m^3	14% 4.0 μg/m^3	14% 2.1 μg/m^3	16% 2.0 μg/m^3
Hog Fuel Boilers (HFB)	6% 0.4 μg/m^3	1% 0.2 μg/m^3	1% 0.5 μg/m^3	1% 0.0 μg/m^3	5% 0.5 μg/m^3	8% 2.3 μg/m^3	6% 0.8 μg/m^3	7% 0.8 μg/m^3
Street Sand	14% 0.9 μg/m^3	7% 1.0 μg/m^3	5% 2.0 μg/m^3	12% 0.7 μg/m^3	3% 0.4 μg/m^3	2% 0.6 μg/m^3	5% 0.7 μg/m^3	5% 0.6 μg/m^3
Autos	0% 0.0 μg/m^3	0% 0.0 μg/m^3	0% 0.0 μg/m^3	0% 0.0 μg/m^3	0% 0.0 μg/m^3	1% 0.1 μg/m^3	0% 0.0 μg/m^3	0% 0.0 μg/m^3
Avg $PM_{2.5}$ Mass	5.8 μg/m^3	14.7 μg/m^3	42.2 μg/m^3	5.6 μg/m^3	10.5 μg/m^3	29.9 μg/m^3	15.4 μg/m^3	13.6 μg/m^3

Both Boyd Park and Frenchtown had similar source contributions to the fine fraction during the 2000/2001 CMB Sampling Program. Tables 3-11 and 3-12 list the source contribution estimates for Boyd Park and Frenchtown for each sample day throughout the entire CMB sampling program. The biggest source contributing to the ambient $PM_{2.5}$ in the Missoula Valley throughout the year was wood combustion, followed by diesel, ammonium nitrate (NH_4NO_3), the kraft recovery boilers from Smurfit-Stone Container, other hog fuel boilers, and street sand. Gasoline powered automobiles were found by the CMB Model 8.0 to be an insignificant contributor to the fine fraction.

Figure 3-9:



Source Contribution Estimates - Boyd Park Spring (3/22/00 - 6/14/00)

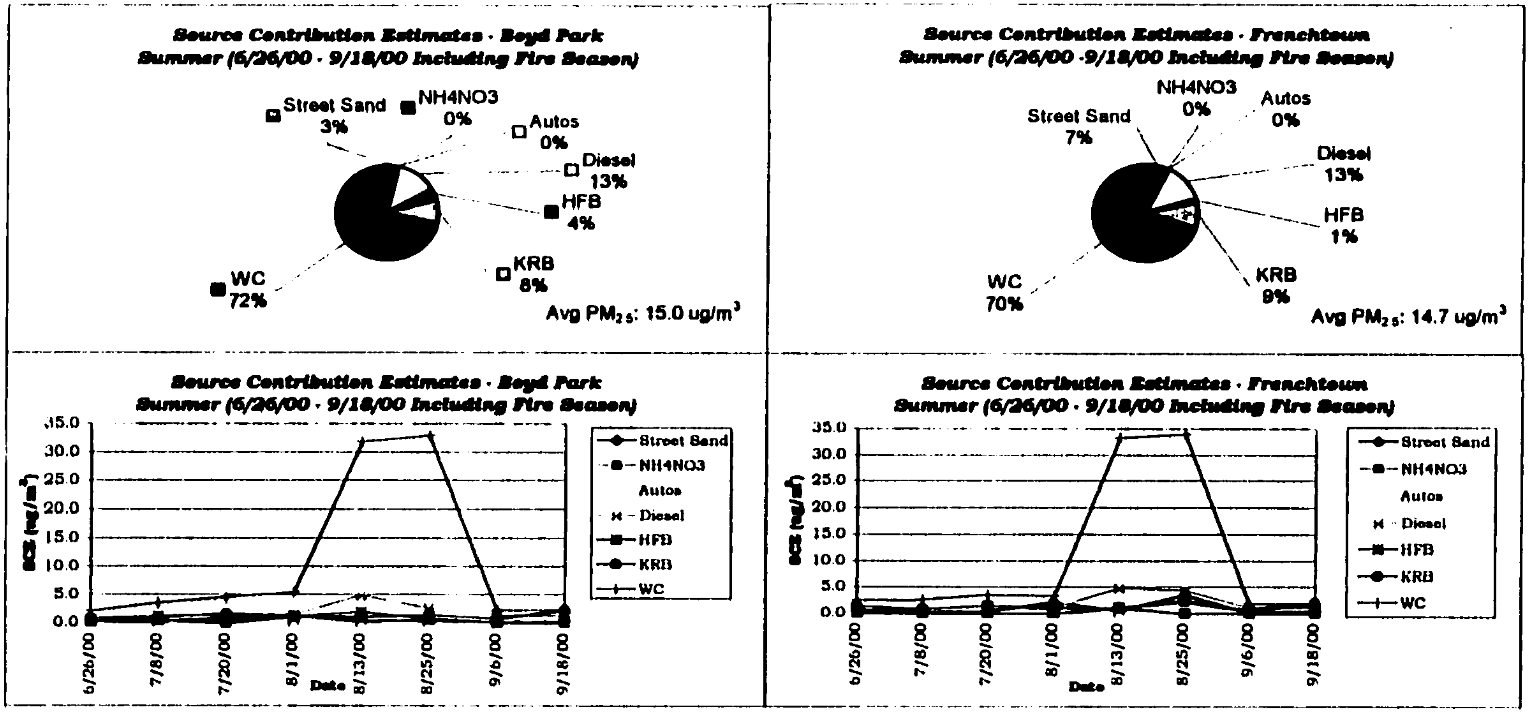
Source Contriubtion Estimates - Frenchtown Spring (3/22/00 - 6/14/00)

Source Contribution Estimates - Boyd Park Spring (3/22/00 - 6/14/00)

Source Contribution Estimates - Frenchtown Spring (3/22/00 - 6/14/00)

Note: Figures 3-9 through 3-15 have different scales on y-axis (ug/m^3).

Figure 3-10:



Source Contribution Estimates - Boyd Park
Summer (6/26/00 - 9/18/00 Including Fire Season)

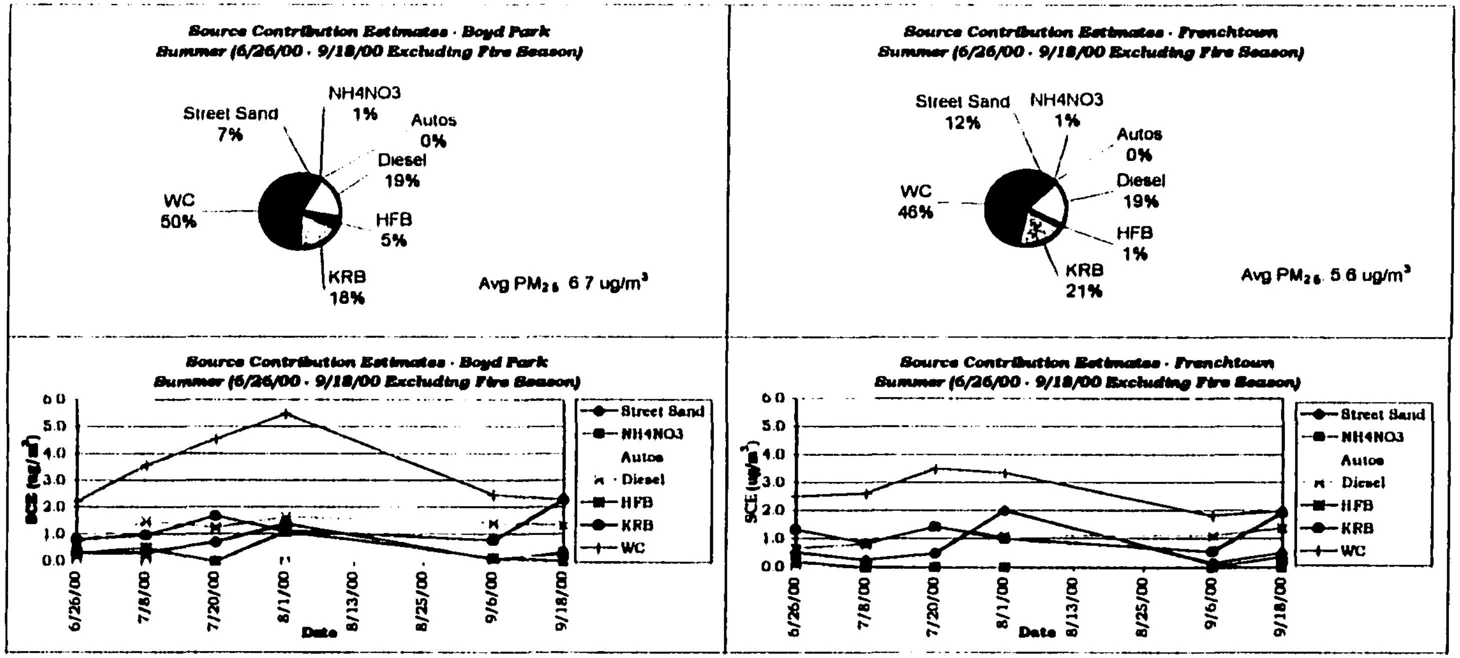
Source Contribution Estimates - Frenchtown
Summer (6/26/00 - 9/18/00 Including Fire Season)

Source Contribution Estimates - Boyd Park
Summer (6/26/00 - 9/18/00 Including Fire Season)

Source Contribution Estimates - Frenchtown
Summer (6/26/00 - 9/18/00 Including Fire Season)

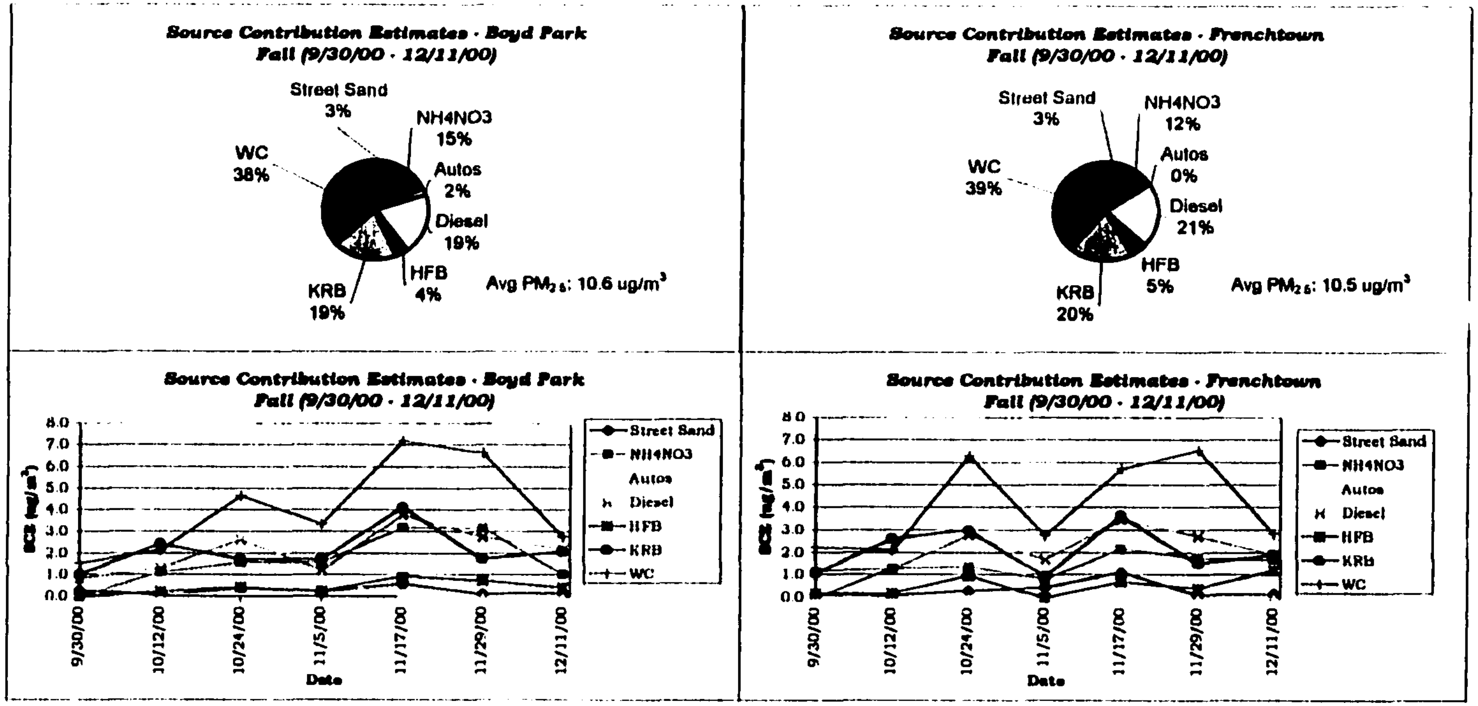
Note: Figures 3-9 through 3-15 have different scales on y-axis (ug/m³).

Figure 3-11:



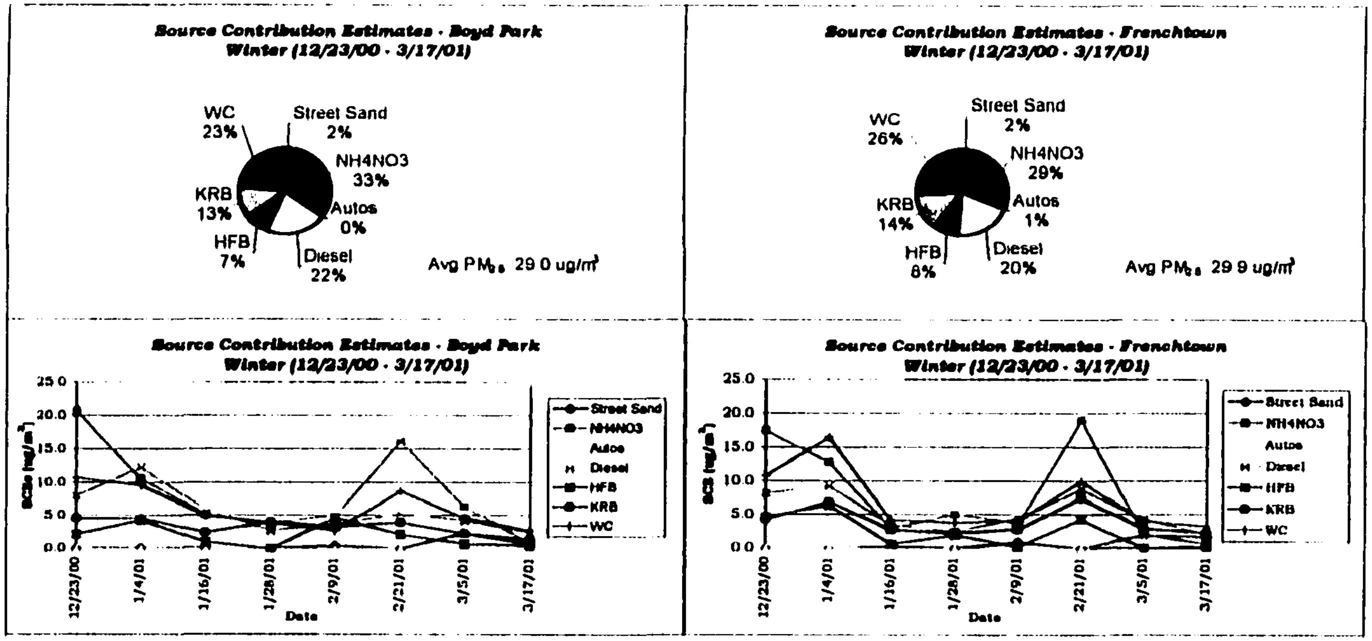
Note: Figures 3-9 through 3-15 have different scales on y-axis (ug/m^3).

Figure 3-12:



Note: Figures 3-9 through 3-15 have different scales on y-axis (ug/m³).

Figure 3-13:



Source Contribution Estimates - Boyd Park
Winter (12/23/00 - 3/17/01)

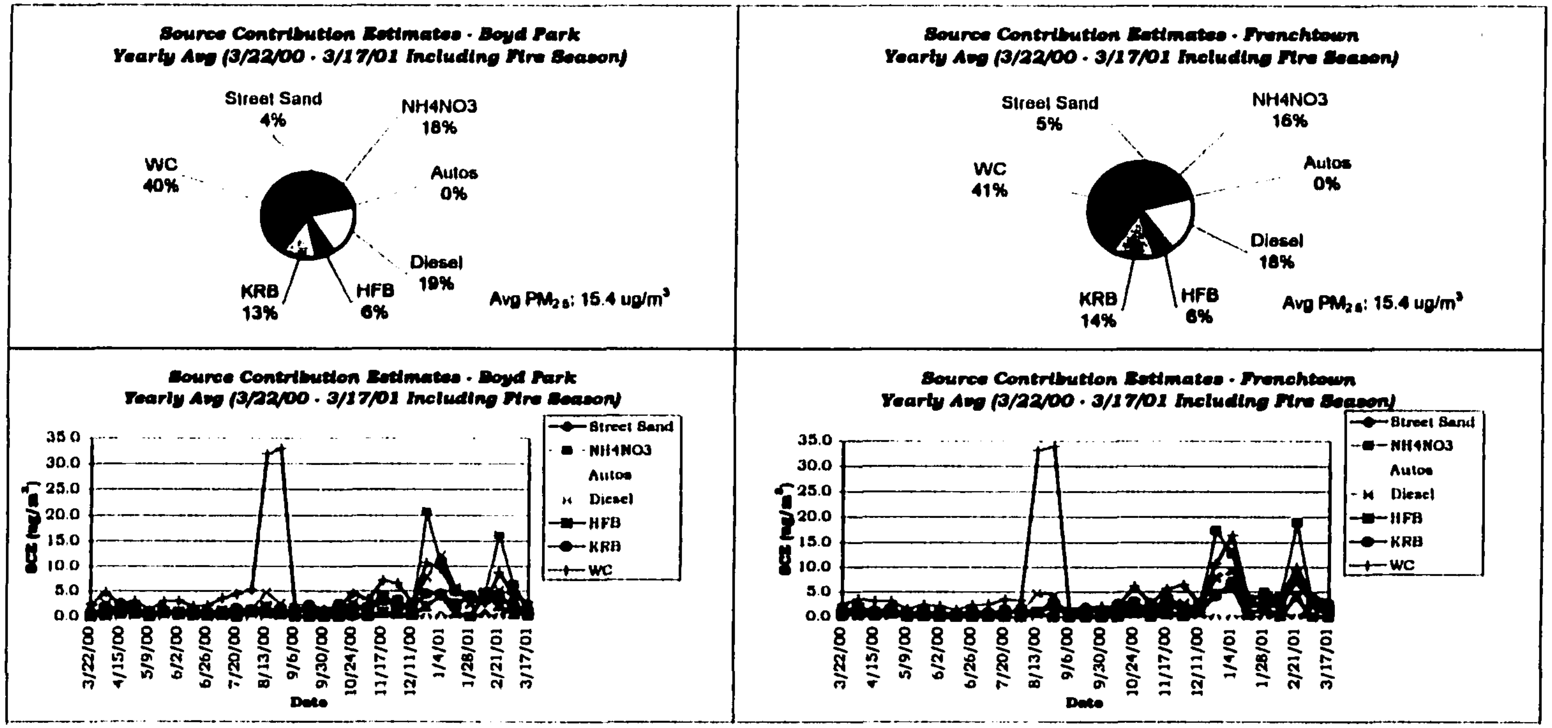
Source Contribution Estimates - Frenchtown
Winter (12/23/00 - 3/17/01)

Source Contribution Estimates - Boyd Park
Winter (12/23/00 - 3/17/01)

Source Contribution Estimates - Frenchtown
Winter (12/23/00 - 3/17/01)

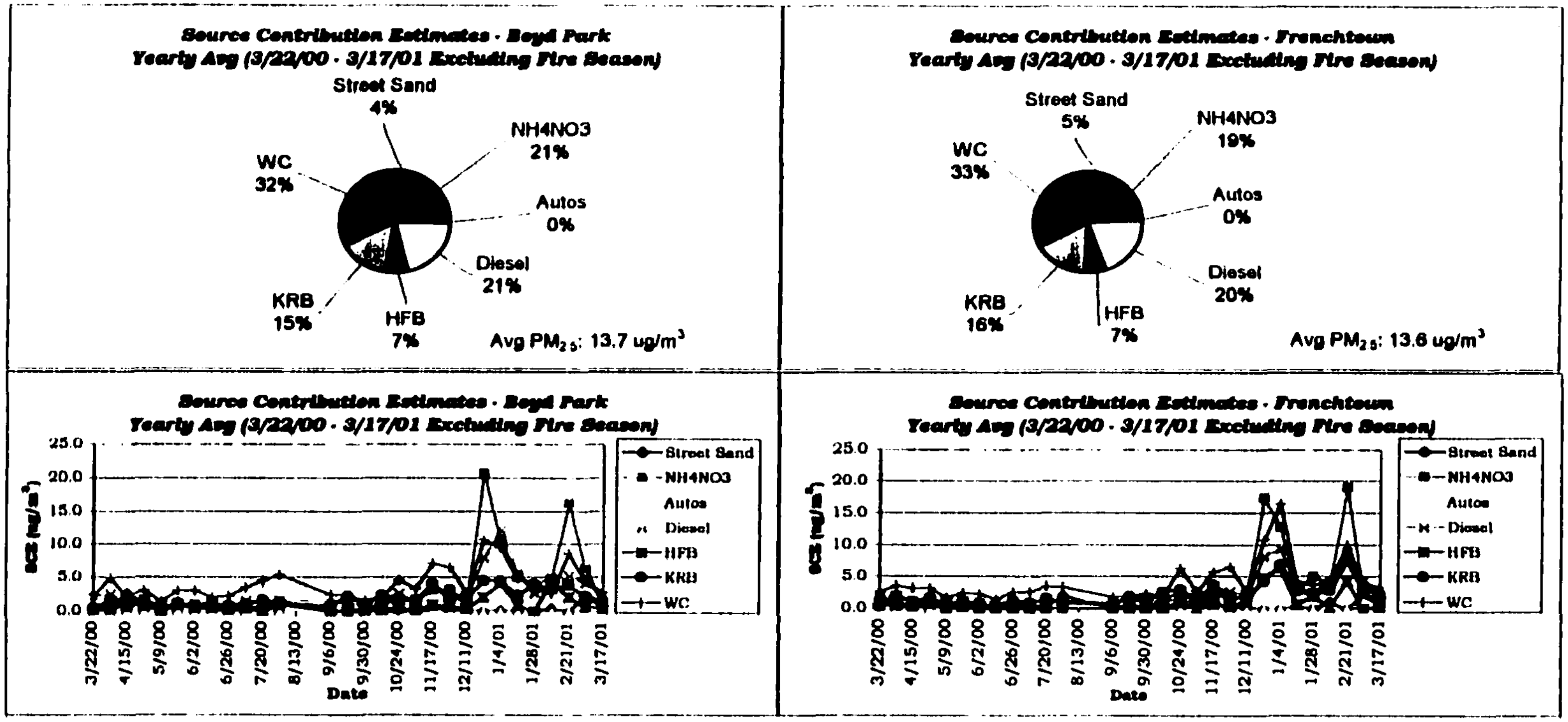
Note: Figures 3-9 through 3-15 have different scales on y-axis (ug/m³).

Figure 3-14:



Note: Figures 3-9 through 3-15 have different scales on y-axis (ug/m³).

Figure 3-15:



Note: Figures 3-9 through 3-15 have different scales on y-axis (ug/m³).

Table 3-11

Source contribution estimates (ug/m^3) for every CMB sample day - Boyd Park.

	Street Sand	Ammonium Nitrate	Autos	Diesel	Hog Fuel Boilers	Kraft Recovery Boilers	Wood Combustion
Spring 2000							
3/22/00	0.6	0.0	0.0	2.3	0.2	0.5	2.4
4/3/00	0.4	0.0	0.0	2.6	0.4	1.6	4.9
4/15/00	2.7	0.0	0.0	1.1	1.2	0.7	2.2
4/27/00	0.9	0.0	0.0	1.7	0.9	1.4	3.1
5/9/00	0.3	0.0	0.0	0.8	0.1	0.3	1.4
5/21/00	0.9	0.0	0.0	1.1	1.0	1.1	3.1
6/2/00	0.6	0.0	0.0	1.2	0.6	0.8	3.1
6/14/00	0.4	0.0	0.0	1.2	0.5	1.1	2.1
Average	0.8	0.0	0.0	1.5	0.6	0.9	2.8
Summer 2000							
6/26/00	0.3	0.0	0.0	0.7	0.3	0.8	2.2
7/8/00	0.3	0.0	0.0	1.5	0.5	1.0	3.6
7/20/00	0.7	0.0	0.0	1.3	0.0	1.7	4.5
8/1/00	1.4	0.0	0.0	1.7	1.1	1.1	5.5
8/13/00	0.3	0.0	0.0	5.0	2.0	1.1	31.9
8/25/00	0.5	0.0	0.0	2.7	0.7	1.4	33.0
9/6/00	0.1	0.0	0.0	1.4	0.1	0.8	2.5
9/18/00	0.3	0.4	0.0	1.4	0.0	2.3	2.3
Average	0.5	0.0	0.0	2.0	0.6	1.3	10.7
Fall 2000							
9/30/00	0.3	0.0	0.0	0.8	0.0	1.0	1.6
10/12/00	0.1	1.1	0.0	1.3	0.3	2.5	2.1
10/24/00	0.4	1.6	0.8	2.7	0.4	1.7	4.7
11/5/00	0.2	1.6	0.8	1.2	0.3	1.7	3.4
11/17/00	0.6	3.2	0.0	3.8	0.9	4.1	7.2
11/29/00	0.1	3.2	0.0	2.8	0.7	1.8	6.6
12/11/00	0.2	1.0	0.0	2.2	0.4	2.1	2.8
Average	0.3	1.7	0.2	2.1	0.4	2.1	4.1
Winter 2000 / 2001							
12/23/00	0.0	20.8	0.0	8.1	2.1	4.6	10.8
1/4/01	0.1	10.6	0.0	12.4	4.3	4.5	9.7
1/16/01	0.1	5.2	0.0	6.0	1.0	2.4	5.0
1/28/01	0.0	3.9	0.0	2.7	0.0	4.0	3.8
2/9/01	0.5	5.0	0.0	3.6	4.6	3.3	2.8
2/21/01	0.0	16.4	0.0	5.3	2.2	4.0	8.7
3/5/01	2.4	6.4	0.0	4.3	0.7	2.2	4.6
3/17/01	0.7	0.8	0.0	2.4	0.4	1.3	2.8
Average	0.5	8.7	0.0	5.6	1.9	3.3	6.0

Street Sand: includes MSLA01 (ST_SANDF), MSLA 02 (ERN_RUSF), MSLA 03 (RUS_STF2), and MSLA04 (DESP_LTF).

Diesel: includes MSLA 11 (LDV_DSLF), MSLA 12 (LDV_DS2F), and MSLA 13 (HDV_DSLF).

Hog Fuel Boilers: includes MSLA18 (HFB_PLYF), MSLA19 (HFB_PL2F), MSLA20 (HFB_DOF2), MSLA21 (HFB_CMPF), MSLA25 (WFB_CMPF), and MSLA27 (LP_CHPDF).

Table 3-12

Source contribution estimates (ug/m^3) for every CMB sample day - Frenchtown.

	Street Sand	Ammonium Nitrate	Autos	Diesel	Hog Fuel Boilers	Kraft Recovery Boilers	Wood Combustion
Spring 2000							
3/22/00	1.5	0.0	0.0	1.7	0.6	0.4	2.8
4/3/00	1.0	0.0	0.0	1.9	0.6	1.9	3.6
4/15/00	0.3	0.3	0.0	1.1	0.4	1.0	3.2
4/27/00	1.4	0.0	0.0	1.3	0.8	1.7	3.2
5/9/00	0.8	0.0	0.0	0.9	0.0	0.4	1.7
5/21/00	1.1	0.0	0.0	1.1	0.4	1.0	2.5
6/2/00	0.4	0.0	0.0	1.0	0.0	0.6	2.3
6/14/00	0.3	0.0	0.0	1.1	0.0	0.3	1.5
Average	0.9	0.0	0.0	1.3	0.4	0.9	2.6
Summer 2000							
6/26/00	0.5	0.0	0.0	0.7	0.2	1.3	2.5
7/8/00	0.3	0.0	0.0	0.8	0.0	0.9	2.6
7/20/00	0.5	0.0	0.0	1.5	0.0	1.5	3.5
8/1/00	2.0	0.0	0.0	1.1	0.0	1.0	3.4
8/13/00	0.6	0.0	0.0	5.0	1.1	1.1	33.2
8/25/00	3.4	0.0	0.0	4.4	0.0	2.3	34.0
9/6/00	0.1	0.0	0.0	1.1	0.0	0.6	1.8
9/18/00	0.5	0.4	0.0	1.4	0.0	1.9	2.0
Average	1.0	0.0	0.0	2.0	0.2	1.3	10.4
Fall 2000							
9/30/00	0.1	0.0	0.0	1.2	0.2	1.1	2.3
10/12/00	0.1	1.3	0.0	1.3	0.2	2.6	2.1
10/24/00	0.3	1.4	0.0	2.8	1.0	3.0	6.3
11/5/00	0.4	0.8	0.0	1.7	0.0	1.0	2.8
11/17/00	1.2	2.2	0.0	3.5	0.7	3.7	5.7
11/29/00	0.1	1.8	0.0	2.8	0.4	1.5	6.5
12/11/00	0.2	1.7	0.0	1.9	1.2	1.9	2.9
Average	0.4	1.3	0.0	2.2	0.5	2.1	4.1
Winter 2000 / 2001							
12/23/00	0.0	17.5	0.0	8.2	4.7	4.3	10.6
1/4/01	0.0	12.9	0.0	9.4	6.4	6.9	16.5
1/16/01	0.2	3.0	0.0	3.5	0.6	2.8	4.3
1/28/01	0.0	5.1	0.0	2.5	2.0	2.2	3.8
2/9/01	0.9	3.8	0.0	4.4	0.3	2.8	4.1
2/21/01	0.0	19.1	0.0	8.9	4.3	7.5	10.0
3/5/01	2.0	2.1	1.1	4.4	0.0	2.9	4.0
3/17/01	1.7	0.7	0.0	2.0	0.2	2.3	3.3
Average	0.6	8.0	0.1	5.4	2.3	4.0	7.1

Street Sand: Includes MSLA01 (ST_SANDF), MSLA 02 (ERN_RUSF), MSLA 03 (RUS_STF2), and MSLA04 (DESP_LTF).

Diesel: Includes MSLA 11 (LDV_DSLF), MSLA 12 (LDV_DS2F), and MSLA 13 (HDV_DSLF).

Hog Fuel Boilers: Includes MSLA18 (HFB_PLYF), MSLA19 (HFB_PL2F), MSLA20 (HFB_DOF2), MSLA21 (HFB_CMPF), MSLA25 (WFB_CMPF), and MSLA27 (LP_CHPDF).

Chapter 4 Discussion

Section 4.1 describes some of the issues encountered while apportioning the sources of $PM_{2.5}$ using the CMB model, while section 4.2 discusses the meteorological conditions in the Missoula Valley. Section 4.3 summarizes the air pollution for each of the four seasons. Sections 4.4 and 4.5 compare this study with other studies that have been conducted in the Missoula Valley in the past, and section 4.6 addresses the current major sources of $PM_{2.5}$ in the Valley identified by the CMB model. Sections 4.7, 4.8, and 4.9 discuss the QA/QC results of the $PM_{2.5}$, SVOC, and VOC sampling and analysis programs, respectively.

4.1 CMB Model Notes

In this CMB model, street sand, diesel, and hog fuel boiler sources each had several different profiles for the same source. Sometimes in conducting the model runs, one source profile type of a particular source provided the best fit, while on another sample day a different source profile for the same source gave a better fit. Therefore, in reporting the data, some source profiles were grouped together. Street sand source profiles MSLA01 (ST_SANDF), MSLA02 (ERN_RUSF), MSLA03 (RUS_STF2), and MSLA04 (DESP_LTF) were reported as "street sand." Diesel source profiles, MSLA11 (LDV_DSLF), MSLA12 (LDV_DS2F), and MSLA13 (HDV_DSLF) were reported as "diesel." Finally, MSLA18 (HFB_PLYF), MSLA19 (HFB_PL2F), MSLA20 (HFB_DOF2), MSLA21 (HFB_CMPF), MSLA25 (WFB_CMPF), and MSLA27

(LP_CHPDF) hog fuel boiler source profiles were all grouped together and reported as "hog fuel boilers."

There were also three source profiles for residential wood combustion to choose from in this CMB model: MSLA28 (RWC_MEDF), MSLA29 (RWC_POCF), and MSLA30 (RWC_F222). These were residential wood combustion source profiles from Medford, Oregon, Pocatello, Idaho, and Missoula, respectively. To be consistent in the model, the Missoula source profile for residential wood combustion (MSLA30, RWC_F222) was used throughout the program. It also gave the best statistical fit compared to the two other profiles - even in spring, summer, and fall when residential wood combustion was not supposed to be a major contributor to the fine fraction. This meant that the Missoula residential wood combustion source profile was likely providing a good fit for slash burning and controlled burns during the spring and fall, and the forest fires during the summer of 2000. Using USEPA's SPECIATE 3.0, source profiles for forest prescribed burning (broadcast conifer #42321), slash burning 1 (#42301), slash burning 2 (#42302), slash burning 3 (conifer flaming phase #42305), and slash burning 4 (conifer smoldering phase #42306) were found and put into the model. In almost every case, the Missoula residential wood combustion source profile gave a better statistical fit than the prescribed burning and slash burning source profiles throughout spring, summer and fall. Therefore, the results from this source profile are defined as "wood combustion." In the spring, summer, and fall it represents slash burning, controlled forest fire burns, and wildland forest fires. In the winter, when outdoor burning is prohibited and wildland fires are not present, the Missoula source profile represents residential wood combustion.

During the smoky days of 8/13/00 and 8/25/00, the residential wood combustion source profile for Pocatello, Idaho gave a better fit for the forest fires than the Missoula source profile. Good statistical fits were also achieved using the smoldering slash burning profile (#42306) as well, but the Pocatello profile was used because it gave a better percent mass statistical fit with less total mass unexplained.

Sulfate was used as a fitting species in the model instead of sulfur in order to get a better fit for the kraft recovery boiler. Only on a few occasions when the average $PM_{2.5}$ mass concentration was extremely low did sulfur give a better fit than sulfate in the model runs. Also, CMB runs were conducted using the source profile for the kraft recovery boiler (MSLA24, KRB_CMPF) as a source profile instead of ammonium sulfate (MSLA07, NH4SO4F2). The kraft recovery boiler source profile usually gave a much better statistical fit than the ammonium sulfate profile during each run. In addition, on some of the higher mass days during the winter, all three diesel source profiles gave excellent (almost indistinguishable) statistical fits. Finally, when conducting the CMB model runs, only sources with TSTATs greater than two were reported. If a TSTAT was below two, then the source was not considered a significant contributor for that sample day.

4.2 Meteorological Data

Meteorological information recorded for each sample day is presented in Table 4-1. Ambient temperature, wind speed and direction, and precipitation amounts were measured by the National Weather Service (NWS) at the Missoula International Airport. The $PM_{2.5}$ samplers also recorded site specific information such as temperature and pressure during sampling. In addition, visual observations were taken during each day of sampling, including documenting any unusual events that might effect pollution levels on that day (ex. rain, snow, forest fire smoke, high winds, visible street sand, etc.). The direction the Smurfit-Stone Container Pulp Mill plume was blowing was also recorded for each sample day during the mid-point check.

Seasonal weather patterns and daily temperatures during the late fall and winter can lead to poor dispersion and create inversion conditions in the Missoula Valley. Overnight, as cold air sinks lower into the valley, boundary layer compression concentrates contaminants in the air column. Low levels of sunlight decrease the removal of air pollution by convection, helping to trap the atmospheric contaminants near ground level. This results in stagnant air episodes with increased levels of pollutants. Three sample days in particular which displayed inversion conditions were 12/23/00, 1/4/01, and 2/21/01. These days were characterized by low temperatures, little wind, and high pollution levels. Sampling during inversion conditions in Logan, Utah showed that the $PM_{2.5}$ was composed mostly of carbonaceous material, ammonium nitrate (NH_4NO_3), and ammonium sulfate ($(NH_4)_2SO_4$). The presence of sulfate (SO_4^{2-}) and nitrate (NO_3^-) are thought to come from the conversion of sulfur dioxide (SO_2) and oxides of nitrogen (NOx) in the presence of excess oxidants to sulfuric (H_2SO_4) and nitric acid (HNO_3) that are neutralized by excess ammonia (NH_3) (Mangelson *et al.*, 1997). In fog conditions when moisture condenses on suspended particles, SO_2 is converted to SO_4^{2-} at a much faster rate and is believed to involve oxidation by hydrogen peroxide (H_2O_2) or ozone (O_3) in water droplets (Finlayson-Pitts and Pitts, 1986; Eatough *et al.*, 1994). Conversion of NO_2 to NO_3^- at night and in clouds or fog likely involves the nitrate radical, NO_3, and O_3 (Mangelson *et al.*, 1997).

Valley wind direction can be a misleading piece of information when used to predict pollution in the airshed, though Wrobel (2000) found that there was a reasonable correlation between high pollutant levels in the Missoula Valley and low wind velocity. Higher winds have a tendency to increase the turbulent mixing and the dilution of SVOCs and VOCs. Levels of $PM_{2.5}$ may be positively biased due to the inclusion of coarse-mode particulate matter during high wind events such as dust storms (Claiborn *et al.*, 2000). The wind direction in the Missoula Valley is also extremely variable. In the 2000/2001 CMB sampling program, at times there were discrepancies between the wind direction recorded by the NWS and the visual observation taken on the Smurfit-Stone plume during the mid-point check. For example, on 9/18/00, the NWS reported the prevailing wind direction blowing from the west to the east. Visual observations recorded from that day report the Stone plume blowing towards Frenchtown (west). On some days, the bottom of the plume was blowing in one direction, and the top of the plume was blowing in the opposite direction. This occurred several times throughout the winter and early spring. Wrobel (2000) found that the wind directions recorded at ambient station #1A near Smurfit-Stone Container and the NWS were often so irregular as to make the determination of the predominant wind direction impossible, and that it was more common for the two weather stations to disagree than agree.

Table 4-1
Meteorological Summary for CMB and Research Sample Days.
March 22, 2000 - March 23, 2001

	$PM_{2.5}$ (ug/m³)		Ambient Temp (°F)			Max Wind					
Date	Boyd Park	Frenchtown	Max	Min	Avg	Speed (mph)	Direction[a]	Plume[b]	Pcpn (in)	Snow[c] (in)	Air[d]
3/22/00	6.2	7.1	66	31	49	21	230 (SW)		0.00	0.0	
3/28/00			47	36	42	24	240 (WSW)		0.08	0.0	
4/3/00	10.2	9.4	63	23	43	14	110 (ESE)		0.00	0.0	
4/9/00			68	28	48	11	300 (WNW)	Missoula	0.00	0.0	C
4/15/00	7.9	6.8	56	35	46	20	250 (WSW)	Frenchtown	0.13	0.0	R
4/21/00			70	42	56	12	340 (NNW)	Missoula	0.00	0.0	C, S
4/27/00	7.4	7.5	80	32	56	25	120 (ESE)	Frenchtown	T	0.0	C
5/3/00			72	35	54	35	300 (WNW)		0.08	0.0	R
5/9/00	2.5	3.1	56	40	48	24	200 (SSW)	Frenchtown	0.16	0.0	R
5/15/00			71	34	53	20	350 (N)	Missoula	0.00	0.0	C
5/21/00	6.6	5.9	76	52	64	21	280 (W)	Missoula	0.00	0.0	C
5/27/00			76	42	59	26	310 (NW)	Missoula	0.08	0.0	R
6/2/00	6.7	3.7	81	38	60	17	290 (WNW)	Frenchtown	0.00	0.0	C
6/8/00			80	50	65	29	240 (WSW)	Missoula	0.00	0.0	
6/14/00	4.7	2.7	66	53	60	13	290 (WNW)	Missoula	0.25	0.0	R
6/20/00			74	44	59	23	280 (W)	Missoula	0.00	0.0	C
6/26/00	3.8	4.5	80	42	61	19	30 (NNE)	Frenchtown	0.00	0.0	
7/2/00			79	48	64	21	290 (WNW)	Missoula	0.00	0.0	
7/8/00	6.8	4.6	81	44	63	25	360 (N)	Missoula	T	0.0	R, S
7/14/00			93	54	74	26	290 (WNW)	Missoula	0.00	0.0	
7/20/00	8.4	6.9	88	51	70	17	290 (WNW)	Missoula	0.00	0.0	
7/26/00			95	51	73	19	290 (WNW)	Missoula	0.00	0.0	H, S
8/1/00	10.2	7.1	96	64	80	20	260 (W)	Missoula	0.00	0.0	H, S
8/7/00			92	50	71	23	260 (W)	Missoula	0.00	0.0	S
8/13/00	40.4	41.9	88	47	68	28	280 (W)	Missoula	0.00	0.0	S
8/19/00			75	47	61	25	290 (WNW)	Missoula	0.00	0.0	S
8/25/00	39.3	42.4	91	49	70	21	270 (W)	Missoula	0.00	0.0	S
8/31/00			81	43	62	17	300 (WNW)	Missoula	T	0.0	S
9/6/00	4.7	3.5	57	42	50	10	300 (WNW)	Missoula	0.02	0.0	R
9/12/00			80	40	60	23	280 (W)	Missoula	0.00	0.0	C
9/18/00	6.6	6.9	72	53	63	23	270 (W)	Frenchtown	T	0.0	
9/24/00			63	23	43	8	340 (NNW)	Frenchtown	0.00	0.0	C
9/30/00	2.9	4.2	61	50	56	23	20 (NNE)	Frenchtown	0.59	0.0	R
10/6/00			56	23	40	12	360 (N)	None	0.00	0.0	C
10/12/00	6.7	7.2	45	40	43	19	130 (SE)	Frenchtown	0.36	0.0	R
10/18/00			60	31	46	16	220 (SW)	Both	T	0.0	
10/24/00	12.2	15.8	54	26	40	6	110 (ESE)	Missoula	0.00	0.0	F
10/30/00			44	29	37	14	340 (NNW)	Missoula	0.00	0.0	
11/5/00	8.7	6.6	37	32	35	11	340 (NNW)	Missoula	0.10	0.3 (T)	R, Sn
11/11/00			26	19	23	18	100 (ESE)	Both	0.00	0.0	
11/17/00	19.9	17.1	31	15	23	11	320 (NW)	Missoula	0.00	0.0	F
11/23/00			24	18	21	11	110 (ESE)	Frenchtown	T	T (0)	F
11/29/00	15.6	13.4	32	17	25	20	120 (ESE)	Missoula	0.03	0.4 (0)	Sn
12/5/00			35	16	26	19	300 (WNW)	Frenchtown	0.00	0.0	F
12/11/00	8.0	9.5	14	-1	7	26	110 (ESE)	Frenchtown	0.01	T (1)	C, F
12/17/00			36	19	28	27	280 (W)	Missoula	0.04	0.6 (6)	Sn
12/23/00	63.1	55.3	28	20	24	8	120 (ESE)	Frenchtown	0.07	0.8 (6)	Sn
12/29/00			26	13	20	8	160 (SSE)	Missoula	0.00	0.0	F
1/4/01	44.8	57.0	38	20	29	10	280 (W)	Both	0.00	0.0	H, F
1/10/01			30	15	23	8	270 (W)	Missoula	0.02	0.2 (3)	Sn, F
1/16/01	21.7	14.6	23	6	15	13	110 (ESE)	Both	T	T (7)	Sn
1/22/01			34	16	25	9	240 (WSW)	Missoula	T	T (6)	F
1/28/01	13.8	15.7	24	9	17	11	130 (SE)	Frenchtown	0.00	0.0	
2/3/01			38	23	31	14	310 (NW)	Missoula	T	0.1 (6)	Sn
2/9/01	19.9	17.7	20	5	13	19	110 (ESE)	Both	0.05	1.0 (5)	Sn
2/15/01			24	13	19	25	100 (ESE)	Frenchtown	0.24	5.7 (6)	Sn
2/21/01	39.3	49.3	36	22	29	8	230 (SW)	Frenchtown	0.02	T (9)	Sn, F
2/27/01			29	4	17	9	330 (NNW)	Frenchtown	0.00	0.0	C, RD
3/5/01	20.6	19.3	46	31	39	19	120 (ESE)	Frenchtown	0.00	0.0	H, RD
3/11/01			39	27	33	17	250 (WSW)	Missoula	0.00	0.0	RD
3/17/01	8.7	10.7	42	29	36	10	350 (N)	Both	T	T (0)	RD
3/23/01			64	24	44	17	110 (ESE)	Both	0.00	0.0	

a: Wind direction is in degrees. Also given is the general direction wind is coming from (North, East, South, West).
b: Visible recording of the direction the Smurfit - Stone Container plume was heading during mid-point check of sampling.
c: Number in () refers to snow pack in inches. T = trace of precipitation.
d: C = Clear; R = Rain; Sn = Snow; H = Haze; S = Smoke; F = Fog / inversion; RD = Road dust.

4.3 Seasonal Air Pollution

4.3.1 Spring 2000

$PM_{2.5}$ averaged 6.5 μg/m^3 at Boyd Park and 5.8 μg/m^3 during the spring (3/22/00 – 6/14/00), with OC comprising 46% of the mass, followed by total ions (27%), EC (15%), and total elements (11%). Wood combustion was the greatest contributor to the fine fraction at both sites, contributing 42% (2.8 μg/m^3) at Boyd Park and 42% (2.6 μg/m^3) at Frenchtown. The Missoula residential wood combustion source profile (MSLA30, RWC_F222) gave a good statistical fit in the CMB model during spring, but this is probably representative of wood smoke emanating from yard waste burning, slash burning, and controlled burns conducted by the Forest Service in the surrounding areas. Diesel was the second biggest source of fine particulate during the spring, contributing about half that of wood combustion at both sites. Street sand had its highest percent source contribution of the entire sampling program during the spring, contributing 13% (0.8 μg/m^3) at Boyd Park and 14% (0.9 μg/m^3) at Frenchtown. During the spring, the snow is starting to melt and the sand that was put down on the icy roads during the colder months is re-entrained. This is supported by the elevated levels of the Class 1 elements (aluminum, silicon, calcium, iron, and copper) during this time period. Industry contributes 22-23% (1.3-1.5 μg/m^3) of the spring fine particulate between the kraft recovery boilers and the hog fuel boilers in the Missoula Valley. There is little to no contribution from ammonium nitrate due to the warmer temperatures, and no contribution from automobiles during the spring.

4.3.2 Summer 2000

The summer of 2000 was characterized by hot, dry, windy weather which contributed to widespread forest fires in Idaho and Montana. Since a full discussion of the air pollution in the Missoula Valley during the forest fires is given in Part III of this document, only summer averages including the fire season are presented here. Summer $PM_{2.5}$ levels averaged 15.0 $\mu g/m^3$ at Boyd Park and 14.7 $\mu g/m^3$ from 6/26/00 – 9/18/00. At Boyd Park, OC contributed 47% of the mass, with total ions contributing 15%, EC at 13%, and total elements contributing 5%. Frenchtown mass was composed of 45% OC, 14% of both total ions and EC, and 6% total elements. An average of 21% of the mass during the summer was unidentified, a result of the smoky days of 8/13/00 and 8/25/00.

Wood combustion dominated the source contribution estimates during the summer of 2000, with 72% (10.7 $\mu g/m^3$) at Boyd Park and 70% (10.4 $\mu g/m^3$) at Frenchtown. Diesel was the second largest source of $PM_{2.5}$ at both sites, contributing 13% (2.0 $\mu g/m^3$) at both Boyd Park and Frenchtown. Industrial sources (kraft recovery boiler and hog fuel boilers) contributed slightly more mass to the fine fraction than they did during the spring, with 12% (1.9 $\mu g/m^3$) at Boyd Park and 10% (1.5 $\mu g/m^3$) at Frenchtown. Automobile emissions and ammonium nitrate were not detected by the CMB model during the warm summer months when emissions were most likely in the gaseous phase. There was more street sand at Frenchtown (7%, 1.0 $\mu g/m^3$) compared to Boyd Park (3%, 0.5 $\mu g/m^3$) during the summer, the result of unpaved areas around the Frenchtown Fire Department parking lot where the sampling station was located. During the fire season, the Frenchtown Fire Department was used as a staging area for startup fires on the west side of the Valley. Extra fire trucks and fire fighting crews were on standby, creating a lot of activity which could have suspended street sand and crustaceous material around the samplers. Levels of Class 1 elements such as aluminum, silicon, and iron are again elevated during this time period at Frenchtown. The low summer VOC and SVOC levels were likely the result of increased atmospheric dilution caused by higher winds and the increased degradation rates as a result of the more active photochemistry prevailing during the summer months.

4.3.3 Fall 2000

During the fall (9/30/00 – 12/11/00), levels of $PM_{2.5}$ traditionally increase after being low throughout the spring and summer (although this was not the case when including the 2000 forest fires). Temperatures get cooler, inversions can occur, and there is an increase in precipitation and snow. Fall levels of $PM_{2.5}$ were 10.6 $\mu g/m^3$ and 10.5 $\mu g/m^3$ at Boyd Park and Frenchtown, respectively. The makeup of the $PM_{2.5}$ between Boyd Park and Frenchtown during this time was similar, with average compositions of 36% OC, 13% EC, and 7% total elements. With the colder weather comes more of the volatile fraction of $PM_{2.5}$ staying in the particle form. During the fall, 40% of the fine particulate was composed of ions (mostly ammonium, nitrate, and sulfate) at both Boyd Park and Frenchtown, and ammonium nitrate was for the first time in the CMB model found to be a significant contributor to the fine fraction. Ammonium nitrate accounted for 15% (1.7 $\mu g/m^3$) and 12% (1.3 $\mu g/m^3$) at Boyd Park and Frenchtown, respectively. The cooler weather also brings the increased use of fireplaces and wood stoves in the Missoula Valley, resulting in wood combustion at Boyd Park (38%, 4.1 $\mu g/m^3$) and Frenchtown (39%, 4.1 $\mu g/m^3$) being the largest source of $PM_{2.5}$ during the fall. Diesel and the kraft recovery boiler each contributed an average of 19% (2.1 μg/m^3) at Boyd Park and 21% (2.2 μg/m^3) at Frenchtown, while hog fuel boilers contributed around 5% (0.5 μg/m^3) at both sites. Street sand and automobiles contributed very little (<3%) to the fall $PM_{2.5}$.

4.3.4 Winter 2000 / 2001

Winter (12/23/00 – 3/17/01) is traditionally the worst air pollution season in Missoula, characterized by cold weather and inversion conditions which frequently form in the Valley. $PM_{2.5}$ during the winter of 2000/2001 was measured at 29.0 μg/m^3 at Boyd Park and 30.0 μg/m^3 at Frenchtown. The fine mass at Boyd Park was composed of 41% total ions, 24% OC, 11% EC, 5% total elements, and 19% unknown, while Frenchtown fines were composed of 42% ions, 27% OC, 11% EC, 6% total elements, and 14% unknown. Ammonium nitrate was the largest contributing source to the fine fraction, with 33% (8.7 μg/m^3) at Boyd Park and 29% (8.0 μg/m^3) at Frenchtown. Figure 3-6 shows how the levels of nitrate and ammonium spiked during the winter at both sites. Wood combustion was the second largest source contributor, with 23% (6.0 μg/m^3) at Boyd Park and 26% (7.1 μg/m^3) at Frenchtown. Diesel was the third largest source of $PM_{2.5}$, contributing 22% (5.6 μg/m^3) at Boyd Park and 20% (5.4 μg/m^3) at Frenchtown, while industry (kraft recovery boiler and hog fuel boilers) contributed 20% (5.2 μg/m^3) at Boyd Park and 22% (6.3 μg/m^3) in Frenchtown. Street sand and automobiles were not significant contributors to the wintertime $PM_{2.5}$. VOCs and SVOCs were also measured at their highest levels of the sampling program during the winter, the result of shorter daylight hours and reduced temperatures which inhibit the photochemical destruction of these compounds.

4.3.5 Yearly Average

Including the fire season, the average $PM_{2.5}$ measured over the entire year (3/22/00 – 3/17/01) was 15.4 $\mu g/m^3$ at both Boyd Park and Frenchtown, and was composed of nearly the same amounts of the speciated compounds. The average percent compositions of the annual fine fraction were 36% OC, 34% total ions, 13% EC, 12% unknown, and 7% total elements. The source contribution estimates at both sites identified by the CMB model were nearly identical as well. Including the fire season in the yearly average discussion, wood combustion accounted for approximately 41% (6.0 $\mu g/m^3$) of the fine fraction at Boyd Park and Frenchtown, doubling the levels of the second biggest contributor, diesel. Ammonium nitrate was the third largest source of $PM_{2.5}$, averaging 17% (2.5 $\mu g/m^3$) at both sites. It should also be noted that almost all of the ammonium nitrate was contributed during the colder fall and winter months. The kraft recovery boiler was the fourth largest contributor to the fine fraction, with slightly more calculated at Frenchtown (14%, 2.1 $\mu g/m^3$) compared to Boyd Park (13%, 1.9 $\mu g/m^3$). Hog fuel boilers contributed an average of 6% (0.9 $\mu g/m^3$) at both sites, with more street sand detected at Frenchtown (5%, 0.7 $\mu g/m^3$) over Boyd Park (4%, 0.5 $\mu g/m^3$). Automobiles contributed very little to the yearly average in the particle form, yet Class 1 VOC levels (benzene, toluene, ethyl benzene, xylenes, and naphthalene) at Boyd Park doubled the levels measured at Frenchtown. SVOC levels were comparable between both sides of the Missoula Valley.

4.4 Past Missoula Valley $PM_{2.5}$ Studies

The Missoula Health Department in the past has conducted other CMB studies in the Missoula Valley. The Rose Park study was conducted during the winter of 1986/1987 to apportion the sources of PM_{10}. Nearly ten years later, another CMB source apportionment study was conducted during the winter of 1995/1996 at Boyd Park to quantify the source contributions to ambient $PM_{2.5}$, PM_c (coarse particulate matter with diameters between 2.5 and 10 μm in diameter), and PM_{10}. A comparison between the PM_{10} results of the two studies showed that residential wood combustion impacts had decreased by as much as 87% while road dust impacts had increased by about 25%. Ammonium nitrate was also discovered to be a significant contributor to the fine fraction in the 1995/1996 CMB (Schmidt, 1996).

The 2000/2001 CMB was the first attempt to quantify the $PM_{2.5}$ source contributions in the Missoula Valley throughout the entire year. Table 4-2 summarizes the source contribution estimates for the 1995/1996 CMB and 2000/2001 CMB.

Table 4-2: 1995/1996 Boyd Park CMB and 2000/2001 Boyd Park CMB average source contribution estimate ($\mu g/m^3$) comparison.

	1995/1996 Boyd Park CMB (%)	1995/1996 Boyd Park CMB (SCE, $\mu g/m^3$)		2000/2001 Boyd Park CMB (%)	2000/2001 Boyd Park CMB (SCE $\mu g/m^3$)	Difference
Source						
Residential Wood Combustion	19%	5.6		26%	5.9	+ 0.3 $\mu g/m^3$
Ammonium Nitrate	25%	7.2		30%	7.0	- 0.2 $\mu g/m^3$
Diesel	25%	7.1		21%	4.9	- 2.2 $\mu g/m^3$
Kraft Recovery Boiler	8%	2.4		14%	3.1	+ 0.7 $\mu g/m^3$
Hog Fuel Boiler	8%	2.2		7%	1.6	- 0.6 $\mu g/m^3$
Road Dust (Street Sand)	15%	4.2		2%	0.4	- 3.8 $\mu g/m^3$
Average Mass	32.1 $\mu g/m^3$	32.1 $\mu g/m^3$		25.0 $\mu g/m^3$	25.0 $\mu g/m^3$	- 7.1 $\mu g/m^3$

Twelve samples were collected at Boyd Park during the 1995/1996 CMB from 11/22/95 through 3/31/96. In order for a direct comparison to be made between these two studies, the 1995/1996 results are presented in Table 4-2 without the unexplained source contributions factored into SCEs. In addition, the 2000/2001 CMB sample dates for only 11/17/00 - 3/17/01 are used to approximate the same seasonal span, and "wood combustion" is called "residential wood combustion." The average $PM_{2.5}$ mass collected during the programs was higher during the 1995/1996 CMB. Residential wood combustion and the kraft recovery boiler source contributions appear to have increased slightly since the last study, with ammonium nitrate, diesel, and hog fuel boilers all decreasing. Road dust (street sand) shows the most significant change between the two studies with a drop from an average of 4.2 $\mu g/m^3$ (15%) contribution to the fine fraction in the 1995/1996 CMB to 0.4 $\mu g/m^3$ (2%) in 2000/2001. The drop in street sand may be due to different amounts of sanding material being applied each winter season. This could be a variable source profile. Comparisons can also be made between the seasonal averages of the two studies. Tables 4-3 and 4-4 list the SCEs for winter and spring for the 1995/1996 and 2000/2001 CMBs.

Table 4-3: 1995/1996 Boyd Park CMB and 2000/2001 Boyd Park CMB average source contribution estimate (µg/m^3) comparison for winter (November through February).

	1995/1996 Boyd Park CMB (%)	1995/1996 Boyd Park CMB (SCE, µg/m^3)		2000/2001 Boyd Park CMB (%)	2000/2001 Boyd Park CMB (SCE, µg/m^3)	Difference
Source						
Residential Wood Combustion	21%	6.5		28%	6.6	+ 0.1 µg/m^3
Ammonium Nitrate	30%	9.0		28%	6.9	- 2.1 µg/m^3
Diesel	26%	8.2		23%	5.4	- 2.8 µg/m^3
Kraft Recovery Boiler	10%	3.2		14%	3.4	+ 0.2 µg/m^3
Hog Fuel Boiler	8%	2.5		6%	1.4	- 1.1 µg/m^3
Road Dust (Street Sand)	5%	1.7		1%	0.2	- 1.5 µg/m^3
Average Mass	37.4 µg/m^3	37.4 µg/m^3		26.7 µg/m^3	26.7 µg/m^3	- 10.7 µg/m^3

Table 4-4: 1995/1996 Boyd Park CMB and 2000/2001 Boyd Park CMB average source contribution estimate ($\mu g/m^3$) comparison for spring (February through March).

	1995/1996 Boyd Park CMB (%)	1995/1996 Boyd Park CMB (SCE, $\mu g/m^3$)		2000/2001 Boyd Park CMB (%)	2000/2001 Boyd Park CMB (SCE, $\mu g/m^3$)	Difference
Source						
Residential Wood Combustion	16%	4.6		22%	4.7	+ 0.1 $\mu g/m^3$
Ammonium Nitrate	18%	5.2		34%	7.2	+ 2.0 $\mu g/m^3$
Diesel	22%	6.2		18%	3.9	- 2.3 $\mu g/m^3$
Kraft Recovery Boiler	3%	1.0		13%	2.7	+ 1.7 $\mu g/m^3$
Hog Fuel Boiler	7%	1.9		9%	2.0	+ 0.1 $\mu g/m^3$
Road Dust (Street Sand)	34%	9.3		4%	0.9	- 8.4 $\mu g/m^3$
Average Mass	28.4 $\mu g/m^3$	28.4 $\mu g/m^3$		22.1 $\mu g/m^3$	22.1 $\mu g/m^3$	- 6.3 $\mu g/m^3$

For the 1995/1996 CMB, winter sampling was conducted between 11/22/95 – 2/5/96 while spring sampling was conducted between 2/12/96 - 3/10/96. The yearlong 2000/2001 CMB seasonal sampling periods for spring and winter were 3/22/00 – 6/14/00 and 12/23/00 – 3/17/01, respectively. Therefore, 2000/2001 sample days were grouped according to the 1995/1996 seasonal designations so that direct comparisons could be made between the two studies. For both the winter and spring, the average $PM_{2.5}$ masses collected are lower for the 2000/2001 CMB. The comparison for the winter months follow the same trends established in comparing averages taken over the entire 1995/1996 sample period (November through March). Residential wood combustion and the kraft recovery boiler sources have slightly elevated contributions while ammonium nitrate, diesel, hog fuel boilers, and road dust all decreased. For the spring data, residential wood combustion, ammonium nitrate, kraft recovery boiler, and hog fuel contributions all increased from 1995/1996 to 2000/2001, while diesel and road dust were lower. The most significant item in the spring comparison is the 8.4 $\mu g/m^3$ reduction in road dust (street sand) since the 1995/1996 CMB, possibly a result of the increased use of deicer in the Missoula Valley during the 2000/2001 winter season. The drop in street sand may also be due to different amounts of street sand applied during the two winters.

Results of the 1995/1996 CMB showed that in addition to the average $PM_{2.5}$ levels significantly decreasing compared with the 1986/1987 study, TC and OC also decreased while EC increased. A summary of the 1986/1987, 1995/1996, and 2000/2001 OC/EC/TC results for the three CMBs is presented in Table 4-5. In comparing the 2000/2001 CMB with the 1995/1996 CMB, average $PM_{2.5}$ levels again decreased, TC and EC both decreased, but OC increased. Levels of 2000/2001 $PM_{2.5}$, TC, and OC were much lower than they were in the 1986/1987 study. However, average EC values are slightly higher, and EC % $PM_{2.5}$ and EC % TC values are nearly four times higher as a result of less OC composing the TC and $PM_{2.5}$. This OC decrease is probably the result of the 1994 ban on wood stove installations in the Missoula Air Stagnation Zone. The increase in EC from the 1986/1987 study is likely the result of more vehicles operating in Missoula. EC is exclusively emitted from combustion sources as a product of incomplete combustion, and a major source in urban areas responsible for EC emissions includes vehicular emissions (Hildemann *et al.*, 1991).

Table 4-5: 1986/1987 Rose Park CMB, 1995/1996 Boyd Park CMB, and 2000/2001 Boyd Park CMB OC/EC/TC comparison.

Species	1986/1987 Rose Park CMB	1995/1996 Boyd Park CMB	2000/2001 Boyd Park CMB	Difference (1995/1996 and 2000/2001)
Avg. $PM_{2.5}$ ($\mu g/m^3$)	55.0 $\mu g/m^3$	32.2 $\mu g/m^3$	25.0 $\mu g/m^3$	- 7.2 $\mu g/m^3$
Avg. TC ($\mu g/m^3$)	25.0 $\mu g/m^3$	9.9 $\mu g/m^3$	9.7 $\mu g/m^3$	- 0.2 $\mu g/m^3$
TC % $PM_{2.5}$	45%	31%	39%	+ 8%
Avg. OC ($\mu g/m^3$)	23.0 $\mu g/m^3$	5.7 $\mu g/m^3$	6.6 $\mu g/m^3$	+ 0.9 $\mu g/m^3$
OC % $PM_{2.5}$	42%	18%	26%	+ 8%
OC % TC	93%	58%	69%	+ 11%
Avg. EC ($\mu g/m^3$)	2.0 $\mu g/m^3$	4.2 $\mu g/m^3$	3.0 $\mu g/m^3$	- 1.2 $\mu g/m^3$
EC % $PM_{2.5}$	3%	13%	12%	- 1%
EC % TC	8%	43%	31%	- 12%

TC = Total Carbon.
OC = Organic Carbon.
EC = Elemental Carbon.

4.5 Past Missoula Valley VOC Studies

Wrobel (2000) conducted a VOC sampling study in the Missoula Valley between 5/98 and 7/99 at five locations throughout the Missoula Valley. Site 1 was located a few blocks east of Reserve Street, and represented the western edge of urban Missoula. Site 2 was located on the eastern edge of the urban airshed near the Hellgate Canyon. A comparison of these two urban sites is made with the Boyd Park 2000/2001 VOC data in Table 4-6. Site 3 was located at Ambient Station 1A, within the Smurfit-Stone Container Corporation mill property boundary. A comparison between the rural Site 3 VOCs with the Frenchtown 2000/2001 VOC data is presented in Table 4-7.

Table 4-6: 1998/1999 and 2000/2001 VOC Comparison: Urban Missoula Valley.

VOC	1998/1999 Site 1 and 2 (pptv)	2000/2001 Boyd Park (pptv)
Benzene[1]	510.0	574.4
Toluene[1]	1070.0	1440.4
Ethyl Benzene[1]	158.0	197.4
1,4-Dimethylbenzene[1]	531.0	364.4
1,2-Dimethylbenzene[1]	185.0	270.9
Naphthalene[1]	39.8	66.6
Trichloromethane[2]	23.3	15.3
Isopropyl Toluene[2]	15.9	35.7

1: Class 1 Automobile Emission VOCs.
2: Class 2 Other VOCs.

Table 4-7: 1998/1999 and 2000/2001 VOC Comparison: Rural Missoula Valley.

VOC	1998/1999 Site 3 (pptv)	2000/2001 Frenchtown (pptv)
Benzene[1]	170.0	326.0
Toluene[1]	247.0	641.4
Ethyl Benzene[1]	37.9	89.9
1,4-Dimethylbenzene[1]	121.0	155.1
1,2-Dimethylbenzene[1]	42.9	124.8
Naphthalene[1]	14.3	47.6
Trichloromethane[2]	57.7	11.3
Isopropyl Toluene[2]	53.1	44.1

1: Class 1 Automobile Emission VOCs.
2: Class 2 Other VOCs.

The urban comparison (Table 4-6) shows that levels of Class 1 VOCs in Missoula were fairly consistent between the two studies, while the rural comparison of Class 1 VOCs in Table 4-7 shows higher levels in the 2000/2001 study. This is because the Frenchtown sampling station was located about 10 meters from a well used road, while Ambient 1A (Site 3) was located much further away from any consistent automobile impacts. The urban Class 1 VOCs measured on the east side of the Missoula Valley were found to be much higher than the west side of the Valley in both studies. Wrobel found that the concentrations of aromatic compounds in urban Missoula were four and six times greater than those found at site 3 (Ambient 1A). In the 2000/2001 CMB, urban Missoula VOCs attributed to automobiles were nearly double what was found at Frenchtown.

The biggest discrepancy between the two studies are the levels of rural trichloromethane (chloroform), with the 1998/1999 levels nearly five times higher than those measured during the 2000/2001 study. These numbers give a great example of the impact the bleaching process at Smurfit-Stone Container had on the Missoula Valley before its closure in February 1999. During the 1998/1999 study, the mean chloroform concentrations at site 3 plummeted 94%, from 109.0 pptv when the bleach plant was in operation to 7.0 pptv afterwards. After the bleach plant closed, the Missoula urban center became a larger source of chloroform releases into the Valley airshed than the pulp mill. This trends also holds for the 2000/2001 study.

4.6 Missoula Valley $PM_{2.5}$ Sources

4.6.1 Wood Combustion

Wood combustion was the largest contributor to the fine particulate in the Missoula Valley throughout the year, contributing 40% in Boyd Park and 41% in Frenchtown to the annual $PM_{2.5}$. This includes residential wood combustion during the winter, and slash and controlled burns during the fall and spring. During the summer, wood combustion from the forest fires in Idaho and Montana contributed an average of 71% of the $PM_{2.5}$ in the Missoula Valley, while during the winter, residential wood combustion contributed 23% at Boyd Park and 26% at Frenchtown to the fine fraction. Residential wood combustion can be a very significant source of atmospheric aerosols containing PAHs, particularly in the winter months (Sexton *et al.*, 1985; Greenberg, *et al.*, 1985).

4.6.2 Diesel

Diesel was the second largest contributor to the fine fraction, averaging 19% of the annual average at Boyd Park and 18% at Frenchtown. The contribution from diesel is at its greatest during the winter months, and lowest during the spring and summer. Compared to the 1995/1996 CMB, diesel source contribution has decreased an average of 2.2 μg/m^3 in Missoula during the winter and spring. A motor vehicle emission inventory model for the San Francisco Bay Area in 1996 reported that heavy-duty diesel trucks contributed 74% of exhaust particulate matter emissions from on-road vehicles (Fanai, 1997; Dreher and Harley, 1998). Diesel fueled vehicles emit hydrocarbons mainly in the form of fine particulate PAHs (Westerholm and Egeback, 1994), with naphthalene, 1-/2-methylnaphthalene and dimethylnaphthalene the most abundant PAHs in both diesel fuel and exhaust (Lee *et al.*, 1992; Lowenthal *et al.*, 1994). Another possible source of diesel in the Missoula Valley are diesel-powered trains. However, this source profile was not detected in the CMB model runs, and not considered a significant source of $PM_{2.5}$ in the Missoula Valley.

4.6.3 Ammonium Nitrate (NH_4NO_3)

Ammonium nitrate was the third largest contributor to the fine fraction in the Missoula Valley. It is an extremely volatile species, and is not detected in the particle form during the warmer months. At temperatures greater than 30 °C, most nitrate will be in the gas phase as nitric acid (HNO_3), while at temperatures lower than 15 °C, most nitrate will be in the particle phase as ammonium nitrate. At intermediate temperatures, there will be varying amounts of both nitric acid and ammonium nitrate in equilibrium. On 9/18/00, ammonium nitrate was detected by the CMB model for the first time, and was consistent as a source throughout the winter months. At Boyd Park, ammonium nitrate was found to contribute an average of 18% to the annual fine fraction, while at Frenchtown this contribution was slightly lower at 16%. During the winter, an average of 31% of the $PM_{2.5}$ was attributed to ammonium nitrate.

Secondary particles such as ammonium nitrate usually form over several hours or days and attain aerodynamic diameters between 0.1 and 1 μm. Ammonia (NH_3) and oxides of nitrogen (NOx) are the precursors for ammonium nitrate particles (Seinfeld and Pandis, 1998), and a mechanism for the formation of ammonium nitrate has been reported by Stockwell *et al.*, (2000). $PM_{2.5}$ has been found to correlate with gaseous emissions of NOx from vehicles, with heavy duty vehicles contributing significantly greater amounts of NOx and particulate matter on a per vehicle basis than light duty vehicles (Gillies *et al.*, 2001). Between 40 and 45% of all NOx emissions in the United States are estimated to come from transportation, with about half of this coming from light-duty gasoline trucks and cars and approximately one-quarter from heavy-duty gasoline and diesel vehicles (Seinfeld and Pandis, 1998; Dreher and Harley, 1998). Other sources of NOx in the Missoula Valley include industry, natural gas furnaces, and residential wood combustion (Schmidt, 1996). Ammonia emissions to the atmosphere arise from many sources including the decay of livestock waste, use of chemical fertilizers, emissions from sewage treatment plants, biological processes in soils, and to a lesser extent, combustion processes (Fraser and Cass, 1998).

4.6.4 Industrial Sources - Kraft Recovery Boiler and Hog Fuel Boilers

The kraft recovery boiler was the fourth largest contributor to $PM_{2.5}$ in the Missoula Valley, averaging 13% in Boyd Park and 14% in Frenchtown of the annual $PM_{2.5}$. Its levels were lowest during the spring at both sites, and highest during the winter. Hog fuel boilers were calculated to be the fifth greatest contributor to the fine particulate in the Missoula Valley. The CMB model gave positive statistical hits for several different types of source profiles for the hog fuel boilers, including plywood manufacturing, a hog fuel boiler Dutch oven, a hog fuel boiler composite from Smurfit - Stone Container, a waste fuel boiler composite from Smurfit - Stone Container, and the Louisiana Pacific chip dryer. Since all of these source profiles are similar, they were grouped together and reported as one. The hog fuel fine particulate contribution was fairly consistent in Boyd Park and Frenchtown from spring through fall, averaging approximately 5% of the $PM_{2.5}$. Hog fuel boilers accounted for approximately 8% of the $PM_{2.5}$ at both sites during the winter.

4.6.5 Street Sand

Street sand is more associated with coarse (PM_{10}) particles, and was not shown to be a significant contributor to the fine fraction in this study. Out of all of the sources identified in the 1995/1996 CMB, street sand showed the biggest decrease as a source of $PM_{2.5}$ in the last five years. This is likely due to the increased use of deicer in the

Missoula City limits during the last decade. Although street sand was low in the yearly averages (4% in Boyd Park, and 5% in Frenchtown), it was detected in all four seasons. At Boyd Park, street sand was most prevalent during spring, when street sand put down to combat icy roads during the winter is re-entrained by melting snow. This same trend holds true at Frenchtown, however, summer levels were also elevated compared to Boyd Park. This is most likely the result of extra fire vehicles and personnel that were stationed at the Frenchtown Fire Department during the 2000 fire season. Some areas around the sampling station were not paved, and many fire trucks were parked in these areas which could have kicked up dust and sand around the samplers. Although liquid deicer ($MgCl_2$) is often used in place of sanding material, it was not detected in the 2000/2001 CMB. This is supported by the fact that the magnesium cation was not detected at either location during the fall or winter.

4.6.6 Automobiles

Automobiles were only detected twice by the CMB model at Boyd Park (10/24/00 and 11/5/00) and once at Frenchtown (3/5/01) during the entire year of sampling, and were not found to be a significant contributor to the Missoula Valley $PM_{2.5}$. The automobile source profile gave good fits in the absence of diesel during the model runs, but rarely gave good fits in the presence of diesel in the model. Automobiles did however contribute a significant amount of VOCs in Missoula, nearly twice the amount found in Frenchtown. Wrobel (2000) found that automobile emissions accounted for 97% of the aromatic VOCs in urban Missoula, with nearly 100% of the m- / p-xylene detected at each of his sampling sites linked to vehicle emissions. The percentages of ethylbenzene attributable to vehicles were also fairly consistent at all sites, ranging from 87 to 93%. In addition, about 80% of the toluene and naphthalene in urban Missoula were estimated to originate from vehicle emissions.

Although automobiles were not found to contribute to the fine fraction in this study, research has shown that most of the emissions from mobile sources are in the $PM_{2.5}$ fraction. Primary particulate emission sources from automobiles include their exhaust (Mulawa *et al.*, 1997; Sagebiel *et al.*, 1997), the mechanical wear of tires and brakes (Pierson and Brachaczek, 1983), and the injection of particles from the pavement (Nicholson *et al.*, 1989) and unpaved road shoulders (Moosmuller *et al.*, 1998) by resuspension processes. Mobile source particulate emissions are among the most difficult to measure with respect to emission rates and chemical composition for several reasons. This includes the different mobile source types within a group, seasonal and annual changes in fuel composition and emission control technology, and the large range of emission characteristics of individual emitters within each mobile source category among others (Gertler *et al.*, 2000). A tire wear source profile was also used in the 2000/2001 CMB model, however, it was never identified as a significant contributor to the fine fraction in the Missoula Valley.

4.7 QAQC Results – $PM_{2.5}$ Sampling and Analyses

4.7.1 $PM_{2.5}$ Filter Blanks

Field blanks showed negligible concentrations of contamination throughout the sampling and analysis program.

4.7.2 $PM_{2.5}$ Sampler Verification, Calibration, and Quarterly Audits

During the yearlong CMB sampling program, the Frenchtown samplers were maintained to ensure proper collection of sample. This included leak checks, flow verifications, ambient and filter temperature verifications, and pressure verifications. Temperature and pressure sensors were stable throughout the year, and did not require recalibration. Only the flow sensors had to be recalibrated due to ambient temperature fluctuations from season to season. Boyd Park $PM_{2.5}$ samplers were calibrated and maintained by the Montana DEQ.

Quarterly audits were conducted on the $PM_{2.5}$ samplers by the Montana DEQ as part of the QA/QC program. During each audit, the samplers were leak checked, and verifications were conducted on the flow sensor, ambient and filter temperature sensors, and the pressure sensors. Montana DEQ conducted quarterly audits on the Frenchtown samplers (Stevie and Mo) on 5/25/00, 9/20/00, 1/9/01, and 3/20/01. The Boyd Park $PM_{2.5}$ samplers (#138, #142, #140, #144, #152, and #150) were audited on 4/26/00, 9/20/00, 10/18/00, and 3/7/01. The results of these audits are presented in Table 4-8 for Frenchtown, and Table 4-9 for Boyd Park.

Table 4-8: Frenchtown quarterly audit results for the $PM_{2.5}$ samplers.

Frenchtown – Stevie	**5/25/00**	**9/20/00**	**1/9/01**	**3/20/01**
Leak Check (<10 cm Hg) Result:	Pass	Pass	Pass	Pass
Flow (± 4%) Result:	-8.8% Fail	-7.5% Fail	+3.8% Pass	+4.8% Fail
Ambient Temperature (± 2 °C) Result:	+0.1 °C Pass	+0.1 °C Pass	-0.5 °C Pass	-0.4 °C Pass
Filter Temperature (± 2 °C) Result:	+0.2 °C Pass	-0.3 °C Pass	-0.1 °C Pass	-0.4 °C Fail
Pressure (± 10 mm Hg) Result:	-5 mm Hg Pass	-8 mm Hg Pass	-7 mm Hg Pass	-2 mm Hg Pass
Frenchtown – Mo	**5/25/00**	**9/20/00**	**1/9/01**	**3/20/01**
Leak Check (<10 cm Hg) Result:	Pass	Pass	Pass	Pass
Flow (± 4%) Result:	-9.3% Fail	-7.6% Fail	+2.9% Pass	+3.8% Pass
Ambient Temperature (± 2 °C) Result:	-1.9 °C Pass	-1.2 °C Pass	+0.5 °C Pass	-0.3 °C Pass
Filter Temperature (± 2 °C) Result:	-0.5 °C Pass	-0.3 °C Pass	-0.3 °C Pass	-0.1 °C Pass
Pressure (± 10 mm Hg) Result:	-4 mm Hg Pass	-7 mm Hg Pass	-9 mm Hg Pass	-3 mm Hg Pass

Table 4-9: Boyd Park quarterly audit results for the $PM_{2.5}$ samplers.

Boyd Park - #138, #142	**4/26/00**	**9/20/00**	**10/18/00**	**3/7/01**
Leak Check (<10 cm Hg) Result:	Pass	*Pass	**Pass	Pass
Flow (± 4%) Result:	+0.5% Pass	-2.3% Pass	-4.2% Pass	-0.1% Pass
Ambient Temperature (± 2 °C) Result:	-0.3 °C Pass	-0.3 °C Pass	0.6 °C Pass	-0.5 °C Pass
Filter Temperature (± 2 °C) Result:	+0.4 °C Pass	+0.3 °C Pass	-0.3 °C Pass	-1.0 °C Pass
Pressure (± 10 mm Hg) Result:	-3 mm Hg Pass	-3 mm Hg Pass	-6 mm Hg Pass	-1 mm Hg Pass
Boyd Park - #140, #144	**4/26/00**	**9/20/00**	**10/18/00**	**3/7/01**
Leak Check (<10 cm Hg) Result:	Pass	Pass	Pass	*Pass
Flow (± 4%) Result:	-1.7% Pass	-0.8% Pass	-1.8% Pass	+0.3% Pass
Ambient Temperature (± 2 °C) Result:	-0.4 °C Pass	-0.6 °C Pass	+0.1 °C Pass	-1.2 °C Pass
Filter Temperature (± 2 °C) Result:	+0.2 °C Pass	+0.2 °C Pass	-0.2 °C Pass	-0.8 °C Pass
Pressure (± 10 mm Hg) Result:	-3 mm Hg Pass	-3 mm Hg Pass	-5 mm Hg Pass	-2 mm Hg Pass
Boyd Park - #152, #150	**4/26/00**	**9/20/00**	**10/18/00**	**3/7/01**
Leak Check (<10 cm Hg) Result:	Pass	Pass	Pass	Pass
Flow (± 4%) Result:	-0.8% Pass	+0.8% Pass	-1.4% Pass	-0.0% Pass
Ambient Temperature (± 2 °C) Result:	-0.3 °C Pass	-0.7 °C Pass	0.0 °C Pass	-1.4 °C Pass
Filter Temperature (± 2 °C) Result:	-0.2 °C Pass	-0.6 °C Pass	-0.5 °C Pass	-0.7 °C Pass
Pressure (± 10 mm Hg) Result:	-3 mm Hg Pass	-3 mm Hg Pass	-5 mm Hg Pass	-2 mm Hg Pass

* Passed leak check with clamp on C. Valve.
** Passed leak check with two clamps on C. Valve. Vandalism at site.

The Frenchtown $PM_{2.5}$ samplers passed the four audits for leak checks, ambient temperatures, filter temperatures, and pressures. However, a discrepancy in flows was discovered between the DEQ flow transfer standard (FTS) and the flow transfer standard employed in the 2000/2001 CMB sampling. This resulted in both Frenchtown $PM_{2.5}$ samplers passing the flow audits on only one occasion (1/9/01). Boyd Park samplers were calibrated and maintained by the Montana DEQ, and passed all of the leak checks, and audits for flow, filter and ambient temperatures, and pressure. Samplers 138, 140, and 152 were replaced with samplers 142, 144, and 150 sometime before the fourth audit was conducted.

The flow discrepancy between flow transfer standards was discovered in the beginning of the sampling program. Many people were involved in trying to identify the source of this discrepancy, including the manufacturers of the $PM_{2.5}$ samplers and flow transfer standards, the Missoula Health Department, the Regional EPA QA/QC officers, and the Montana DEQ. Several meetings with the DEQ at Frenchtown and the Missoula Health Department determined that the source of discrepancy did not come from the verification methods, but from the different types of flow transfer standards employed. For CMB sampling by The University of Montana, a Goohsneck Prototype FTS was initially used (later replaced with an updated model of the Goohsneck FTS) while the DEQ used a Chinook FTS. After getting reproducible results in several experiments, the Goohsneck FTS and Chinook FTS were shipped to Bob Gussman of BGI for a side-by-side comparison. The results of these experiments revealed that the Goohsneck Prototype FTS was reading a little high (17.37 LPM, or 3.9% off) while the DEQ's Chinook was reading low (15.73 LPM, or 6.2% off). There also seems to be some variation between the Goohsnecks themselves. A difference of approximately 4% was found between the Goohsneck Prototype and a third Goohsneck FTS in auditing the same $PM_{2.5}$ samplers.

To control the size-fractionating cutpoints and to measure the total volume correctly, the $PM_{2.5}$ sampler's flow rate must be maintained at a constant value that is within ±5% of the design flow rate of 16.67 LPM. If a single-point verification check of the $PM_{2.5}$ sampler flow rate is outside the tolerance of ±4%, a multipoint verification / calibration must be performed. Multipoint flow calibrations on the Frenchtown samplers were conducted on 6/12/00, and the third Goohsneck FTS was used throughout the remainder of the sampling program. After the flow issue was investigated and solved, the Frenchtown samplers passed the third quarterly audit for flow (1/9/01). However, only Mo passed the fourth audit. The flow audit for Stevie was outside of the ±4% range, yet still within the ±5% range. This meant that the flow readings were good, but the sampler needed to be recalibrated. It was noted, however, that these audits were conducted on an unusually warm day in early spring while the samplers were initially calibrated at much colder temperatures.

4.7.3 Contracted Laboratories

Chester LabNet conducted a full range of QA/QC analytical procedures during the $PM_{2.5}$ sample analyses. These include conducting precision and accuracy tests for the XRF, IC, and KHP standard analyses, OC/EC split analyses, and duplicate analyses on the carbon analyzer. No major problems were encountered with the Chester LabNet analyses. Edglo Laboratories of Fort Wayne, Indiana was originally contracted to conduct the ion analyses on the quartz samples. From the beginning of the analysis program, Edglo reported high concentrations of both chloride and sulfate. These values showed no consistency or patterns in the reports. After several experiments involving both Chester LabNet and Edglo, the source of the contamination was determined. Both Chester LabNet and Edglo used the same Method (EPA 300.0) for anion analysis. However, the discrepancy in the concentrations reported on the same samples came from the methods in which the filters were extracted, with Edglo inadvertently contaminating each filer sample. The last batch of quartz samples was sent to Edglo on 9/11/00. After that, Chester LabNet conducted all of the analyses, including the ion analyses.

The data reported by Edglo Laboratories on the $PM_{2.5}$ quartz filter samples were useless. However, archived $PM_{2.5}$ Teflon filter samples were analyzed by Chester LabNet to obtain concentrations of anions and cations from samples collected between 3/22/00 through 9/6/00. Even though these archived Teflon filters were stored at room temperature before analysis, ion measurements reported by Chester LabNet on these samples should be accurate with the possible exception of nitrate. Nitrate is a volatile compound at room temperature, therefore, the calculated concentrations could actually be slightly higher than reported here. However, these samples were collected during late spring and summer when nitrate is likely in the gaseous (not particle) form, and therefore not a major component of the fine fraction.

4.8 QAQC Results – SVOC Sampling and Analyses

4.8.1 Field Blanks

PUF field blanks were collected with every CMB sample run. The only compound that showed a consistent background concentration was phenol. The final data were corrected for this background level.

4.8.2 PUF Sampler Flow Verification, Calibration, and Quarterly Audits

Flow verifications were routinely conducted on the Frenchtown and Boyd Park PUF samplers before and after each sampling event. Both samplers also passed the quarterly flow audits conducted by the Montana DEQ on 5/25/00, 9/20/00, 1/9/01, and

3/20/01. For the PUF audits, The University of Montana orifice flow transfer standard was used because the DEQ did not have access to one. This orifice transfer standard was NIST traceable, with initial calibration by Tisch Environmental on 12/22/99 and recertification on 12/11/00. Table 4-10 presents the results of these audits:

Table 4-10: Frenchtown and Boyd Park quarterly audit results for the PUF samplers.

Frenchtown – Archie (#1454)	**5/25/00**	**9/20/00**	**1/9/01**	**3/20/01**
Flow (± 10%)	-8.00 %	+2.40 %	+6.21 %	+4.20 %
Result:	Pass	Pass	Pass	Pass
Boyd Park – Scooter (#0794)	**5/25/00**	**9/20/00**	**1/9/01**	**3/20/01**
Flow (± 10%)	-6.83 %	0.00 %	+4.67 %	+6.70 %
Result:	Pass	Pass	Pass	Pass

4.8.3 Field and Lab Surrogates

Field and lab surrogates were spiked into each PUF sample to monitor sampling and analysis efficiencies. Surrogate recoveries were evaluated by determining whether the measured concentrations fell within the acceptance limits of 60-120%. For both the field and lab surrogate solutions, 20 μl of a 50 μg/ml solution was spiked onto the PUF cartridge to yield a final concentration of 1 μg. The field surrogates were spiked before sampling, and the lab surrogates were spiked just prior to extraction. Table 4-11 presents the average percent recovery results for the field and lab surrogates for all of the PUF samples collected during the yearlong sampling program.

Table 4-11: Average percent recovery results for PUF sampling field and lab surrogates.

Field Surrogates	**%Recovery**
D_{10}-Fluoranthene	91%
D_{12}-Benzo(a)pyrene	97%
Lab Surrogates	**%Recovery**
D_{10}-Fluorene	83%
D_{10}-Pyrene	73%

The recovery efficiencies for the field and lab surrogates were all well within the 60-120% range. PUF field blanks were not included in the field surrogate calculations because they were not actually used for sampling.

4.8.4 PUF Batches

For each batch of PUF cartridges, a PUF batch certification, solvent blank, laboratory method blank (LMB), and laboratory control spike (LCS) were analyzed. Background levels of SVOC analytes were generally not detected in the blanks, with only phenol showing a consistent background presence during the analyses. For the LCS, a clean, unused, and certified PUF was spiked with the target analytes (1 μg) and carried through the extraction process. The percent recovery range for target analytes is between 60-120%. Table 4-12 presents the average LCS percent recoveries for the SVOC analytes for batches one through seven.

Table 4-12: Percent recovery results for PUF laboratory control spikes.

SVOC Analyte	%Recovery
Phenol	43%
2-methylphenol	42%
4-methylphenol	53%
2,4-dimethylphenol	52%
Naphthalene	59%
2-methylnapthalene	66%
Acenaphthylene	60%
Acenaphthene	64%
Dibenzofuran	61%
Fluorene	63%
Phenanthrene	73%
Anthracene	72%
Fluoranthene	85%
Pyrene	89%
Benzo(a)anthracene	102%
Chrysene	81%
Benzo(b)fluoranthene	88%
Benzo(k)fluoranthene	85%
Benzo(a)pyrene	96%

The first five compounds in Table 4-12 show an LCS percent recovery below 60%. This is a result of the volatile nature of these lighter molecular weight species. It states in Compendium Method TO-13A that naphthalene, acenaphthylene, and acenaphthene have demonstrated significant breakthrough using PUF cartridges, especially at summer ambient temperatures. Compared to PUF, XAD-2 resin has shown a higher collection efficiency (Lewis *et al.*, 1977; Lewis and Jackson, 1982; Chuang^{1} *et al.*, 1986; Chuang^{2} *et al.*, 1986) for volatile PAHs such as naphthalene, as well as a higher retention efficiency. However, PUF cartridges are easier to handle in the field and maintain better flow characteristics during sampling. Also, since VOC sampling already collected some of the more volatile PAHs such as naphthalene during the 2000/2001 sampling program, a focus was placed more on the heavier PAHs during PUF sampling.

Therefore, PUF was used in the sampling instead of XAD-2, and a lower collection efficiency for the lighter SVOCs is to be expected.

4.8.5 GC/MS Continuing Calibration

To document that the GC/MS met tuning and standard mass spectral abundance criteria, 1μl of a 50 ng/μl solution of decafluorotriphenylphosphine (DFTPP) was analyzed at the start of each day of SVOC analyses. Daily continuing calibration results were generally well within the desired range of ±30%. Table 4-13 presents the average continuing calibration percent differences for each SVOC analyte throughout the entire SVOC analytical program.

Table 4-13: Average continuing calibration percent differences for the SVOC analysis.

SVOC Analyte	% Difference
Phenol	+14%
2-methylphenol	+6%
4-methylphenol	+4%
2,4-dimethylphenol	+8%
Naphthalene	-1%
2-methylnapthalene	+15%
Acenaphthylene	+8%
Acenaphthene	-3%
Dibenzofuran	0%
Fluorene	+1%
Phenanthrene	+5%
Anthracene	+11%
Fluoranthene	+7%
Pyrene	+9%
Benzo(a)anthracene	+12%
Chrysene	-3%
Benzo(b)fluoranthene	+7%
Benzo(k)fluoranthene	-1%
Benzo(a)pyrene	+12%

4.8.6 SVOC Minimum Instrument Responses and Minimum Detection Limits

The minimum instrument response (MIR) necessary for the reliable identification of the measured SVOCs is given in Table 4-14. The associated minimum detection limit (MDL) was calculated using the average volume of air collected while sampling and the average ambient air temperatures and pressures for the sample days.

Table 4-14: Minimum instrument responses (MIR) and minimum detection limits (MDL) for SVOC analytes.

SVOC Analyte	MIR (ng)	MDL (pptv)
Phenol	0.28	0.24
2-methylphenol	0.14	0.10
4-methylphenol	0.21	0.15
2,4-dimethylphenol	0.16	0.10
Naphthalene	0.00	0.00
2-methylnapthalene	0.04	0.02
Acenaphthylene	0.02	0.01
Acenaphthene	0.00	0.00
Dibenzofuran	0.09	0.04
Fluorene	0.06	0.03
Phenanthrene	0.07	0.03
Anthracene	0.12	0.05
Fluoranthene	0.16	0.06
Pyrene	0.08	0.03
Benzo(a)anthracene	0.17	0.06
Chrysene	0.12	0.04
Benzo(b)fluoranthene	0.20	0.06
Benzo(k)fluoranthene	0.20	0.06
Benzo(a)pyrene	0.34	0.11

4.8.7 SVOC Analytical Uncertainty

The relative uncertainty for each SVOC analyte was determined by statistical analysis of replicate, mid-range (0.5 ng) standards. These uncertainties are listed in Table 4-15. The minimum relative uncertainty was 3.6% for fluorene, while the maximum uncertainty was 18.6% for benzo(k)fluoranthene. The average uncertainty for all SVOC analytes studied was 8.8%.

Table 4-15 The relative uncertainties associated with the SVOC analytical method.

SVOC Analyte	%Relative Uncertainty
Phenol	9.8
2-methylphenol	14.8
4-methylphenol	10.4
2,4-dimethylphenol	10.5
Naphthalene	5.1
2-methylnapthalene	5.5
Acenaphthylene	6.7
Acenaphthene	5.7
Dibenzofuran	5.4
Fluorene	3.6
Phenanthrene	5.1
Anthracene	6.2
Fluoranthene	9.0
Pyrene	10.1
Benzo(a)anthracene	13.3
Chrysene	6.0
Benzo(b)fluoranthene	18.6
Benzo(k)fluoranthene	11.2
Benzo(a)pyrene	9.0

4.9 QAQC Results – VOC Sampling and Analyses

4.9.1 Field Blanks

Field blanks were collected with every CMB sample run. Chloroform, benzene, toluene, ethylbenzene, 1,4-dimethylbenzene, 1,2-dimethylbenzene, *n*-propylbenzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, isopropylbenzene, and naphthalene showed low but consistent background levels in the blanks. The final data were corrected for these background levels.

4.9.2 Duplicate Samples and Backup Sorbent Tubes

Duplicate VOC samples were collected for nearly every CMB sampling episode at both Boyd Park and Frenchtown. Backup sorbent tubes were used in the beginning of the sampling program, however, the use of these tubes was suspended after the first few sampling episodes due to a lack of VOC breakthrough during sampling.

4.9.3 Solvent and System Blanks

Solvent and system blanks were analyzed to monitor for analytical artifacts. VOC analytes on these blanks were generally not detected.

4.9.4 GC/MS Continuing Calibration / Spike

BFB was analyzed at the start of each day of VOC analyses to document that the GC/MS met tuning and standard mass spectral abundances. Daily continuing calibration results were generally well within the desired range of ±30%. These continuing calibrations were also used as spikes to monitor analytical recovery efficiencies. Table 4-16 presents the average continuing calibration percent differences for the entire VOC analytical program.

Table 4-16: Average continuing calibration percent differences for the VOC analysis.

VOC Analyte	**%Difference**
Trichloromethane	-12%
Tetrachloromethane	-11%
Benzene	-6%
Toluene	2%
Ethyl Benzene	-2%
1,4-Dimethylbenzene	-3%
1,2-Dimethylbenzene	-1%
Isopropylbenzene	2%
n-Propylbenzene	0%
1,3,5-Trimethylbenzene	2%
1,2,4-Trimethylbenzene	2%
Isopropyl Toluene	2%
Naphthalene	0%

4.9.5 VOC Minimum Instrument Responses and Minimum Detection Limits

The minimum instrument response (MIR) necessary for the reliable identification of the measured VOCs is given in Table 4-17. The associated minimum detection limit (MDL) was calculated using the average volume of air collected while sampling and the average ambient air temperatures and pressures for the sample days.

Table 4-17: Minimum instrument responses (MIR) and minimum detection limits (MDL) for VOC analytes.

VOC Analyte	MIR (ng)	MDL (pptv)
Trichloromethane	1.05	3.54
Tetrachloromethane	9.06	23.71
Benzene	5.66	29.17
Toluene	12.13	53.00
Ethyl Benzene	13.46	51.05
1,4-Dimethylbenzene	13.26	50.28
1,2-Dimethylbenzene	12.92	48.99
Isopropylbenzene	14.04	47.02
n-Propylbenzene	12.70	42.54
1,3,5-Trimethylbenzene	16.19	54.23
1,2,4-Trimethylbenzene	15.67	52.49
Isopropyl Toluene	17.24	51.71
Naphthalene	13.93	43.76

4.9.6 VOC Analytical Uncertainty

The relative uncertainty for each VOC analyte was determined by statistical analysis of replicate, mid-range (200 ng) standards. These uncertainties are listed in Table 4-18. The minimum relative uncertainty was 6.42% for isopropyltoluene, while the maximum uncertainty was 23.99% for tetrachloromethane. The average uncertainty for all VOC analytes studied was 11.01%.

Table 4-18 The relative uncertainties associated with the VOC analytical method.

VOC Analyte	%Relative Uncertainty
Trichloromethane	21.62
Tetrachloromethane	23.99
Benzene	20.92
Toluene	8.26
Ethyl Benzene	7.73
1,4-Dimethylbenzene	9.29
1,2-Dimethylbenzene	8.34
Isopropylbenzene	8.13
n-Propylbenzene	6.95
1,3,5-Trimethylbenzene	6.88
1,2,4-Trimethylbenzene	7.45
Isopropyl Toluene	6.42
Naphthalene	7.08

4.10 QAQC Results – CMB Model

Most of the CMB fitting parameters were well within EPA target ranges. Table 4-19 presents the average key goodness-of-fit parameters for Boyd Park and Frenchtown as well as the EPA target ranges for each parameter. Boyd Park and Frenchtown goodness-of-fit parameters for each sample day are presented in Tables 4-20 and 4-21.

Table 4-19: Average goodness-of-fit parameters for the 2000/2001 CMB.

Goodness-of-Fit Parameter	**Boyd Park**	**Frenchtown**	**EPA Target**
R^2	0.96	0.95	0.8 - 1.00
Chi^2	0.62	0.64	0.00 - 4.00
Degrees of Freedom	17	17	> 5
% Mass Explained	102%	102%	80 - 120%
TSTAT	>2	>2	>2

R^2, Chi^2, and DF values for each CMB model run were well within the EPA target ranges. If the measured mass is very low (< 5 to 10 µg/m^3), percent mass explained may be outside of the target range because the precision of the mass measurement is on the order of 1 to 2 µg/m^3. Only on three occasions out of 62 model runs did the percent mass go outside of the range of 100 ±20%. These were 9/30/00 (Boyd Park), 12/23/00 (Boyd Park), and 5/9/00 (Frenchtown), with values of 127.6, 73.6, and 123.4, respectively. These three days either had extremely low concentrations (9/30/00 and 5/9/00) or high concentrations (12/23/00). In reporting source contribution estimates, all TSTATS were kept above 2 to ensure that they were above the detection limits. Collinearity did not appear to be a problem in the 2000/2001 CMB, and diesel exhaust and residential wood combustion were not intermixed in this model. The C/M and R/U ratios were for the most part all below 2, although a few species for each run (copper and chlorine) were almost always above 2. In summary, although there were a few cases where the fit parameters were outside the EPA target range, none of these cases were considered invalid, and all of the fits were quite strong.

The sensitivity of the CMB model's results to the errors in the source profiles were evaluated by using different chemical abundances of a source type, by changing the fitting species used in the source type, and by varying different types of sources. The results of the sensitivity tests showed that the CMB calculations carried out in this study were acceptable.

Table 4-20: Boyd Park Goodness-of-fit summary for each sample run in 2000/2001 CMB.

Date	TSTAT Target >2.0	R^2 Target 0.8-1.0	Chi^2 Target 0.0-0.4	% Mass Target 100%+-20%	DF Target >5	Ration C/M Target 0.5-2.0	Ration R/U Target abs<2.0
3/22/00	OK	0.99	0.26	95.6	12	OK	OK
4/3/00	OK	0.98	0.39	96.6	14	OK	OK
4/15/00	OK	0.97	0.93	99.9	16	OK	OK
4/27/00	OK	0.96	0.58	108.3	16	OK	OK
5/9/00	OK	0.93	0.92	116.9	23	OK	OK
5/21/00	OK	0.95	1.22	108.4	13	OK	OK
6/2/00	OK	0.98	0.37	93.0	15	OK	OK
6/14/00	OK	0.94	0.52	111.3	24	OK	OK
6/26/00	OK	0.90	1.43	115.5	23	OK	OK
7/8/00	OK	0.93	0.63	101.2	24	OK	OK
7/20/00	OK	0.95	0.46	97.7	23	OK	OK
8/1/00	OK	0.97	0.80	106.0	16	OK	OK
8/13/00	OK	0.93	0.81	99.8	22	OK	OK
8/25/00	OK	0.88	1.06	97.6	22	OK	OK
9/6/00	OK	0.92	0.77	105.8	23	OK	OK
9/18/00	OK	0.88	1.23	100.9	21	OK	OK
9/30/00	OK	0.98	0.17	**127.6**	19	OK	OK
10/12/00	OK	0.95	0.65	111.6	19	OK	OK
10/24/00	OK	0.99	0.22	100.0	12	OK	OK
11/5/00	OK	0.94	1.32	107.2	13	OK	OK
11/17/00	OK	0.98	0.53	99.8	14	OK	OK
11/29/00	OK	0.99	0.30	98.3	14	OK	OK
12/11/00	OK	0.98	0.42	109.1	15	OK	OK
12/23/00	OK	0.99	0.15	**73.6**	22	OK	OK
1/4/01	OK	0.97	0.76	92.9	15	OK	OK
1/16/01	OK	0.99	0.29	90.5	12	OK	OK
1/28/01	OK	0.98	0.28	105.0	14	OK	OK
2/9/01	OK	0.99	0.32	99.8	12	OK	OK
2/21/01	OK	0.97	0.45	93.0	15	OK	OK
3/5/01	OK	0.99	0.53	100.0	14	OK	OK
3/17/01	OK	0.99	0.30	98.6	14	OK	OK
Average	**OK**	**0.96**	**0.62**	**102**	**17**	**OK**	**OK**

Table 4-21: Frenchtown Goodness-of-fit summary for each sample run in 2000/2001 CMB.

Date	TSTAT Target >2.0	R^2 Target 0.8-1.0	Chi^2 Target 0.0-0.4	% Mass Target 100%+-20%	DF Target >5	Ration C/M Target 0.5-2.0	Ration R/U Target abs<2.0
3/22/00	OK	1.00	0.17	95.7	13	OK	OK
4/3/00	OK	0.96	0.68	94.9	14	OK	OK
4/15/00	OK	0.97	0.61	94.0	14	OK	OK
4/27/00	OK	0.98	0.60	113.1	15	OK	OK
5/9/00	OK	0.99	0.20	123.4	16	OK	OK
5/21/00	OK	0.92	1.09	104.7	25	OK	OK
6/2/00	OK	0.95	0.33	117.5	22	OK	OK
6/14/00	OK	0.93	0.61	119.1	21	OK	OK
6/26/00	OK	0.85	1.46	117.6	23	OK	OK
7/8/00	OK	0.92	0.71	100.0	22	OK	OK
7/20/00	OK	0.90	0.83	100.7	23	OK	OK
8/1/00	OK	0.93	1.22	105.5	24	OK	OK
8/13/00	OK	0.94	0.80	97.8	22	OK	OK
8/25/00	OK	0.88	1.17	104.0	16	OK	OK
9/6/00	OK	0.93	0.59	103.2	22	OK	OK
9/18/00	OK	0.84	1.64	90.5	22	OK	OK
9/30/00	OK	0.91	0.91	116.8	25	OK	OK
10/12/00	OK	0.94	0.85	106.1	20	OK	OK
10/24/00	OK	0.96	0.68	94.0	14	OK	OK
11/5/00	OK	0.97	0.54	101.2	14	OK	OK
11/17/00	OK	0.97	0.70	99.2	14	OK	OK
11/29/00	OK	0.97	0.51	98.3	14	OK	OK
12/11/00	OK	0.97	0.51	102.8	13	OK	OK
12/23/00	OK	0.97	0.67	82.6	15	OK	OK
1/4/01	OK	0.99	0.17	91.6	13	OK	OK
1/16/01	OK	0.99	0.26	98.3	14	OK	OK
1/28/01	OK	0.99	0.23	99.2	13	OK	OK
2/9/01	OK	0.99	0.19	92.5	12	OK	OK
2/21/01	OK	0.99	0.12	101.2	13	OK	OK
3/5/01	OK	0.97	0.60	86.3	15	OK	OK
3/17/01	OK	0.99	0.11	94.6	15	OK	OK
Average	OK	0.95	0.64	101	17	OK	OK

Chapter 5 Conclusion

This study provides the first, comprehensive appraisal of $PM_{2.5}$ sources throughout all four seasons in the Missoula Valley. Results showed that ambient levels of $PM_{2.5}$ and the amounts contributed by sources to the fine fraction were nearly identical between both Boyd Park and Frenchtown during the 2000/2001 sampling program, which verifies the findings in other studies that $PM_{2.5}$ concentrations in an airshed are uniform (Wilson and Suh, 1997; Chen *et al.*, 2001). $PM_{2.5}$ was collected every 12 days at two locations in the Missoula Valley from 3/22/01 – 3/17/01. From these samples, levels of trace elements, ions, and OC, EC, and TC were quantified and used in an EPA CMB Model (Version 8) to apportion the sources of $PM_{2.5}$ in the Missoula Valley. In addition to collecting $PM_{2.5}$, SVOCs and VOCs were also measured throughout the program. The biggest source contributing to the ambient $PM_{2.5}$ in the Missoula Valley throughout the year was wood combustion, contributing an average of 41% to the fine fraction. The residential wood combustion source profile used in the CMB model provided excellent fits for residential wood combustion during the winter months, slash and controlled burns during the spring and fall, and wildfires during the summer. The second largest source of $PM_{2.5}$ was diesel (19%), followed by ammonium nitrate (17%), the kraft recovery boilers from Smurfit-Stone Container (14%), other hog fuel boilers (6%), and street sand (5%). In a comparison between the 1995/1996 CMB and the 2000/2001 CMB, road dust (street sand) showed the most significant drop in contributions to the fine fraction, decreasing from an average of 4.2 $\mu g/m^3$ in the 1995/1996 CMB to 0.4 $\mu g/m^3$ in 2000/2001. Gasoline powered automobiles were found to be an insignificant contributor to the fine fraction, but the contribution to VOCs in Missoula was significant, with measured levels nearly double that found in Frenchtown.

Winter was the worst air pollution season in the Missoula Valley, with ammonium nitrate composing a major portion of the wintertime fine fraction. Levels of PAHs and VOCs were also elevated during the wintertime due to a reduction of the photochemical processes that destroy these compounds. As a result of the wildfire season during the summer of 2000, annual averages of $PM_{2.5}$ were measured above the 15 μg/m^3 annual standard, with an annual average of 15.4 μg/m^3 at both Boyd Park and Frenchtown. Without the fire season included in the annual average, levels at Boyd Park were 13.7 μg/m^3 and 13.6 μg/m^3 at Frenchtown. At no time during these sample days did the ambient $PM_{2.5}$ exceed the daily standard of 65 μg/m^3.

Part II

INVESTIGATION OF THE RELATIONSHIP BETWEEN $PM_{2.5}$, SEMI-VOLATILE ORGANIC COMPOUNDS, AND VOLATILE ORGANIC COMPOUNDS

Chapter 6 Introduction

Since 1997, states have been required to measure the mass of ambient $PM_{2.5}$ particles. Now that $PM_{2.5}$ sampling and weighing techniques have been refined, the next step is to determine what types of compounds actually compose the $PM_{2.5}$ particles in individual airsheds. In March 2001, the Missoula County began the operation of a speciation sampler at Boyd Park, measuring mass, anions, cations, trace elements, and organic carbon (OC), elemental carbon (EC), and total carbon (TC). EPA mandated speciation testing of individual organics and differentiation of the Semi-Volatile Organic Compound (SVOC) fraction from total carbon in the $PM_{2.5}$ sampling program is still optional for states. However, as research continues, SVOCs may be added to the routine $PM_{2.5}$ speciation program as the methodology is further developed (EPA^2, 1999).

Exploratory and research organic speciation sampling and analyses enhance our understanding of the various organic and chemical components of the $PM_{2.5}$ particles, which, in turn, lead to improved source apportionment techniques. Chemical speciation also helps in determining the effectiveness of emissions reduction strategies and in understanding the $PM_{2.5}$ temporal and spatial variations. Currently, there are a few types of research sampling systems that have been developed and evaluated using the basic FRM (Federal Reference Method) $PM_{2.5}$ sampling components. Because several different speciation sampler designs could be used in the overall $PM_{2.5}$ speciation sampling program, studies are needed to collect data which show intercomparisons between the samplers (EPA[1], 1999). On May 18-19, 1999, the Expert Panel for the EPA Speciation Network met in Las Vegas, Nevada to review the EPA's revised guidance document on the speciation network. The Expert Panel reported that further development is required to have an adequately characterized, accurate FRM $PM_{2.5}$ sampler for carbonaceous aerosols and more accurate organic carbon sampling methods (Koutrakis, 1999).

6.1 Relationship Between $PM_{2.5}$ and SVOCs

Organic compounds are important components of particulate matter, whether in urban, rural, or remote areas. Most of the particulate organic carbon is believed to reside in the fine particle fraction. In Missoula, the organic fraction composes approximately 48% (35% OC, 13% EC) of the annual $PM_{2.5}$. Particulate organic carbon consists of thousands of separate compounds that contain more than 20 carbon atoms ($>C_{20}$), such as acids, waxy materials, and ringed structures. Rogge *et al.* (1993) identified and quantified over 80 individual organic compounds in the $PM_{2.5}$ fraction, including *n*-alkanes, *n*-alkanoic acid, *n*-alkanal, aliphatic dicarboxylic acids, aromatic polycarboxylic acids, polycyclic aromatic hydrocarbons (PAHs), polycyclic aromatic ketones (PAKs), polycyclic aromatic quinones (PAQs), diterpenoid acids, and some nitrogen-containing compounds. In other studies where individual organic compounds were quantified from $PM_{2.5}$, the sum of the measured compounds amounted to only a few percent of the total organic mass (Bennett and Stockburger, 1994).

$PM_{2.5}$ research has investigated the volatility of some compounds which compose fine particles, including ammonium nitrate and some organic carbon materials. Previous studies using denuder based technology showed that $PM_{2.5}$ FRM sampling using a Teflon filter undermeasured $PM_{2.5}$ total mass by 20-40%. The loss of semi-volatile material from particles collected on these filters was dominated by the loss of organic semi-volatiles, which accounted for ~80% of the total loss (Eatough *et al.*, 1999; Pang[1] *et al.*, in press; Pang[2] *et al.*, in press). In another study, the FRM was found to undermeasure $PM_{2.5}$ nitrate by ~20% and total organic carbon by 27% in sampling with a Teflon filter (Pang *et al.*, 2001). The loss of particulate SVOCs is a function of the composition of the collected particles, temperature, humidity, and other effects (Zhang and McMurry, 1987; Eatough *et al.*, 1999; Pang[1] *et al.*, in press). The loss of this mass from $PM_{2.5}$ Teflon filters using EPA mandated sampling equipment and technology (FRM) could have biased regulatory effects, and the accuracy of these mass measurements remains in question.

6.2 Current $PM_{2.5}$ Speciation Samplers for Organics

EPA compliance sampling for $PM_{2.5}$ is performed using either a quartz or Teflon filter. However, since many organic compounds composing $PM_{2.5}$ are distributed between the gas and particle phases, the gaseous fraction will not be collected by the filter. Also, any gaseous species that revolatize off of the particles during sampling will be lost. To accurately collect the gaseous fraction, additional sampling techniques are required. There are several sampling designs that are currently investigating the organic composition of $PM_{2.5}$ filter samples. These systems employ different types of inlets, denuders, filters in series and parallel, and absorbing materials to accurately measure volatile compounds and to quantify the precursors of secondary aerosols.

The sequential filter sampler (SFS) and California Acid Deposition Monitoring Program (CADMP) dry deposition samplers (Chow *et al.*, 1993) draw air through medium-volume inlets into a plenum. Several samples can then be drawn simultaneously from the plenum, through denuders, and onto various filter media (Chow and Egami, 1997). Novel sampling and analysis techniques for organic carbon using XAD and carbon-impregnated filter denuders, which remove gaseous organic compounds before the filter, are currently being evaluated in Seattle, Washington. Here, two quartz filters down-flow of the denuder collect the particle-phase organic carbon. The first filter collects particle phase organic carbon (EC, OC, and a very small fraction of gas phase organic carbon) while the second collects the gas phase organic carbon volatized from the first quartz filter. The total particle carbon concentration is determined by adding the concentrations of the first and second filter, respectively. It is not known whether removing gas phase organics prior to particle collection enhances the volatilization of organic carbon from the quartz filter.

The combination of technologies used in the BOSS diffusion denuder sampler and the Harvard particle concentrators has resulted in the Particle Concentrator – Brigham Young University Organic Sampling System (PC-BOSS) for the 24 hour (or less) integrated collection of $PM_{2.5}$, including ammonium nitrate and semi-volatile organic material (Eatough *et al.*, 1999; Pang[1] *et al.*, in press; Pang[2] *et al.*, in press). A combination of BOSS denuder and tapered element oscillating microbalance (TEOM) monitor technology resulted in the real-time ambient mass sampler (RAMS) for the continuous measurement of $PM_{2.5}$, including the semi-volatile components (Eatough *et al.*, 1999; Obeidi[1] *et al.*, 2000; Obeidi[2] *et al.*, 2000; Eatough *et al.*, in press; Pang *et al.*, 2001). Finally, both gaseous and particle phases of SVOCs can be measured during $PM_{2.5}$ sampling using a filter followed by solid adsorbents such as polyurethane foam (PUF), Tenax, or XAD resins.

Chapter 7 Experimental Methods

The Research portion (Part II) of this sampling program was designed to investigate the organic fraction that composes the $PM_{2.5}$ in the Missoula Valley. On days offset from CMB testing, Research sampling was conducted only at the Frenchtown site to evaluate an innovative $PM_{2.5}$ instrument design which collected SVOCs in addition to $PM_{2.5}$ using an FRM sampler. A high-volume PUF (Hi-vol PUF) and two VOC samplers were operated in addition to the modified $PM_{2.5}$ sampler in 24 hour intervals starting at midnight and ending at midnight the next night. Research sampling was conducted every 12 days throughout the yearlong program.

SVOC and VOC sampling, analysis, and QA/QC methodologies are described in Part I of this document. A detailed description of the Research sampling, analysis, and QA/QC program is discussed here. Table 7.1 presents methodologies followed in conducting the Research program.

Table 7-1: Research sampling, analysis, and QA/QC methodologies.

Sampling	
PM$_{2.5}$ Research	40 CFR Part 50, Appendix L (EPA[1], 1997), 40 CFR Part 53, Subpart E, and 40 CFR part 58, Appendix A (EPA[2], 1997; EPA[3], 1997). Development of new sampling methodology.
PUF (SVOCs)	Compendium Method TO-13A. Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography / Mass Spectrometry (GC/MS). January, 1999 (TO-13A, 1999).
VOCs	Method TO-2, Method for the Determination of Volatile Organic Compounds in Ambient Air by Carbon Molecular Sieve Adsorption and Gas Chromatography / Mass Spectrometry (GC/MS). Revision 1.0, April, 1984 (TO-2, 1984).
Analyses	
PM$_{2.5}$ Research	Development of new analytical methodology.
PUF (SVOCs)	Compendium Method TO-13A.
VOC	Modified Method TO-2.
QA/QC – Sampling and Analyses	
PM$_{2.5}$ Research	EPA QA Guidance Document "Field SOPs for the PM$_{2.5}$ Performance Evaluation Program," section 10 (EPA[1], 1998), EPA's QA Guidance Document 2.12 sections 7 and 10 (EPA[2], 1998), EPA "Guideline on Speciated Particulate Monitoring," section 6.0 and 7.0 (EPA[4], 1998). Compendium Method TO-13A.
PUF (SVOCs)	Compendium Method TO-13A.
VOCs	Modified Method TO-2.

7.1 PM$_{2.5}$ Research Sampling

7.1.1 Summary

PM$_{2.5}$ Research sampling was conducted every 12 days during the yearlong sampling program at Frenchtown. 24 hour samples (midnight to midnight) were collected by the modified PM$_{2.5}$ FRM sampler using a 47 mm quartz filter and two PUF cartridges. Air was drawn at a controlled flow rate of 16.67 Liters Per Minute (LPM) through a specially designed particle-size discriminating WINS (Well Impactor Ninety-

Six) $PM_{2.5}$ inlet, with approximately 24,000 liters of sample collected during each sample run.

7.1.2 $PM_{2.5}$ Sampler and Media Description

Although $PM_{2.5}$ sampling with denuders has predominantly been used to investigate the revolatilization of SVOCs from filter samples, more sampling using the FRM speciation sampler with one quartz filter and no denuder is needed before the use of the denuder speciation sampler can be recommended by the EPA (Koutrakis, 1999). Research sampling was conducted with a modified BGI Inc., PQ200 FRM sampler. The collection media included a 47 mm quartz glass filter followed by two miniature PUF cartridges installed down-flow of the $PM_{2.5}$ filter to collect any gaseous organics that might revolatize from the filter during sampling. In studies of different types of media used in SVOC sampling (Westerholm, 1991), the PUF sampling technique was found to be the most suitable for sampling of SVOC constituents in diluted heavy-duty diesel exhausts. The $PM_{2.5}$ quartz filters (Whatman QMA) were purchased from Chester LabNet who prefired the filters at 800 °C for 6 hours before shipping them to The University of Montana. The miniature PUF cartridges were purchased from SKC, and contained 76 mm of PUF sorbent in a glass cartridge with a 22 mm outside diameter and length of 110 mm. These smaller PUF cartridges are significantly smaller than the ones used in TO-13A Hi-vol PUF sampling, and are normally used in EPA Methods IP-8, TO-10A, ASTM D 4861, and ASTM D4947 for organochlorine and organophosphorus pesticides testing. Figure 7-1 presents a Hi-vol quartz glass filter and PUF plug (left side) and the Research $PM_{2.5}$ quartz glass filter and PUF plugs on the right.

The PQ200 $PM_{2.5}$ sampler was modified with ChemFluor 367 tubing (Norton Plastics) and Kynar fittings and elbows (Cole Parmer). First, the rubber hose normally attached to the back of the filter assembly was taken off and ChemFluor tubing was connected. Then, using elbows, reducers, and straight pieces, the flow pathway past the filter was extended outside of the sampler's casing to the bottom of the sampler where two PUF cartridges could be installed. This allowed for easy access in installing and removing the PUF cartridges. A piece of rubber hose was connected to the back end of the PUF cartridges, with the other end of the hose connected to a piece of Tygon tubing which ran back inside of the sampler casing and into the water trap. The two PUF cartridges were joined in series downstream of the quartz filter using a silicon stopper. Please see Figure 7-2 for pictures of the modified $PM_{2.5}$ sampler.

Figure 7-1: Hi-vol quartz glass filter and PUF (left) and Research $PM_{2.5}$ quartz glass filter and PUF (right).

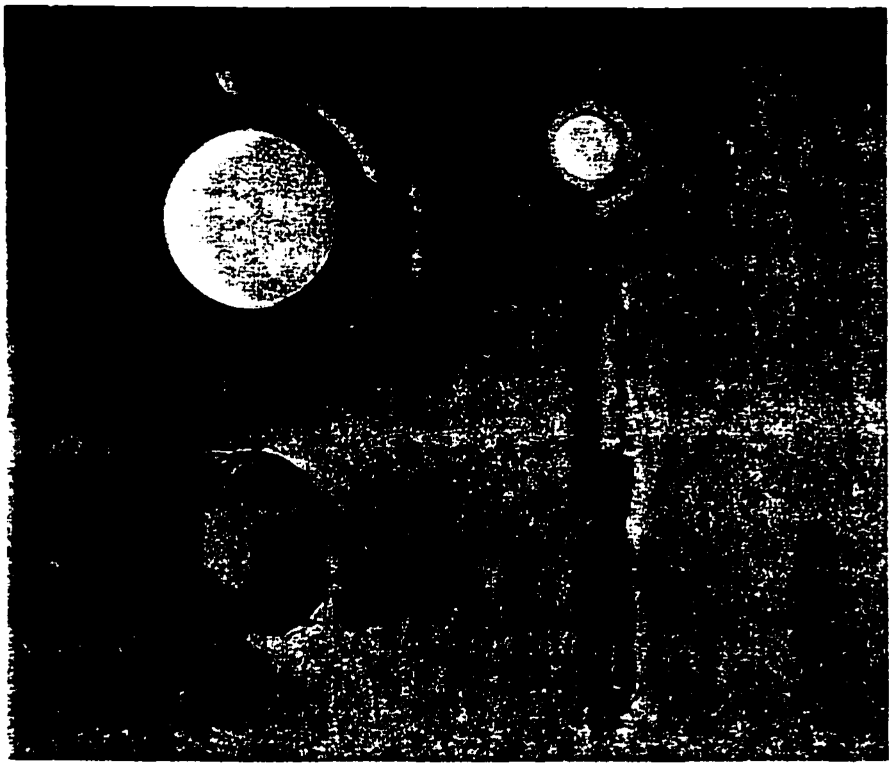


Figure 7-2: Modified $PM_{2.5}$ Sampler.

Inside of the PQ200 $PM_{2.5}$ sampler displaying ChemFluor tubing extending from the back of the filter assembly down and out the bottom of the sampler.

Bottom of the modified $PM_{2.5}$ sampler showing where Research PUF plugs are installed during sampling.

7.1.3 Conducting a Sample Run

For each Research sample run, a $PM_{2.5}$ quartz glass filter and two PUF cartridges were prepared at The University of Montana laboratory. Just prior to sampling, surrogate compounds (field surrogates) were added to the center of the PUF plug. Using a microsyringe, 20 μl of a 50 μg/ml surrogate solution was spiked onto the PUF plug to yield a final concentration of 1 μg. The field surrogates added were d_{10} -fluoranthene and d_{12} –benzo(a)pyrene.

The PQ200 $PM_{2.5}$ samplers had to successfully pass a leak check, and barometric pressure, temperature (ambient and filter), and flow rate verifications before sampling. $PM_{2.5}$ data sheets were filled out documenting date, time, weather conditions, etc.. for each sampling event. On the day of sampling, the modified PQ200 was visually checked to verify that it was functioning properly and to document any unusual conditions that might influence the data (ex. weather conditions, sampler malfunction, etc.). The filter samples were retrieved on the day after the sampling event, and the sample run data parameters (pressure, temperature, flows during sampling) were downloaded from the memory of the PQ200 using a BGI Datatrans downloader. Samples were transported back to The University of Montana laboratory in a cooler, with the PUF plug samples stored in a glass container with Teflon lid and the quartz glass filter samples kept in a Millipore plastic container. All samples were kept in the freezer until analysis.

7.2 Research Analyses

7.2.1 Summary

All research analyses were conducted at The University of Montana laboratory. The $PM_{2.5}$ quartz filter and plugs were extracted together in a Soxhlet apparatus using a solvent combination of diethyl ether and hexane. The extract was concentrated using a Kuderna-Danish (K-D) evaporator prior to analysis by Gas Chromatography / Mass Spectrometry (GC/MS). A suite of 61 organic contaminants was originally quantified but was refined to the following 19 compounds:

Phenol
2,4-Dimethylphenol
2-Methylnaphthalene
Dibenzofuran
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
2-Methylphenol
Naphthalene
Acenaphthylene
Fluorene
Fluoranthene
Chrysene
4-Methylphenol
Benzo(b)fluoranthene
Acenaphthene
Phenanthrene
Pyrene
Benzo(k)fluoranthene

7.2.2 Cleaning of PUF Sampling Media

The miniature PUF plugs were purchased uncleaned from Supelco, and had to be cleaned before being used. At The University of Montana laboratory, the PUF plugs were placed in a Soxhlet apparatus and extracted overnight with acetone for 16 hours at approximately 4 cycles per hour for initial cleanup. The cleaned PUF plugs were stored in a freezer until use. All $PM_{2.5}$ quartz filters were purchased clean (prefired) from Chester LabNet.

7.2.3 Aggregate Samples

In the beginning of the Research analysis program, individual Research samples (3/28/00, 4/9/00, and 4/21/00) were extracted. However, results from these analyses showed that the analytes were present at or below the detection limits of the GC/MS. Research samples were then aggregated to ensure enough sample for each analysis. Each Aggregate sample (Aggregates A – D) consisted of six Research sample days (six $PM_{2.5}$ quartz glass filters and 12 miniature PUF plugs), with Aggregate E containing three.

7.2.4 Sample Extraction and Concentration

The $PM_{2.5}$ quartz filter and PUF plugs for each Aggregate run were extracted together in the Soxhlet apparatus in order to reach detection limits, avoid questionable interpretation of the data, and minimize costs. Before the extraction began, 20 µl of a 50 µg/ml laboratory surrogate standard solution was spiked onto the sample to yield a final concentration of 1 µg. The laboratory surrogate standards used were d_{10} -fluorene and d_{10}-pyrene.

Samples were extracted in 700 ml of a 10 percent diethyl ether in hexane solution. The Soxhlet apparatus refluxed overnight for 18 hours at a rate of at least 3 cycles per hour. After being cooled, the extract was dried by passing it though a drying column containing about 10 grams of anhydrous sodium sulfate. 100 ml of the 10 percent diethyl ether / hexane solution was used as a wash to complete the quantitative transfer into a K-D concentrator with 10 ml concentrator tube. When the liquid was evaporated to an approximate volume of 5 ml, the K-D apparatus was removed from the water bath and the solvent was allowed to drain for at least 5 minutes while cooling.

The K-D flask was then washed with 5 ml of cyclohexane, and further concentrated to 1.0 ml by nitrogen blowdown. The internal wall of the concentrator was rinsed down several times with hexane during the nitrogen blowdown. The final extract was then transferred to an amber vial with Teflon septa and stored in a refrigerator until analysis.

7.2.5 Standard Preparation

In the beginning of the Research analysis program, a PAH standard mix containing 19 compounds was used for quantitation of compounds in the sample extracts. Later, the analysis was improved by using a different SVOC standard mix that contained 65 compounds, including the initial 19 PAHs plus phenols. Using these SVOC stock mixes, a series of calibration standards were generated containing 2.50 ng/µl, 1.25 ng/µl, 0.50 ng/µl, 0.25 ng/µl, and 0.10 ng/µl of the target analytes. The stock standard solutions and standards were kept in amber vials with Teflon septa and stored in a refrigerator. New standards were prepared before each set of PUF sample extracts were analyzed by GC/MS.

7.2.6 Internal Standards

Before the GC/MS analysis, each 1 ml aliquot of the five calibration standards and sample extracts were spiked with deuterated internal standards to yield a final concentration of 0.5 ng/µl. The following internal standards were used for this procedure: d_8 –naphthalene, d_{10} –acenaphthene, d_{10} –phenanthrene, d_{12} –chrysene, and d_{12} –perylene. These compounds were selected because they were similar in analytical behavior to the compounds of interest in the samples. In making up the original internal standard mix, d_8 –naphthalene, d_{10} –acenaphthene, d_{12} –chrysene, and d_{12} –perylene were used. However, d_{12} –perylene had a poor response in the mass spectrum because it came out so late in the run and interfered with the rising baseline due to increasing temperatures. Therefore it was replaced with d_{10} -phenanthrene which had an earlier retention time and came out before the rise in baseline. The response from the internal standards were used in the quantitation of the target analytes by using the target response relative to the calibration curve.

7.2.7 Instrument Description

All Research SVOC analyses were conducted in The University of Montana laboratory. Two different kinds of GC/MSs were used for this analysis. The first is a Hewlett Packard GCD 5890 series II Gas Chromatograph with 5973 Mass Spectrometer. The second GC/MS employed was a Hewlett Packard 6890 series Gas Chromatograph with a 5973 Mass Spectrum Detector (MSD). Analyte separations were accomplished on a 0.32 mm ID X 30.0 meter Restek XTI-5 column. PUF sample extracts were analyzed using the instrument conditions and temperature program in Table 7-2.

Table 7-2: GC/MS instrument operating conditions – Research SVOC analysis.

Inlet Temperature	220 °C
Detector Temperature	270 °C
Injection Mode	Splitless
Initial Oven Temperature	40 °C
Initial Oven Hold	4.0 minutes
Oven Ramp Rate 1	10 °C / minute
Oven Ramp Final Temp 1	300 °C
Oven Ramp Rate 1 Final Time	5.0 minutes
Oven Ramp Rate 2	10 °C / minute
Oven Ramp Final Temp 2	330 °C
Oven Ramp Rate 2 Final Time	2.0 minutes
Total Run Time	40.0 minutes
Carrier Gas	Helium
Flow	1.0 ml / minute

7.3 QA/QC Program – Research Sampling and Analyses

7.3.1 Field Surrogates

Immediately before field deployment, 20 µl of a 50 µg/ml field surrogate solution was spiked onto the PUF plug to yield a final concentration of 1 µg. The recovery of the field surrogate standard was used to monitor for matrix effects, breakthrough, sampling errors, etc. The field surrogates used were d_{10} -fluoranthene and d_{12} –benzo(a)pyrene. After the sample analysis, the field surrogate recovery was determined, with acceptable limits between 60-120%.

7.3.2 Field Blanks

One field blank (quartz filter and PUF plugs) was collected for approximately every 16 samples. The field blanks were shipped to the field, installed in the sampler, and returned to the laboratory without drawing air through the sampler.

7.3.3 $PM_{2.5}$ Sampler Verification and Calibration

In conducting $PM_{2.5}$ sampling, the barometric pressure, ambient and filter temperatures, and flows were all initially calibrated and later verified with National Institute of Standards and Technology (NIST) traceable standards. For the Frenchtown $PM_{2.5}$ sampler, barometric pressure, ambient temperature, and filter temperatures were initially calibrated in the laboratory, with a full multipoint flow calibration conducted in the field upon installation. Field verifications were performed to determine if the sensor readings had drifted since initial calibration. Only if the sampler sensor reading was not acceptable would a full multipoint calibration be conducted. During the yearlong Research sampling program at Frenchtown, only the flows had to be recalibrated due to ambient temperature fluctuations throughout the year. Also, a leak check had to be passed before sampling could be begin. All data and calculations were recorded in calibration logbooks.

7.3.4 $PM_{2.5}$ Sampler Performance Evaluations – Quarterly Audits

Quarterly audits were conducted by the Montana DEQ to verify the sampler's flow rate, temperatures (both filter and ambient), and barometric pressures. The audit consisted of one measurement made at the sampler's operational flow rate (16.67 LPM). The flow rate transfer standard used in the audit was not the same one used to verify or calibrate the sampler during the sampling program, however it was traceable to a primary standard. The barometric pressure and temperature verification devices used by the DEQ were traceable to standards as well. Results of these audits are discussed in Section 4.7.2.

7.3.5 Lab Surrogates

Just before the analytical extraction of the $PM_{2.5}$ PUF sample filter and plug, 20 µl of a 50 µg/ml laboratory surrogate standard solution was spiked into the sample (giving a final concentration of 1 µg) to monitor for unusual matrix effects, gross sample processing errors, etc. The lab surrogates used were d_{10} -fluorene and d_{10} -pyrene. Surrogate recovery was evaluated for acceptance by determining if the measured concentration fell within the acceptance limits of 60-120% recovery.

7.3.6 Aggregate Batches

To determine how many blanks, spikes, etc. to run during the Research analysis program, the sampling and analysis program was divided into Aggregate batches. Each Aggregate analytical batch consisted of 16 cleaned PUF cartridges. A solvent blank, method blank, matrix spike, and Aggregate batch certification were analyzed for every two Aggregate batches.

7.3.7 Aggregate Batch Certifications

To verify that each batch of clean $PM_{2.5}$ quartz glass filters and miniature PUF plugs were free of background contaminants prior to sampling, each batch had to be certified. For this certification, one set of PUF plugs and quartz glass filter were Scxhlet extracted, concentrated, and then analyzed by GC/MS. For the batch to be acceptable, each target PAH analyte had to be less than the detection limit requirements. In general, the following guidelines were used in determining whether a PUF plug batch was acceptable for sampling:

- Naphthalene	<500 ng/cartridge
- Other PAHs	<200 ng total/cartridge

Cartridges were considered clean for up to 30 days from date of certification when sealed in their containers.

7.3.8 Solvent Blanks

One solvent blank was used in the beginning of the Research analytical program to monitor for laboratory and solvent contamination. For the solvent blank analysis, a Soxhlet extraction and evaporation procedure was conducted without a PUF plug or filter. No contaminants were discovered in this solvent blank, so the use of solvent blanks was suspended after the first one. Solvent and instrument contamination were also monitored when conducting the Hi-vol PUF analyses.

7.3.9 Laboratory Method Blanks (LMB)

Lab method blanks were used to monitor for analytical artifacts. For each lab method blank analysis, an unused, certified PUF filter / plug assembly was carried though the same extraction and evaporation procedures as the samples. The LMB also contained the same amount of surrogate compounds and internal standards that were added to each sample. One lab method blank (quartz filter and PUF plugs) was collected for approximately every 16 samples.

7.3.10 Laboratory Control Spikes (LCS)

Lab control spikes were used to monitor the extraction efficiency of the SVOC target analytes. For each LCS, a certified PUF filter and plug were spiked with the target SVOC analytes (1 µg) and carried through the same extraction and evaporation procedures as the field samples. The LCS also contained the same amount of surrogate compounds and internal standards that were added to each sample. All target analytes spiked on the certified PUF cartridge were expected to have a 100 ± 20% recovery efficiency. One spike (quartz filter and PUF plugs) was collected for approximately every 16 samples.

7.3.11 GC/MS Continuing Calibration

To document that the GC/MS met tuning and standard mass spectral abundance criteria prior to sample analyses, 1µl of a 50 ng/µl solution of decafluorotriphenylphosphine (DFTPP) was analyzed at the start of each day of SVOC analyses. For acceptance, the GC/MS had to meet the mass spectral ion abundance criteria established for DFTPP. For each day that SVOC samples were analyzed, a continuing calibration standard was also analyzed to verify the initial calibration. SVOC standard number 3 (0.5 µg/ml) was used for the daily continuing calibration. For an acceptable continuing calibration, the percent difference between the measured target SVOC in standard number 3 and the mean value calculated during initial calibration had to be within ±30%.

Chapter 8 Results

8.1 Calculations

The temperatures and pressures used in calculating the concentrations of SVOCs in both the $PM_{2.5}$ PUF and the Hi-vol PUF samples were those logged by the BGI PQ200 during Research sampling. After determining the flow rate for both samplers during the 24 hour sample run, the concentrations of each analyte were calculated in parts per trillion by volume (pptv).

8.2 $PM_{2.5}$ SVOCs

Initially, SVOC analyses were conducted on individual $PM_{2.5}$ PUF samples for the first three $PM_{2.5}$ Research sample days (3/28/00, 4/9/00, and 4/21/00). After conducting the analyses, it was determined that the amount of sample collected by these individual runs was not sufficient to meet the minimum detection limits for many of the target analytes. Therefore, $PM_{2.5}$ PUF samples were aggregated starting on 5/3/01. Aggregate samples A, B, C, and D each contain six sample runs, while Aggregate E contains three. The dates per Aggregate samples are as follows:

Aggregate A: 5/3/00, 5/15/00, 5/27/00, 6/8/00, 7/2/00, and 7/14/00.
Aggregate B: 7/26/00, 8/7/00, 8/19/00, 8/31/00, 9/12/00, and 9/24/00.
Aggregate C: 10/6/00, 10/18/00, 10/30/00, 11/11/00, 11/23/00, and 12/5/00.
Aggregate D: 12/17/00, 12/29/00, 1/10/01, 1/22/01, 2/3/01, and 2/15/01.
Aggregate E: 2/27/01, 3/11/00, and 3/23/01.

Table 8-1 gives the levels of PAHs measured in the first three individual $PM_{2.5}$ PUF runs, and Table 8-2 gives the results of the Aggregated sample SVOC analyses. Tables 8-1 and 8-2 also present the SVOC concentrations measured from the Hi-vol PUF samples collected during these same time periods. Not surprisingly, the SVOCs measured in the $PM_{2.5}$ PUF samples are also detected in the Hi-vol PUF samples. Brook *et al.* (1997) has shown that $PM_{2.5}$ composes approximately 50% of the mass collected of PM_{10}, while PM_{10} has been measured to account for 44% of TSP.

For 3/28/00, 4/9/00, and 4/21/00, a 1:1 comparison is made between the $PM_{2.5}$ PUF and the Hi-vol PUF samples (Table 8-1). The blank cells in Table 8-1 show which SVOCs were not quantified in the original analysis. Starting on 5/3/00, $PM_{2.5}$ PUF samples were aggregated for comparisons with the Hi-vol PUF, with this data presented in Table 8-2. Figure 8-1 presents the $PM_{2.5}$ PUF and Hi-vol PUF comparison for the lighter molecular weight SVOCs (phenol – dibenzofuran), while Figure 8-2 presents the comparison for the heavier SVOCs (fluorene – benzo(a)pyrene).

Table 8-1: Research SVOC Comparison - $PM_{2.5}$ PUF vs. Hi-vol PUF (pptv).
3/28/00, 4/9/00, and 4/21/00 1:1 comparison.

Frenchtown	3/28/00		Diff	4/9/00		Diff	4/21/00		Diff
	$PM_{2.5}$ PUF	Hi-vol PUF		$PM_{2.5}$ PUF	Hi-vol PUF		$PM_{2.5}$ PUF	Hi-vol PUF	
Phenol									
2-methylphenol (o-cresol)									
4-methylphenol (p-cresol)									
2,4-dimethylphenol									
Naphthalene	0.00	0.00	**0.00**	0.00	0.00	**0.00**	0.00	0.02	**0.02**
2-methylnaphthalene				0.00	0.00				
Acenaphthylene	0.00	0.00	**0.00**	0.00	0.00	**0.00**	0.00	0.00	**0.00**
Acenaphthene	0.00	0.00	**0.00**	0.00	0.05	**0.05**	0.00	0.07	**0.07**
Dibenzofuran									
Fluorene	0.52	0.38	**-0.13**	0.78	0.46	**-0.33**	0.92	0.50	**-0.43**
Phenanthrene	1.26	1.13	**-0.13**	1.34	1.50	**0.16**	1.48	1.61	**0.13**
Anthracene	0.54	0.08	**-0.46**	0.61	0.14	**-0.47**	0.62	0.17	**-0.45**
Fluoranthene	0.69	0.21	**-0.48**	0.64	0.35	**-0.29**	0.65	0.27	**-0.38**
Pyrene	0.42	0.10	**-0.32**	0.48	0.20	**-0.29**	0.43	0.18	**-0.25**
Benzo(a)anthracene	0.00	0.00	**0.00**	0.00	0.07	**0.07**	0.00	0.06	**0.06**
Chrysene	0.00	0.02	**0.02**	0.00	0.02	**0.02**	0.00	0.03	**0.03**
Benzo(b)fluoranthene	0.51	0.03	**-0.48**	0.52	0.06	**-0.46**	0.52	0.05	**-0.47**
Benzo(k)fluoranthene	0.13	0.02	**-0.11**	0.13	0.02	**-0.11**	0.09	0.02	**-0.07**
Benzo(a)pyrene	0.00	0.00	**0.00**	0.00	0.06	**0.06**	0.00	0.06	**0.06**
Total	**4.07**	**1.97**	**-2.10**	**4.50**	**2.92**	**-1.58**	**4.71**	**3.05**	**-1.66**

Note: Blank cells indicate that target analyte was not quantified.

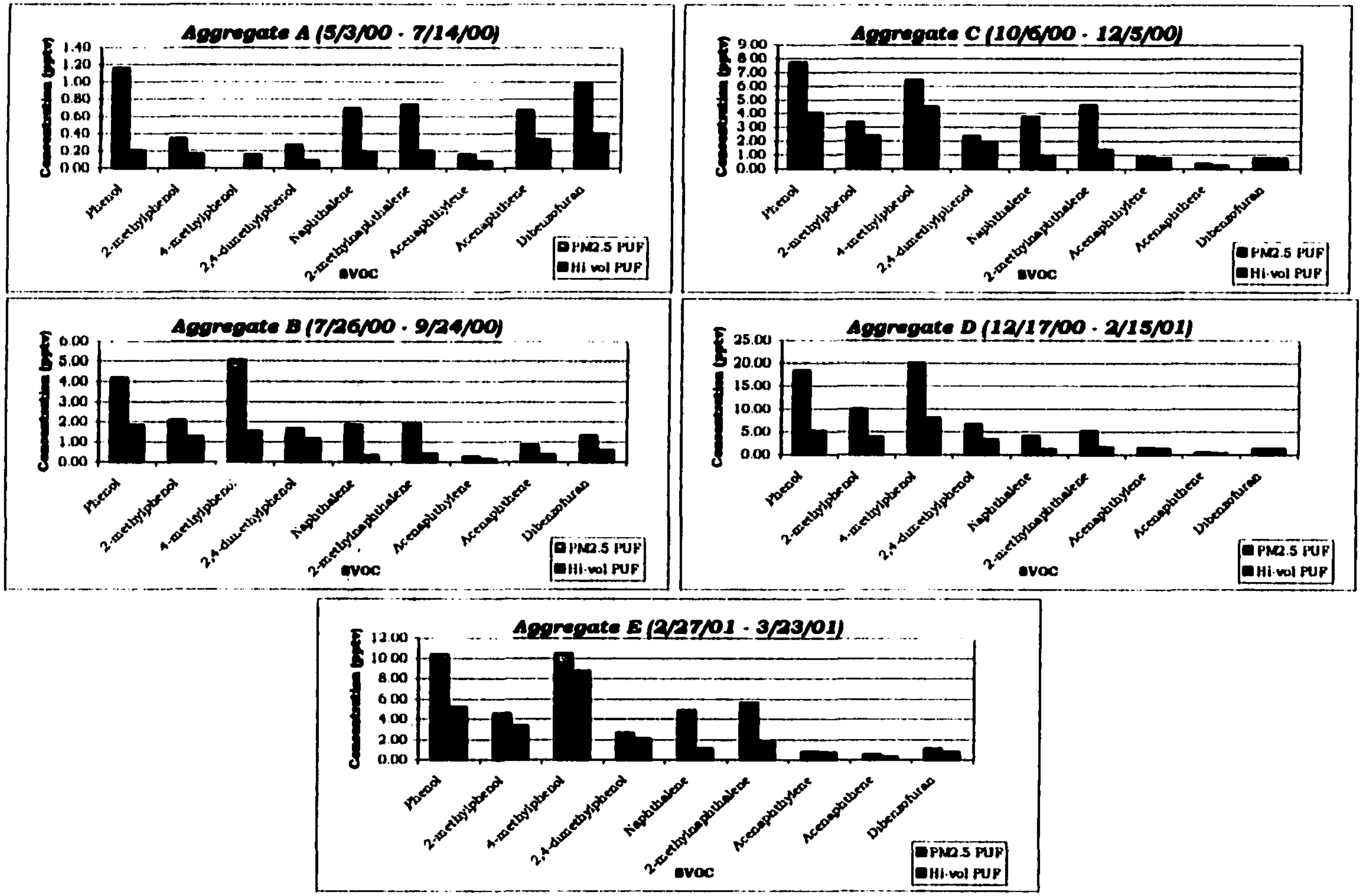
Table 8-2; Research SVOC Comparison - $PM_{2.5}$ PUF vs. Hi-vol PUF (pptv).

Aggregate PUF Comparison.

	Aggregate A			Aggregate B			Aggregate C			Aggregate D			Aggregate E		
Frenchtown	$PM_{2.5}$ PUF	Hi-vol PUF	Diff	$PM_{2.5}$ PUF	Hi-vol PUF	Diff	$PM_{2.5}$ PUF	Hi-vol PUF	Diff	$PM_{2.5}$ PUF	Hi-vol PUF	Diff	$PM_{2.5}$ PUF	Hi-vol PUF	Diff
Phenol	1.16	0.21	**-0.95**	4.19	1.82	**-2.37**	7.72	4.04	**-3.68**	18.57	5.24	-13.33	10.43	5.24	**-5.18**
2-methylphenol (o-cresol)	0.34	0.16	**-0.18**	2.08	1.27	**-0.81**	3.38	2.39	**-1.00**	10.05	3.89	**-6.16**	4.59	3.37	**-1.22**
4-methylphenol (p-cresol)	0.00	0.15	**0.15**	5.05	1.51	**-3.54**	6.45	4.50	**-1.95**	19.99	8.03	**-11.96**	10.45	8.75	**-1.70**
2,4-dimethylphenol	0.27	0.09	**-0.18**	1.65	1.16	**-0.49**	2.37	1.95	**-0.42**	6.71	3.38	**-3.33**	2.67	2.16	**-0.51**
Naphthalene	0.69	0.18	**-0.51**	1.83	0.34	**-1.48**	3.77	0.96	**-2.81**	4.14	1.18	**-2.96**	4.92	1.17	**-3.75**
2-methylnaphthalene	0.74	0.21	**-0.53**	1.91	0.42	**-1.48**	4.60	1.41	**-3.19**	5.21	1.71	**-3.51**	5.66	1.76	**-3.90**
Acenaphthylene	0.16	0.08	**-0.07**	0.27	0.18	**-0.09**	0.86	0.78	**-0.09**	1.57	1.30	**-0.27**	0.82	0.74	**-0.08**
Acenaphthene	0.67	0.33	**-0.34**	0.85	0.38	**-0.47**	0.37	0.26	**-0.11**	0.50	0.41	**-0.09**	0.54	0.35	**-0.19**
Dibenzofuran	0.98	0.41	**-0.57**	1.32	0.57	**-0.74**	0.78	0.77	**-0.01**	1.31	1.37	**0.06**	1.15	0.80	**-0.35**
Fluorene	1.04	0.51	**-0.53**	1.46	0.66	**-0.81**	0.63	0.67	**0.03**	0.96	1.22	**0.26**	0.92	0.69	**-0.23**
Phenanthrene	2.18	2.65	**0.47**	3.07	2.77	**-0.30**	1.05	1.68	**0.63**	2.36	3.07	**0.71**	1.83	1.98	**0.15**
Anthracene	0.29	0.30	**0.01**	0.35	0.33	**-0.02**	0.16	0.23	**0.06**	0.39	0.38	**-0.01**	0.35	0.25	**-0.10**
Fluoranthene	0.32	0.52	**0.20**	0.47	0.55	**0.07**	0.20	0.42	**0.22**	0.62	0.75	**0.13**	0.69	0.58	**-0.11**
Pyrene	0.20	0.30	**0.10**	0.30	0.35	**0.05**	0.18	0.36	**0.19**	0.54	0.63	**0.09**	0.53	0.50	**-0.03**
Benzo(a)anthracene	0.00	0.00	**0.00**	0.00	0.02	**0.02**	0.09	0.12	**0.03**	0.28	0.18	**-0.10**	0.33	0.16	**-0.17**
Chrysene	0.00	0.01	**0.01**	0.00	0.00	**0.00**	0.04	0.08	**0.04**	0.16	0.20	**0.04**	0.12	0.14	**0.02**
Benzo(b)fluoranthene	0.00	0.00	**0.00**	0.00	0.00	**0.00**	0.05	0.04	**-0.01**	0.13	0.10	**-0.03**	0.18	0.09	**-0.09**
Benzo(k)fluoranthene	0.00	0.00	**0.00**	0.00	0.00	**0.00**	0.02	0.04	**0.02**	0.15	0.10	**-0.04**	0.16	0.09	**-0.08**
Benzo(a)pyrene	0.00	0.00	**0.00**	0.00	0.00	**0.00**	0.05	0.05	**-0.01**	0.25	0.11	**-0.14**	0.37	0.14	**-0.23**
Total	**9.05**	**6.11**	**-2.93**	**24.80**	**12.34**	**-12.46**	**32.79**	**20.73**	**-12.06**	**73.90**	**33.23**	**-40.66**	**46.71**	**28.97**	**-17.74**

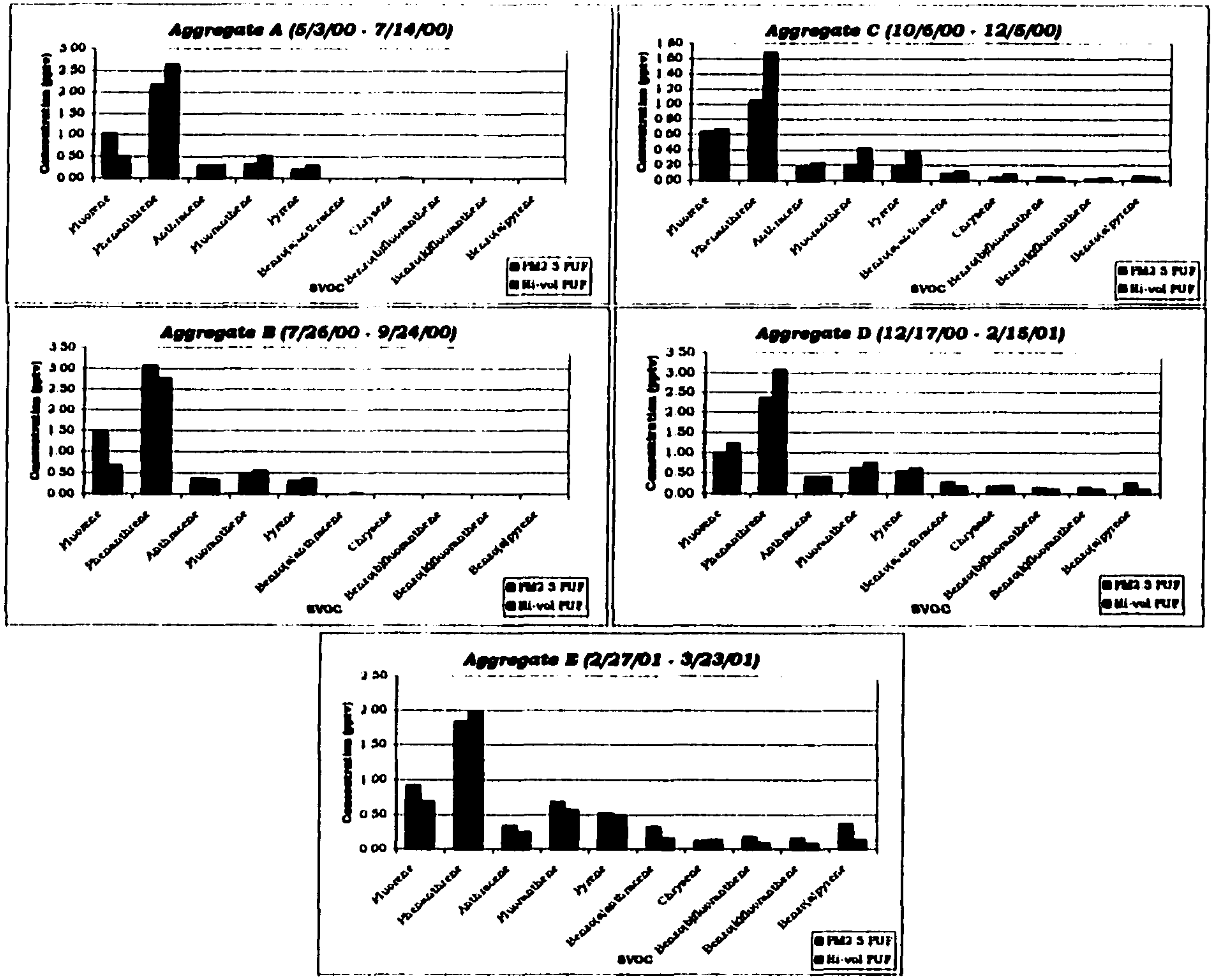
Aggregate A: 5/3/00, 5/15/00, 5/27/00, 6/8/00, 7/2/00, and 7/14/00.
Aggregate B: 7/26/00, 8/7/00, 8/19/00, 8/31/00, 9/12/00, and 9/24/00
Aggregate C: 10/6/00, 10/18/00, 10/30/00, 11/11/00, 11/23/00, and 12/5/00
Aggregate D: 12/17/00, 12/29/00, 1/10/01, 1/22/01, 2/3/01, and 2/15/01.
Aggregate E: 2/27/01, 3/11/00, and 3/23/01.

Figure 8-1: Research SVOC Comparison – $PM_{2.5}$ PUF vs. Hi-vol PUF (pptv) – Lighter SVOCs. Phenol - Dibenzofuran.



Note: Above charts have different scales on y-axis (pptv).

Figure 8-2: Research SVOC Comparison – $PM_{2.5}$ PUF vs. Hi-vol PUF (pptv) – Heavier SVOCs, Fluorene - Benzo(a)pyrene.



Note: Above charts have different scales on y-axis (pptv).

Chapter 9 Discussion

Table 8.1 presents the first three $PM_{2.5}$ PUF sample runs (3/28/00, 4/9/00, and 4/21/00) compared with the Hi-vol PUF sample runs for those days. In looking at the results of these analyses, very little sample was collected. This is true for both the $PM_{2.5}$ PUF samples and for the Hi-vol PUF samples. In fact, naphthalene, acenaphthylene, acenaphthene, benzo(a)anthracene, chrysene, and benzo(a)pyrene were not even detected in the $PM_{2.5}$ PUF, compared with detectable (but low) amounts in the Hi-vol PUF sample. $PM_{2.5}$ levels measured by the Montana DEQ at Boyd Park on these days showed low ambient concentrations of 1.5 $\mu g/m^3$, 7.5 $\mu g/m^3$, and 5.3 $\mu g/m^3$ for 3/28/00, 4/9/00, and 4/21/00, respectively. The compounds that were detected in the $PM_{2.5}$ PUF samples were at greater concentrations than the corresponding Hi-vol samples for almost every analyte, giving the $PM_{2.5}$ PUF more total mass calculated per each of the three runs compared to the Hi-vol PUF from the same days - even with 12.5 times less sample volume collected than the $PM_{2.5}$ PUF. The $PM_{2.5}$ PUF collects ~24,000 Liters of air (per 24 hour sample) compared to the Hi-vol PUF at 300,000 Liters of air collected (per 24 hour sample).

Starting on 5/3/00, $PM_{2.5}$ PUF samples were aggregated in order to collect more sample for the SVOC analysis. Table 8-2 and Figures 8-1 and 8-2 present the analytical results for Aggregates A – E and the corresponding Hi-vol PUF samples taken during these same time periods. Here, the amount of flow collected for each $PM_{2.5}$ PUF sample run is six times what it was in the first three runs, providing each Aggregate (with the exception of Aggregate E) with ~144,000 Liters of sample, which is roughly half of the volume collected by each Hi-vol sample run. The measured SVOC concentrations for the six samples which compose an Aggregate sample are compared with the average SVOC concentrations for the six Hi-vol PUF samples taken over the same time periods. The results show that even with half of the amount of volume collected, the SVOC total mass collected by the $PM_{2.5}$ PUF is consistently higher compared to the average SVOCs that were collected by the Hi-vol PUF samples.

The differences between analyte concentrations are also calculated in each table per sample comparison. For Table 8-1, it is hard to establish trends because the SVOC concentrations are so low. However, in the Aggregates comparison Table 8-2, the lighter compounds (phenol through dibenzofuran) have mostly negative differences, meaning that there was more mass per analyte on the $PM_{2.5}$ PUF compared to the Hi-vol PUF. This is illustrated in Figure 8-1. Fluorene through anthracene (Figure 8-2) have a combination of positive and negatives, and fluoranthene through chrysene have positive values (more mass on the Hi-Vol PUF). The heavy PAHs (benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(a)pyrene) are either not detected or have mostly negative values.

Gas adsorption and particle volatilization both compete during $PM_{2.5}$ mass and organic carbon measurements, and it is not yet known which ones dominate in a particular environment. Volatilization of individual semi-volatile organic species depends on both temperature and filter face velocity due to flow rate. Eatough *et al.* (1989) and Tang *et al.* (1994) found that desorption of organic gases from particles on the front quartz-fiber filter was the dominant sampling artifact (negative bias). Chow *et al.* (1996) found that organic carbon concentrations on the backup filter were frequently 50% or more of the front quartz fiber filter concentrations in a San Joaquin Valley study.

Others (Turpin *et al.* 1994; Cui *et al.*, 1997) have found that the adsorption of organic gases by quartz fiber filters (positive bias) was the prevalent interferent for mass and organic carbon concentrations, with adsorbed organic gases 50% of the organic carbon measured in a study in southern California. Chow and Egami (1997) reported that the extent of gaseous organic carbon adsorption was dependent upon the source mixture in the atmosphere. In using two filters in series, the ratio of backup to front organic carbon becomes fairly constant at $PM_{2.5}$ concentrations greater than 30 μg/m^3, but the ratio varies and is frequently higher at lower $PM_{2.5}$ concentrations. This suggests the adsorbed gas reached equilibrium with the particles and adsorption sites as the front filter became saturated (Turpin *et al.*, 1994). Similar relationships were also found during the winter in northwestern Colorado (Watson *et al.*, 1998).

The volatility of the lighter SVOC compounds make the Hi-vol method less efficient in sampling for these compounds compared to the $PM_{2.5}$ PUF. Also, the higher flow rates seem to have a stripping effect on the compounds. This is observed in the lighter compounds in Table 8-2 and Figure 8-1, where Aggregate samples at half the sample volume have more analyte mass than the Hi-vol PUF samples taken over the same time periods. Loss of SVOCs during sampling has proved to be a problem during high-volume sampling with fiber filters (Wang and John, 1988), and is prone to sampling losses (Van Vaeck *et al.*, 1979; Van Vaeck *et al.*, 1984). The filter face velocity is the volumetric flow rate divided by the exposed areas of the filter. Face velocity experiments have shown that measurements of carbon from low volume sampling yield higher concentrations than high volume sampling (EPA, 2001), especially in quartz fiber filter experiments where measured carbon exhibited a significant decrease with increasing filter face velocity (McDow and Huntzicker, 1990). Miguel and Andrade (1986) also observed similar face velocity dependence in the filter collection of two PAHs normally considered to be in the particulate phase.

Figure 8-3 presents a plot of the SVOC analyte total masses for the $PM_{2.5}$ PUF versus the Hi-vol PUF. The highest SVOC levels measured for both the $PM_{2.5}$ PUF and Hi-vol PUF were collected during Aggregate D, which is 12/17/00 – 2/15/01. This was during the winter when SVOC levels were at their highest. These data are then plotted against DEQ $PM_{2.5}$ mass data (Figure 8-4) collected at Boyd Park and the Missoula Health Department roof on the same days that the PUF samples were collected. Results show that the highest $PM_{2.5}$ mass levels also occurred during 12/17/00 – 2/15/01. In fact, the SVOC mass totals (pptv) have the same overall trend as the levels of airborne $PM_{2.5}$ ($\mu g/m^3$) for these sample days, displaying the relationship between $PM_{2.5}$ and SVOCs.

Figure 8-3:

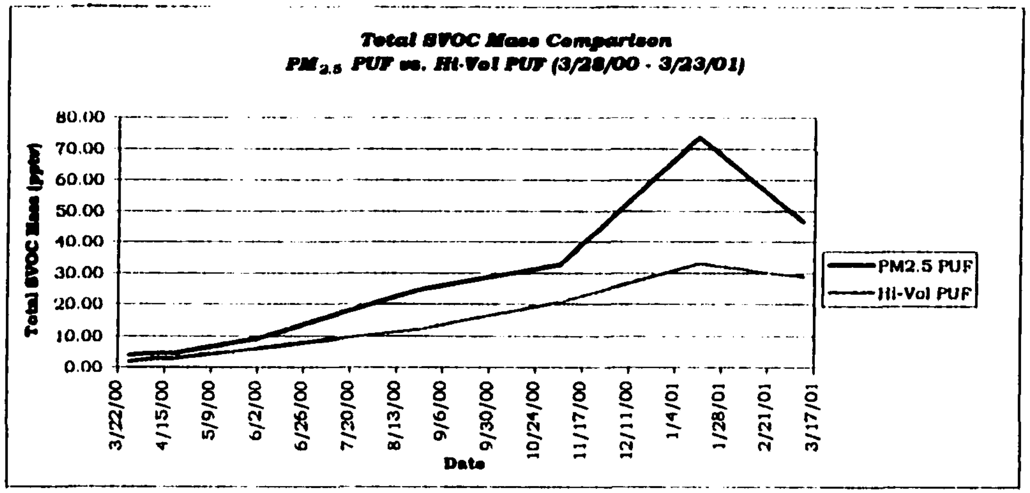
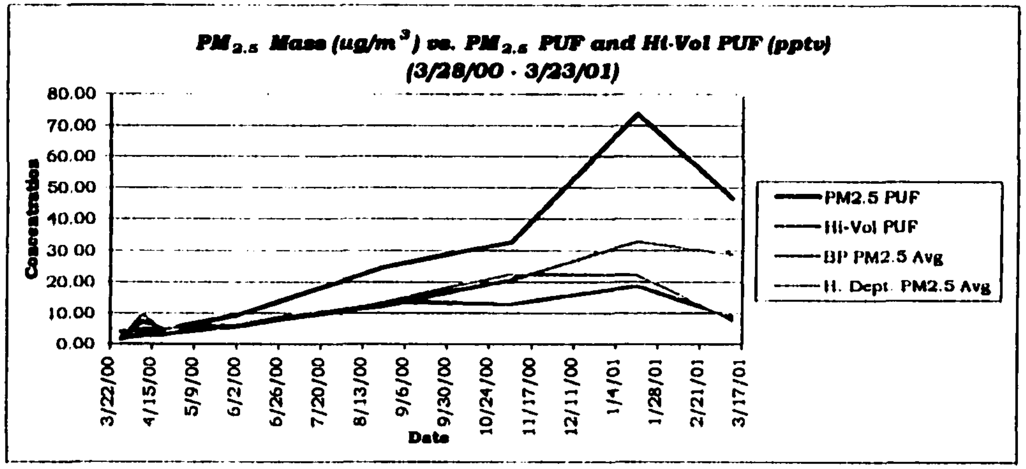


Figure 8-4:



Note: y-axis units are ug/m^3 for $PM_{2.5}$ Avg Data, and pptv for PUF data.

9.1 QAQC Results – Research PM$_{2.5}$ Sampling and Analyses

9.1.1 Field and Lab Surrogates

Field and lab surrogates were spiked into each PUF sample to monitor for sampling and analysis efficiencies. Table 8-3 presents the percent recovery results for the field and lab surrogates for samples collected on 3/28/00, 4/9/00, and 4/21/00, as well as Aggregate Samples A – E.

Table 8-3: Percent recovery results for Research Sampling field and lab surrogates.

Field Surrogates	**3/28/00**	**4/9/00**	**4/21/00**	**Average**
D$_{10}$-Fluoranthene	None	61%	71%	66%
D$_{12}$-Benzo(a)pyrene	None	94%	99%	97%
Lab Surrogates				
D$_{10}$-Fluorene	105%	50%	56%	70%
D$_{10}$-Pyrene	74%	45%	51%	57%

Field Surrogates	**Aggregate A**	**Aggregate B**	**Aggregate C**	**Aggregate D**	**Aggregate E**	**Average**
D$_{10}$-Fluoranthene	118%	93%	93%	117%	None	105%
D$_{12}$-Benzo(a)pyrene	112%	114%	87%	70%	None	96%
Lab Surrogates						
D$_{10}$-Fluorene	71%	83%	87%	110%	None	88%
D$_{10}$-Pyrene	71%	77%	70%	83%	None	75%

The recovery efficiencies for the field and lab surrogates were generally well within the 60-120% range. The lab surrogate recoveries were low for the individual runs (4/9/00 and 4/21/00) due to a higher helium flow rate used during the GC/MS analysis. PUF field blanks were not included in the field surrogate calculations because they were not actually used for sampling.

9.1.2 $PM_{2.5}$ Filter Blanks

Field blanks were collected to monitor for sampling artifacts. Results showed negligible concentrations of contamination throughout the Research sampling and analysis programs.

9.1.3 $PM_{2.5}$ Sampler Verification, Calibration, and Quarterly Audits

During the yearlong sampling program, the $PM_{2.5}$ sampler (Stevie) was maintained to ensure proper collection of sample. This included leak checks, flow verifications, ambient and filter temperature verifications, and pressure verifications. Temperature and pressure sensors were stable throughout the year, and did not require recalibration. Only the flow sensors had to be recalibrated due to ambient temperature fluctuations from season to season. The Frenchtown $PM_{2.5}$ sampler passed all of the audit requirements with the exception of flow. A full discussion of the quarterly audits is given is section 4.7.2 of this document.

9.1.4 PUF Batches

For each batch of PUF cartridges, a PUF batch certification, solvent blank, laboratory method blank (LMB), and laboratory control spike (LCS) were analyzed. Target analytes were generally not detected in the blanks. For the LCS, two clean, unused, and certified Research PUF plugs were spiked with the target analytes (1 μg) and carried through the extraction process. Table 8-4 presents the average percent recoveries for the SVOC analytes from the $PM_{2.5}$ PUF spikes.

Table 8-4: Percent recovery results for $PM_{2.5}$ PUF spikes.

SVOC Analyte	**% Recovery**
Phenol	**41%**
2-methylphenol	63%
4-methylphenol	73%
2,4-dimethylphenol	68%
Naphthalene	61%
2-methylnapthalene	63%
Acenaphthylene	65%
Acenaphthene	63%
Dibenzofuran	66%
Fluorene	65%
Phenanthrene	73%
Anthracene	72%
Fluoranthene	92%
Pyrene	92%
Benzo[a]anthracene	116%
Chrysene	76%
Benzo[b]fluoranthene	100%
Benzo[k]fluoranthene	99%
Benzo[a]pyrene	101%

Only phenol showed a percent recovery below 60% due to its volatility. Overall, the spiked efficiencies were well within the desired range of 60-120%.

9.1.5 GC/MS Continuing Calibration

Daily continuing calibration results were generally well within the desired range of ±30%. Please see Table 4-13 in Section 4.8.5 for results.

Chapter 10 Conclusions

In Part II of this program, a trade off between Hi-vol PUF sampling and $PM_{2.5}$ PUF sampling was revealed. Even though each Hi-vol sample run provides enough material on which to conduct an SVOC analysis on, the results of this analysis may not accurately quantify the levels of the lighter molecular weight SVOCs in the airshed. Part II of this program investigated the SVOC contribution to the $PM_{2.5}$ fraction in the Missoula Valley by using a modified FRM sampler. A method comparison was also made between sampling for SVOCs using the modified $PM_{2.5}$ sampler and in using an EPA Method TO-13A Hi-volume PUF sampler. Results showed that the sum of the individual sample runs that compose an Aggregate $PM_{2.5}$ PUF sample (~144,000 Liters of sample) measured more of the lighter SVOCs compared to the SVOC analyte averages of the six Hi-vol PUF runs collected over the same time period (~300,000 Liters of sample). This is most likely the result of the higher flows through the Hi-vol PUF which "strip" the lighter organics from the surface of the filter. However, the use of a Hi-vol PUF sampler allows for the collection of ~300,000 Liters of sample during one episode in comparison to having to aggregate the $PM_{2.5}$ samples together in order to meet analytical detection limits. The SVOC levels measured with the modified $PM_{2.5}$ sampler also tracked well with the ambient $PM_{2.5}$ as measured by the Montana DEQ on the same sample days, displaying the relationship between $PM_{2.5}$ and PAHs.

This research sampling is important because it used a modified FRM sampler to investigate the organic makeup of the fine fraction so that a more accurate accounting of the mass and risk of airborne particulates could be established. FRM samplers are normally used in $PM_{2.5}$ compliance sampling as mandated by the EPA. The results of this study should also make it possible to develop performance criteria for organic carbon samplers, including criteria for evaluating the capacity and efficiency of the PUF cartridges and $PM_{2.5}$ quartz filter. The extent to which SVOCs are lost from particles during $PM_{2.5}$ sampling is not well known. However, it can be expected that samplers will substantially undermeasure $PM_{2.5}$ in any environment where a significant concentration of SVOC material is present. Traditional single-filter particle mass measurement methods cannot accurately determine particulate SVOC material, and there is a significant negative bias if only a single filter is used to determine particulate carbonaceous material (Pang *et al.*, 2001).

Part III

AIR SAMPLING STUDY OF THE 2000 MONTANA WILDFIRE SEASON

Chapter 11 Introduction

During the summer of 2000, record-low fuel moisture and persistently hot, dry weather caused drought conditions throughout much of the West. The fire season began early, became intense, and lasted well into the fall. Until the end of August, fire activity was focused mostly in Idaho and Montana where more than half of the nation's fires were burning. Several wildfires were burning in close proximity to Missoula during the summer of 2000. Approximately 60 miles to the south, the Sula Complex, Valley Complex, and the Blodgett Canyon fires burned in the Bitterroot mountains. About an hour to the west, the Flat Creek Complex, Clear Creek, and Ninemile Divide Complex fires burned. Frequently, smoke moved downwind directly into the Missoula Valley filling it up, where accumulations of smoke led to nine Stage 1 and five Stage 2 air alerts called in Missoula. The local Air Pollution Control Board had to enact an emergency order to help industry avoid unnecessary shut downs and schools to adjust outdoor athletic activities. Just before Labor Day, rain, cooler temperatures, and higher humidity finally came to the Northern Rockies ending the 2000 wildfire season.

The statistics from the 2000 wildfire season are staggering. From January through the end of October, wildland fires burned 6,966,995 acres across the United States. In Montana and Idaho alone, more than 4000 fires burned an estimated 2.2 million acres. With fire fighting assistance from Australia, New Zealand, Canada, Mexico, and six battalions of the military, fire suppression costs through October totaled an estimated $877,847,296 (NIFC Home Page, 1999; Montana Fires Home Page, 1999).

11.1 Smoke Related Air Pollution

Smoke is composed of a complex mixture of particles, liquids, and gaseous compounds. These include carbon monoxide, hydrocarbons, oxygenates, particulate matter, nitrogen oxides (NO_x), sulfur oxides (SO_x), and oxidants (including small amounts of ozone). Carbon monoxide (CO) is second in abundance to carbon dioxide (CO_2) and water vapor, and the most abundant air pollutant emitted from burning wildland fuels (Ward *et al.*, 1993). Coupled with carbon dioxide (CO_2) and methane (CH_4), CO emissions from fires have been found to be a significant source of greenhouse gases (Crutzen and Andreae, 1990). Hydrocarbons, including ethylene, alkynes, aldehydes, furans, and carboxylic acids, are products of incomplete combustion. Oxygenated species, such as formaldehyde (CH_2O), methanol (CH_3OH), acetic acid (CH_3COOH), formic acid (HCOOH), hydroxyacetaldehyde ($HOCH_2CHO$), and phenol (C_6H_5OH) have been measured by Fourier transform infrared (FTIR) spectroscopy (Griffith *et al.*, 1991; Yokelson^1 *et al.*, 1996; Yokelson^2, 1996; Yokelson, 1997; Yokelson, 1999; Goode *et al.*, 1999; Goode *et al.*, 2000). Particulate matter, comprised of a complex mixture of soot, tars, and volatile organic substances, is another major component of smoke (Ryan and McMahon, 1976). NO_x and SO_x are found in smaller concentrations. Some NO_x forms at lower temperatures, but the amount of NO_x produced depends primarily on the nitrogen content of the fuels burned by the fire (Hao *et al.*, 1991). SO_x are usually produced in negligible quantities because forest fuels generally have a low sulfur content (Ward *et al.*, 1993).

Fires also emit a large number of SVOCs which are partitioned between the gaseous and liquid or solid phase at ambient temperatures. PAHs can condense or be adsorbed onto the surface of fine particles. They are assembled from carbon fragments into larger structures in low-oxygen environments, such as occurs inside the flame envelope in the fuel-rich region of the flame structure (Ward, 1997).

11.2 Smoke Research

Most of the things known about smoke come from either research conducted with prescribed burns or burns conducted in a controlled laboratory environment. Because of the logistics and wide variety of compounds emitted from forest fires, it is very difficult to conduct a comprehensive study of the pollutants emitted from wildfires. Even though samples were collected during the fire season, $PM_{2.5}$ speciated samples were collected only every 12 days. A more comprehensive study would have collected samples every 3 days or more. Because of the breadth of analyses performed on each sample, a shorter sampling interval was not feasible. It is also difficult to determine accurate concentrations of oxygenates from fires without specialized sampling equipment. Some of these compounds when captured on solid media often transform from reactive species to more stable forms (Griffith *et al.*, 1991; Yokelson[1] *et al.*, 1996; Yokelson[2], 1996; Yokelson, 1997; Yokelson, 1999; Goode *et al.*, 1999; Goode *et al.*, 2000).

Chapter 12 Experimental Methods

All methods of sampling, analysis, and QA/QC for measuring $PM_{2.5}$, SVOCs, and VOCs are described in Part I.

12.1 Montana DEQ $PM_{2.5}$ Data

In addition to $PM_{2.5}$ data collected during this sampling program, Montana DEQ $PM_{2.5}$ compliance data for Missoula (Boyd Park and the Missoula City/County Health Department) and Hamilton is presented here. Data were collected at the three DEQ sites every three days throughout the fire season.

Chapter 13 Results and Discussion

13.1 $PM_{2.5}$ Mass

$PM_{2.5}$ levels reached extreme heights during the 2000 wildfire season in western Montana. Figure 13.1 presents the Montana DEQ $PM_{2.5}$ data for Missoula and Hamilton because they possess a higher temporal resolution (3-days) than the 2000/2001 CMB Sampling Program (12 days). The three traces correspond to the two Missoula sites and the solitary Hamilton site. For the entire month of August, $PM_{2.5}$ concentrations were above the annual $PM_{2.5}$ ambient air quality standard of 15 $\mu g/m^3$. On only two occasions (on days that collected samples) did the Missoula sites exceed the 24 hour $PM_{2.5}$ standard of 65 $\mu g/m^3$. On 8/10/00, Boyd Park collected 179.13 $\mu g/m^3$ and the Health Department collected 165.53 $\mu g/m^3$. And on 8/22/00, Boyd Park and the Missoula Health Department collected 82.72 and 90.64 $\mu g/m^3$, respectively. In Hamilton, immediately adjacent to the Bitterroot fire complexes, the concentrations were much higher. In fact, the concentrations were so high that on several occasions the filters became clogged with so much material that the $PM_{2.5}$ sampler shut down. The days in which the sampler was overloaded are indicated on Figure 13.1 by "RL", which stands for run length (hrs:min). For the entire month of August, the $PM_{2.5}$ concentrations were above both the daily and annual $PM_{2.5}$ ambient air quality standards in Hamilton.

Table 13.1 presents $PM_{2.5}$ levels as measured by the 2000/2001 CMB Sampling Program. Although the 8/13/00 and 8/25/00 samples show elevated levels of $PM_{2.5}$, these sample days were not the "high smoke" days experienced during other parts of August. Figure 13.2 presents a picture of $PM_{2.5}$ quartz glass Research sample filters that were collected every 12 days during the summer of 2000. From left to right, the sample dates are 7/26/00, 8/7/00, 8/19/00, 8/31/00, 9/12/00, and 9/24/00. The bottom picture is a closeup of the 8/31/00 filter sample.

Table 13.1: $PM_{2.5}$ mass averages ($\mu g/m^3$) for Boyd Park and Frenchtown during the Summer (6/26/00 – 9/18/00).

	Summer (6/26/00 – 9/18/00)	2000 Fire Season (8/13/00 – 8/25/00)	Summer (Excluding Fire Season)
Boyd Park	15.0	39.9	6.7
Frenchtown	14.7	42.2	5.6

Figure 13-1: Montana DEQ $PM_{2.5}$ Data for Missoula and Hamilton Summer (7/8/00 - 9/30/00)

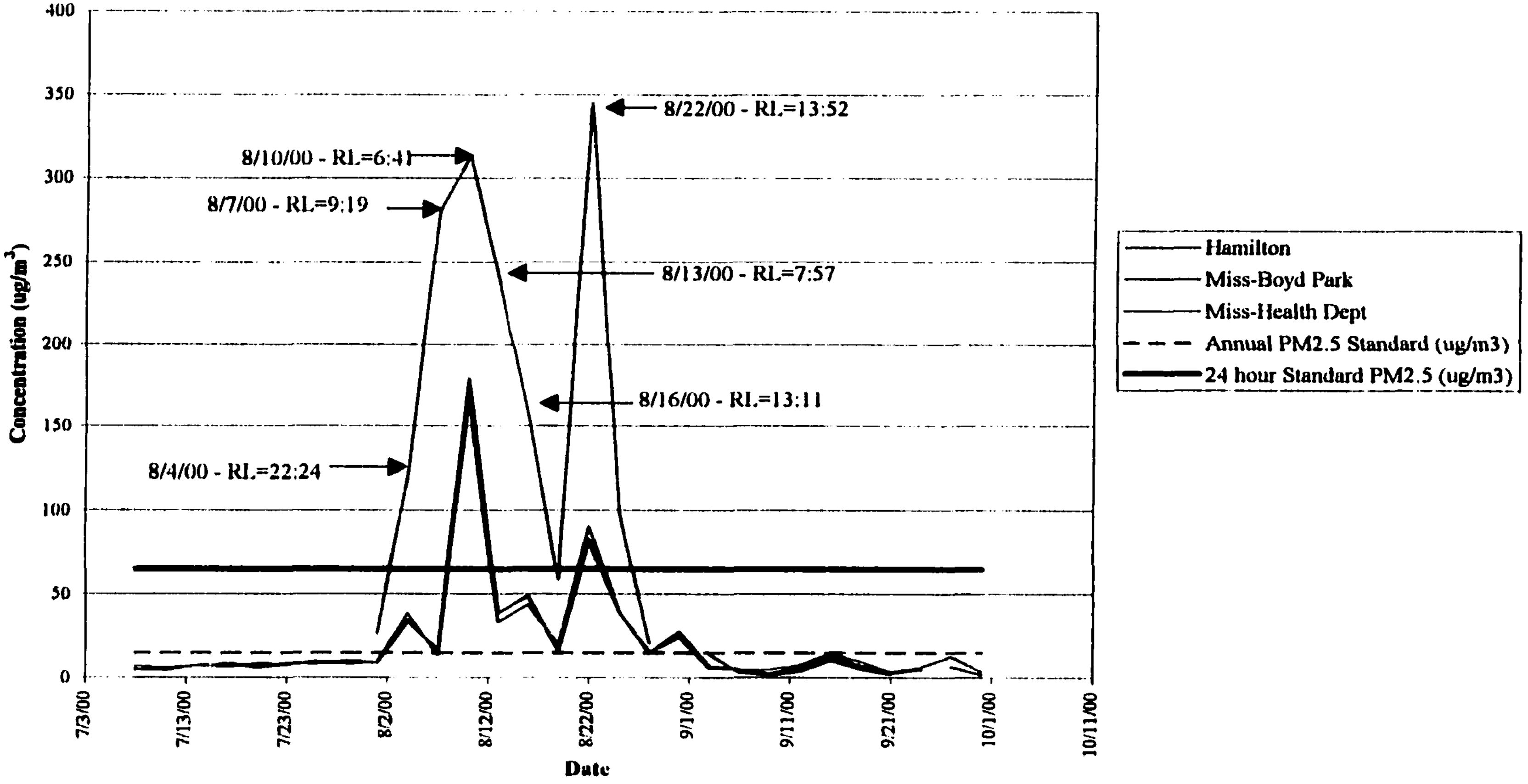
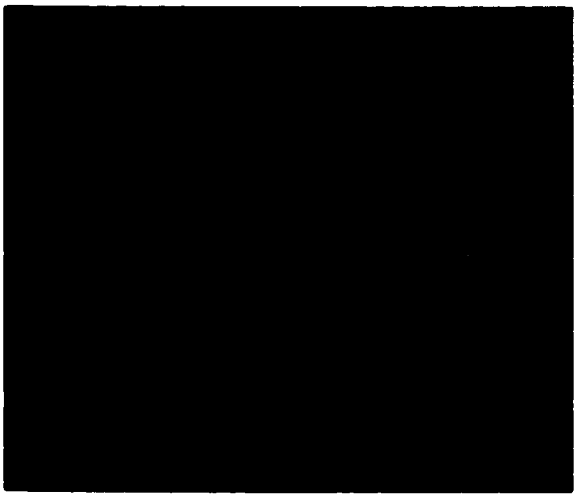
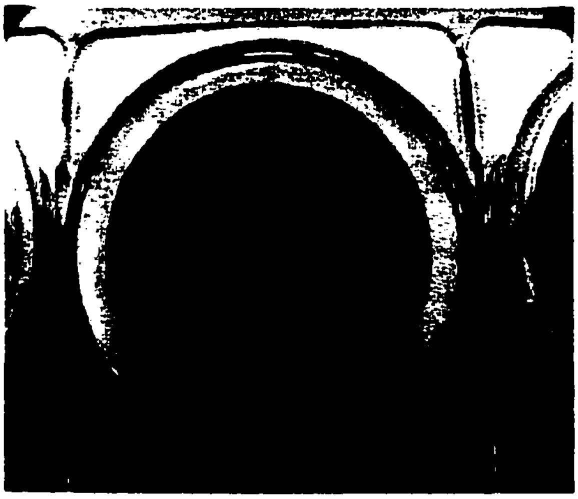


Figure 13.2: PM$_{2.5}$ quartz glass Research samples collected every 12 days during the summer of 2000 in Missoula, Montana.

From left to right, the sample dates are 7/26/00, 8/7/00, 8/19/00, 8/31/00, 9/12/00, and 9/24/00.



Close-up of the 8/31/00 filter sample.



13.2 Organic Carbon (OC), Elemental Carbon (EC), and Total Carbon (TC)

Table 13.2: OC, EC, and TC averages (µg/m^3) for Boyd Park and Frenchtown during the Summer (6/26/00 – 9/18/00).

	Summer (6/26/00 – 9/18/00)	**2000 Fire Season (8/13/00, 8/25/00)**	**Summer (Excluding Fire Season)**
Boyd Park			
OC	7.04	18.02	3.38
EC	2.02	5.18	0.97
TC	9.06	23.19	4.35
Frenchtown			
OC	6.72	18.77	2.71
EC	2.03	5.72	0.81
TC	8.76	24.49	3.51

All forms of carbon showed a 5- to 7-fold increase in $PM_{2.5}$ filter samples during the active fire season. Table 13-2 and Figure 13-3 present the combined results of Boyd Park (BP) and Frenchtown (Fr) concentrations before, during, and after the fire season. Before the fire season, EC averaged approximately 1.00 µg/m^3, OC averaged 3.82 µg/m^3, and TC averaged approximately 4.77 µg/m^3 at Boyd Park. At Frenchtown, EC measured about 0.78 µg/m^3, with OC and TC averaging 3.02 µg/m^3 and 3.80 µg/m^3 before the fire season. On 8/13/00 and 8/25/00, EC concentrations averaged 5.18 µg/m^3 at Boyd Park and 5.72 µg/m^3 at Frenchtown. OC and TC averages on these dates were 18.02 and 23.19 µg/m^3 at Boyd Park, and 18.77 and 24.49 µg/m^3 at Frenchtown. By the end of August, EC, OC, and TC values dropped below their pre-fire season levels.

The average $PM_{2.5}$ collected on 8/13/00 and 8/25/00 was composed of 46% OC and 13% EC at Boyd Park, while the Frenchtown $PM_{2.5}$ was composed of 44% OC and

14% EC. Figure 13-4 presents the $PM_{2.5}$ average compositions for summer (including the fire season), the fire season itself (8/13/00 and 8/25/00), and the summer average without the fire season. Fire research has shown that smoke fine particles consist of 60-70% OC (Ward and Hardy, 1989), 2-15% EC, with the remainder inorganic ash material (Ward and Core, 1984).

Figure 13-3:

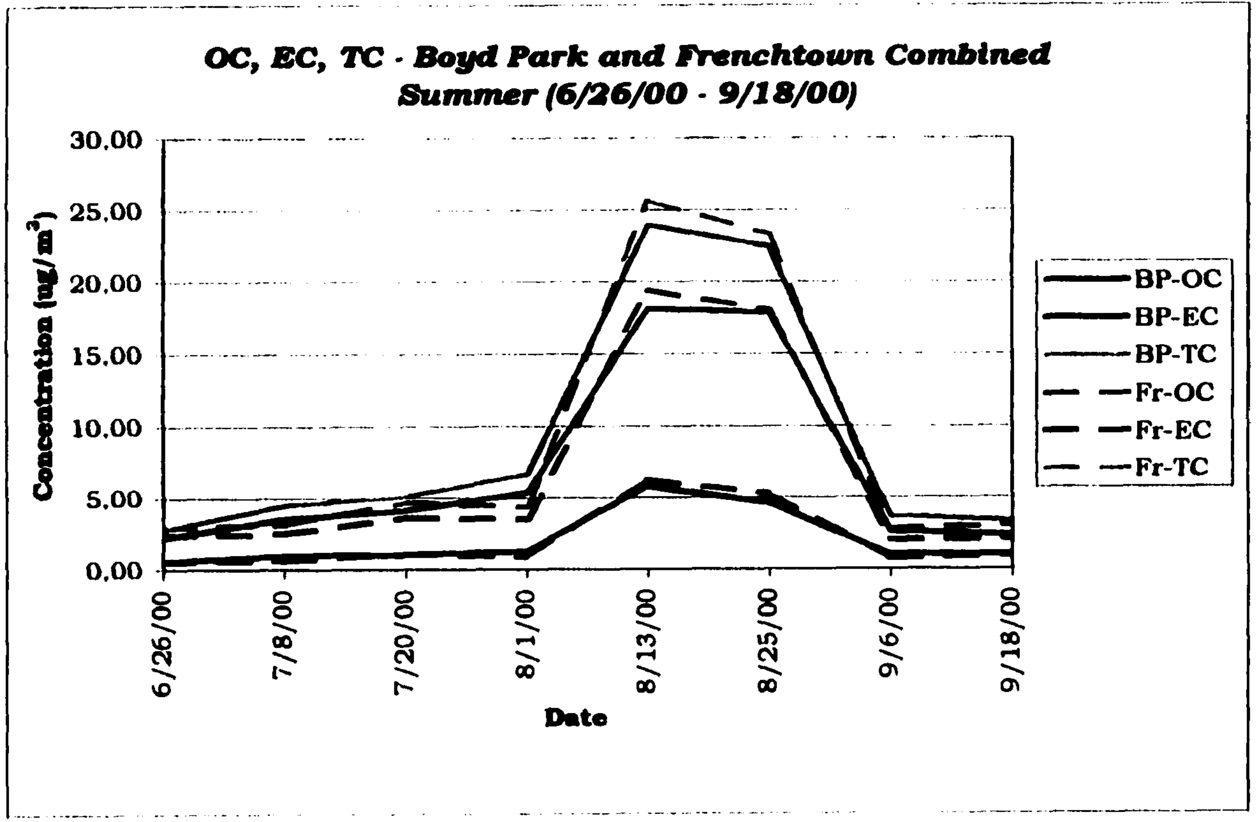
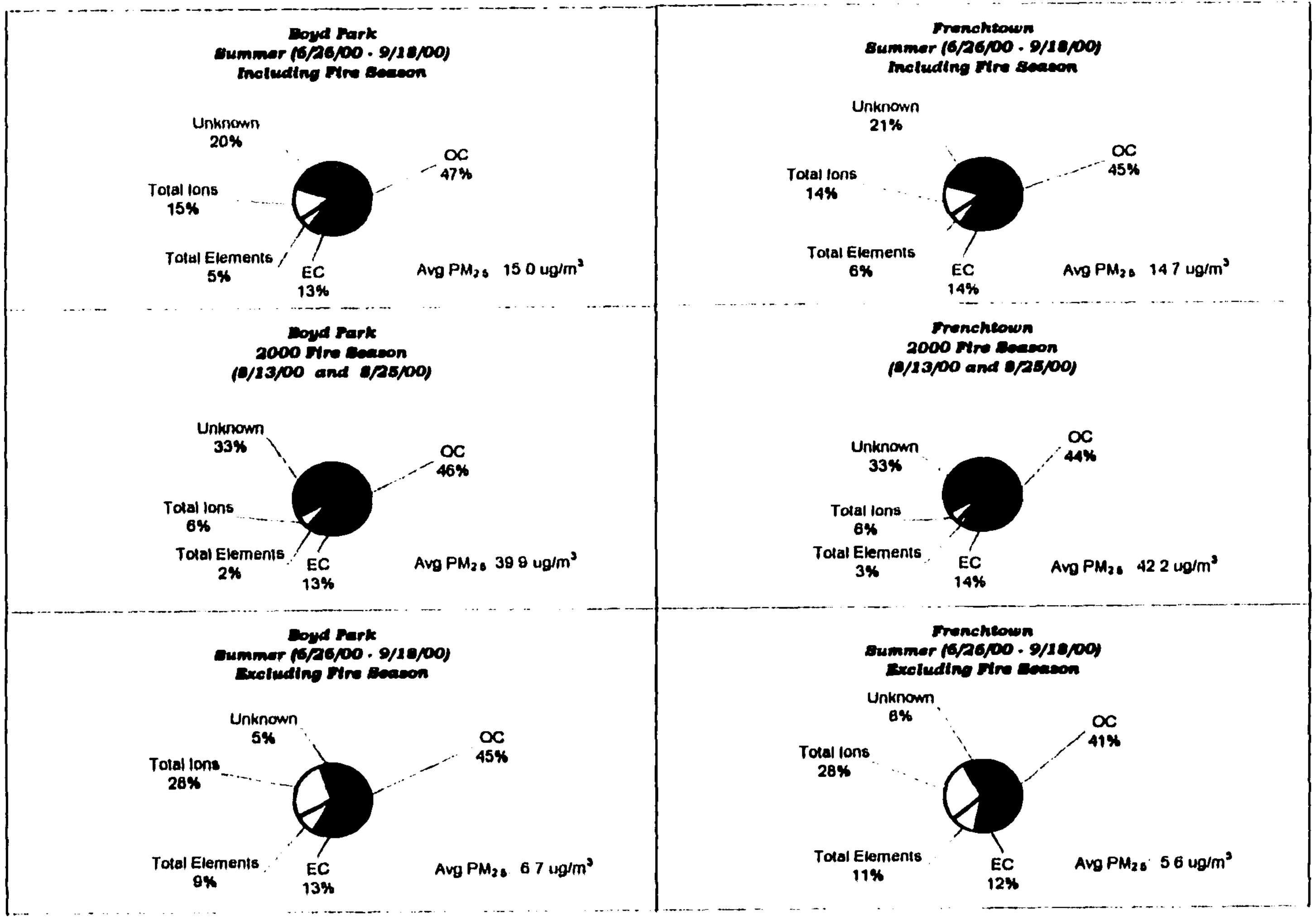

OC, EC, TC - Boyd Park and Frenchtown Combined
Summer (6/26/00 - 9/18/00)
Concentration (ug/m^3)
30.00
25.00
20.00
15.00
10.00
5.00
0.00
6/26/00
7/8/00
7/20/00
8/1/00
8/13/00
8/25/00
9/6/00
9/18/00
Date
BP-OC
BP-EC
BP-TC
Fr-OC
Fr-EC
Fr-TC

Figure 13-4: $PM_{2.5}$ Average Compositions for Boyd Park and Frenchtown.



13.3 Trace Elements

Table 13.3: Trace elemental averages (ug/m^3) for Boyd Park and Frenchtown during the Summer (6/26/00 – 9/18/00).

Boyd Park	Summer (6/26/00 – 9/18/00)	2000 Fire Season (8/13/00, 8/25/00)	Summer (Excluding Fire Season)	Frenchtown	Summer (6/26/00 9/18/00)	2000 Fire Season (8/13/00 8/25/00)	Summer (Excluding Fire Season)
Aluminum, Al[1]	0.022	0.019	0.023		0.043	0.061	0.037
Silicon, Si[1]	0.111	0.118	0.109		0.165	0.243	0.139
Sulfur, S[2]	0.319	0.318	0.320		0.304	0.332	0.295
Chlorine, Cl[3]	0.006	0.016	0.002		0.004	0.013	0.001
Potassium, K[3]	0.141	0.322	0.080		0.120	0.291	0.062
Calcium, Ca[1]	0.050	0.075	0.042		0.043	0.069	0.034
Titanium, Ti[4]	0.003	0.003	0.003		0.004	0.006	0.003
Iron, Fe[1]	0.041	0.043	0.040		0.087	0.110	0.079
Copper, Cu[1]	0.004	0.003	0.004		0.003	0.002	0.004
Zinc, Zn[3]	0.004	0.006	0.003		0.003	0.007	0.002
Bromine, Br[4]	0.002	0.004	0.001		0.002	0.003	0.001
Palladium, Pd[4]	0.002	0.004	0.001		0.002	0.004	0.001
Silver, Ag[4]	0.001	0.002	0.001		0.003	0.004	0.003
Lead, Pb[4]	0.003	0.004	0.003		0.002	0.004	0.002

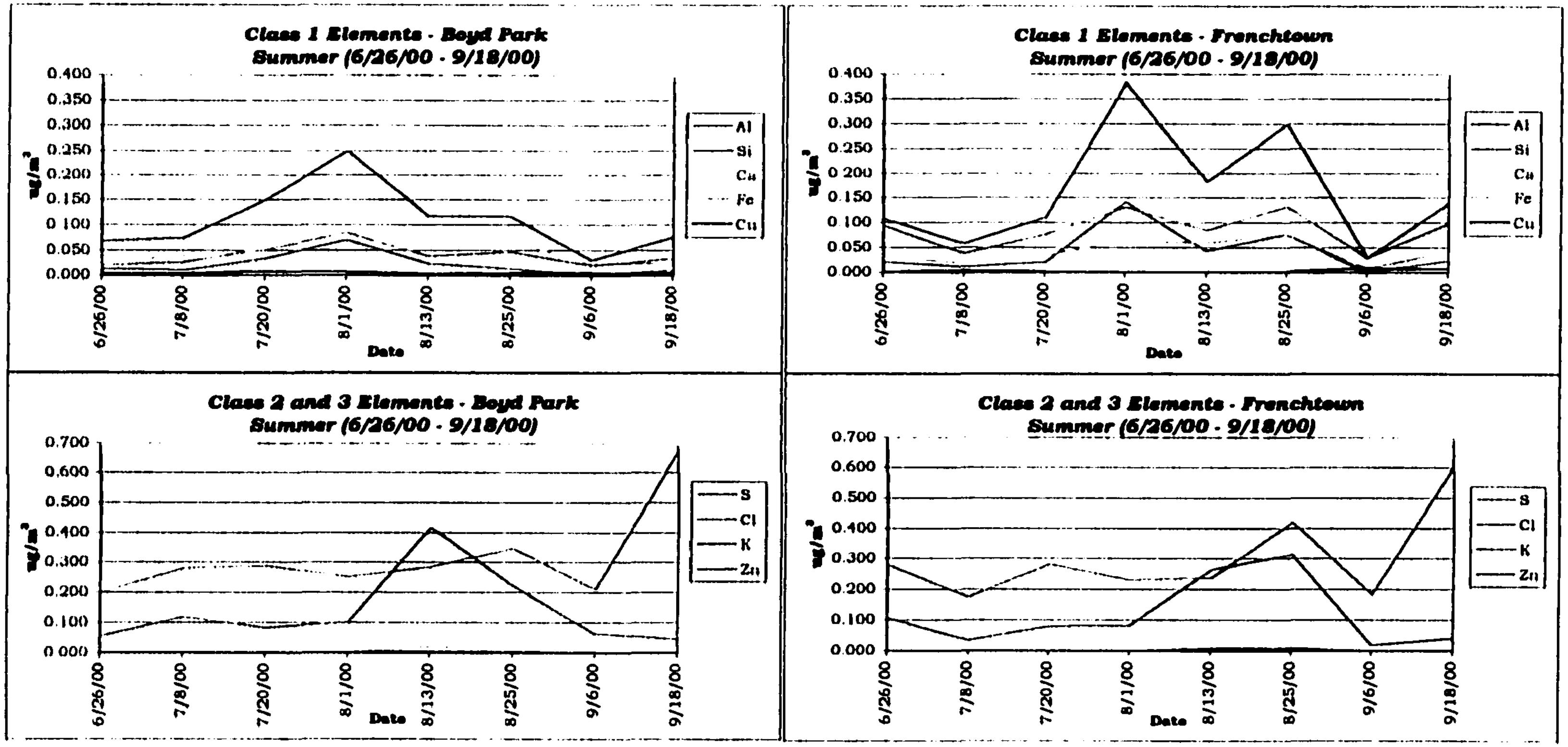
1: Class 1 Elements.
2: Class 2 Elements.
3: Class 3 Elements.
4: Other Notables.

A total of 36 elements were tracked from 6/26/00 – 9/18/00, and these can be further broken down into three classes. The first class contains crustal elements such as aluminum, silicon, calcium, iron, and copper. Class 2 contains sulfur, and Class 3 contains chlorine, potassium, and zinc. Table 13-3 presents the averages of these elements throughout the summer of 2000.

Class 1 elements at Boyd Park did not show a significant increase during the fire season, however, Frenchtown Class 1 elements did show a slight increase in average levels. This is most likely due to the increased fire traffic at the Frenchtown Fire Department during the fire season, resuspending dirt and dust in the unpaved areas around the samplers. Titanium, another element associated with soil, stayed at the same levels during the fire season at Boyd Park, but increased at Frenchtown. Class 2 sulfur at Boyd Park was not affected by the smoke, but Frenchtown sulfur did barely increase above baseline levels on 8/13/00 and 8/25/00. It is difficult to tell if this increase is a result of the smoke or just "normal" daily fluctuations. Figure 13-5 presents the traces for the Class 1, 2, and 3 elements throughout the summer.

Only Class 3 potassium and chlorine displayed significant increases during the fire season at both Boyd Park and Frenchtown. Before August, potassium concentrations averaged 0.092 $\mu g/m^3$ at Boyd Park and 0.078 $\mu g/m^3$ at Frenchtown. During August, Boyd Park potassium concentrations were measured at 0.419 and 0.226 $\mu g/m^3$ on August 13 and 25, respectively. On August 13 and 25 at Frenchtown, potassium concentrations of 0.267 and 0.315 $\mu g/m^3$ were measured. Potassium concentrations dropped back down to baseline levels in September. Potassium has been used as a tracer for wood combustion in other studies (Kavouras, 2001). The chlorine spike was less pronounced. It was measured at low levels at Boyd Park (0.003 $\mu g/m^3$) and not detected at Frenchtown before August. However, during the fire season, chlorine averaged approximately 0.016 $\mu g/m^3$ at Boyd Park, and 0.013 $\mu g/m^3$ at Frenchtown. Chlorine was not detected for the remainder of the summer at Boyd Park while Frenchtown chlorine dropped back down to an average of 0.002 $\mu g/m^3$. Zinc doubled in concentrations during the fire season, but did not have the significant spike that Class 3 potassium and chlorine displayed. Levels of other elements such as bromine, palladium, silver, and lead also had small increases as measured from the 8/13/00 and 8/25/00 Teflon filter samples.

Figure 13-5:



Note: Class 1 and Class 2 / 3 Elements have different scales on y-axis (ug/m³).

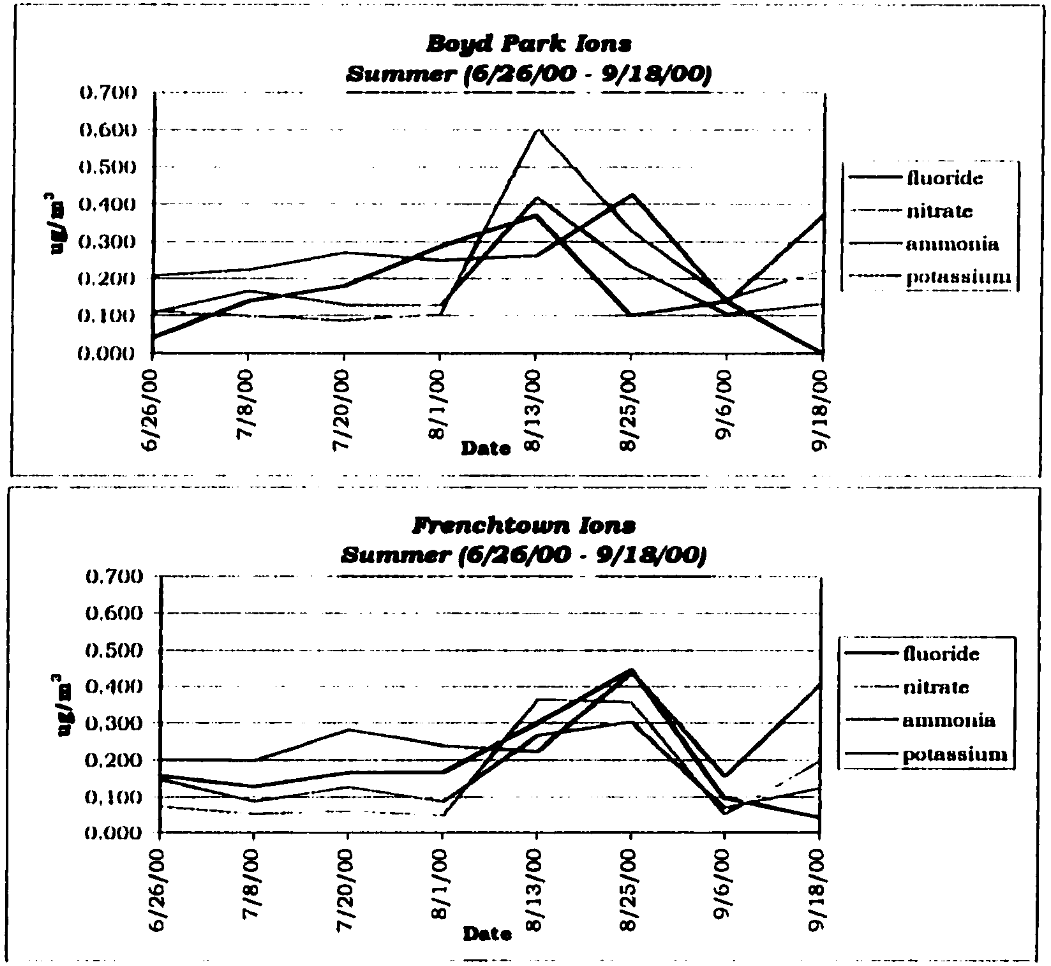
13.4 Anions and Cations

Composing 6% of the 8/13/00 and 8/25/00 fine fraction at Boyd Park and Frenchtown, only four ions showed an increase during the 2000 fire season. These are fluoride. nitrate, ammonia, and potassium. The potassium ion has been shown to be a good marker for the combustion of agricultural biomass and wood (Watson *et al.*, 2001; Park *et al.*, 2001). Even though the trace element chlorine was found to increase significantly during the fire season, chloride did not show the same increase. Table 13-4 presents the averages of these compounds during the summer of 2000, while Figure 13-6 presents the traces.

Table 13-4: Anion and cation averages (µg/m^3) for Boyd Park and Frenchtown during the Summer (6/26/00 – 9/18/00).

Boyd Park	**Summer (6/26/00 – 9/18/00)**	**2000 Fire Season (8/13/00 – 8/25/00)**	**Summer (Excluding Fire Season)**
Fluoride	0.157	0.235	0.130
Nitrate	0.214	0.468	0.129
Ammonium	0.270	0.346	0.244
Potassium	0.178	0.327	0.128
Frenchtown			
Fluoride	0.188	0.373	0.126
Nitrate	0.152	0.362	0.083
Ammonia	0.270	0.333	0.249
Potassium	0.152	0.285	0.108

Figure 13-6:


Boyd Park Ions
Summer (6/26/00 - 9/18/00)
ug/m³
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
6/26/00
7/8/00
7/20/00
8/1/00
8/13/00
8/25/00
9/6/00
9/18/00
Date
fluoride
nitrate
ammonia
potassium
Frenchtown Ions
Summer (6/26/00 - 9/18/00)
ug/m³
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
6/26/00
7/8/00
7/20/00
8/1/00
8/13/00
8/25/00
9/6/00
9/18/00
Date
fluoride
nitrate
ammonia
potassium

13.5 SVOCs

The largest spike of SVOCs collected during the fire season came from phenolic compounds. SVOC data were collected every 12 days at Boyd Park, and every 6 days in Frenchtown, with 19 SVOCs tracked during the summer (6/26/00 – 9/18/00). These 19 can be further broken down into three classes by molecular weights: 1) phenolics (94.12 – 122.17 g/mol) 2) lighter PAHs (128.18 – 202.26 g/mol), and 3) heavier PAHs (228.30 – 252.32 g/mol). Levels for the Class 1 phenolics and the Class 2 PAHs are presented for Boyd Park and Frenchtown in Figure 13-7, with the averages shown in Table 13-5. Four phenolic compounds showed spikes in their concentrations during the fire season. These are phenol, 2-methylphenol (*o*-cresol), 4-methylphenol (*p*-cresol), and 2,4-dimethylphenol. Phenolics are not an unexpected by-product of biomass combustion since the lignin content of wood is characterized by phenolic units joined by propane linkers (Smook, 1992). Substituted phenols are abundant in wood smoke (Hawthorne *et al.*, 1989) and react rapidly with PAHs (Odum *et al.*, 1994). High concentrations of methoxyphenols have also been identified in wood smoke (Hawthorne *et al.*, 1989). 4-methylphenol showed the highest concentrations during the fire seasons, followed by phenol, while 2-methylphenol and 2,4-dimethylphenol showed a strong correlation with one another.

The Class 2 PAHs showed slight increases at both sites during the fire season, but none of the increases were significant compared to the phenolics. Class 3 PAHs were not detected during the summer at Boyd Park, but showed a barely detectable increase at Frenchtown. Perhaps the reason Missoula did not detect higher levels of PAHs during the smoke events was because of photolytic degradation. Rapid photolytic degradation of

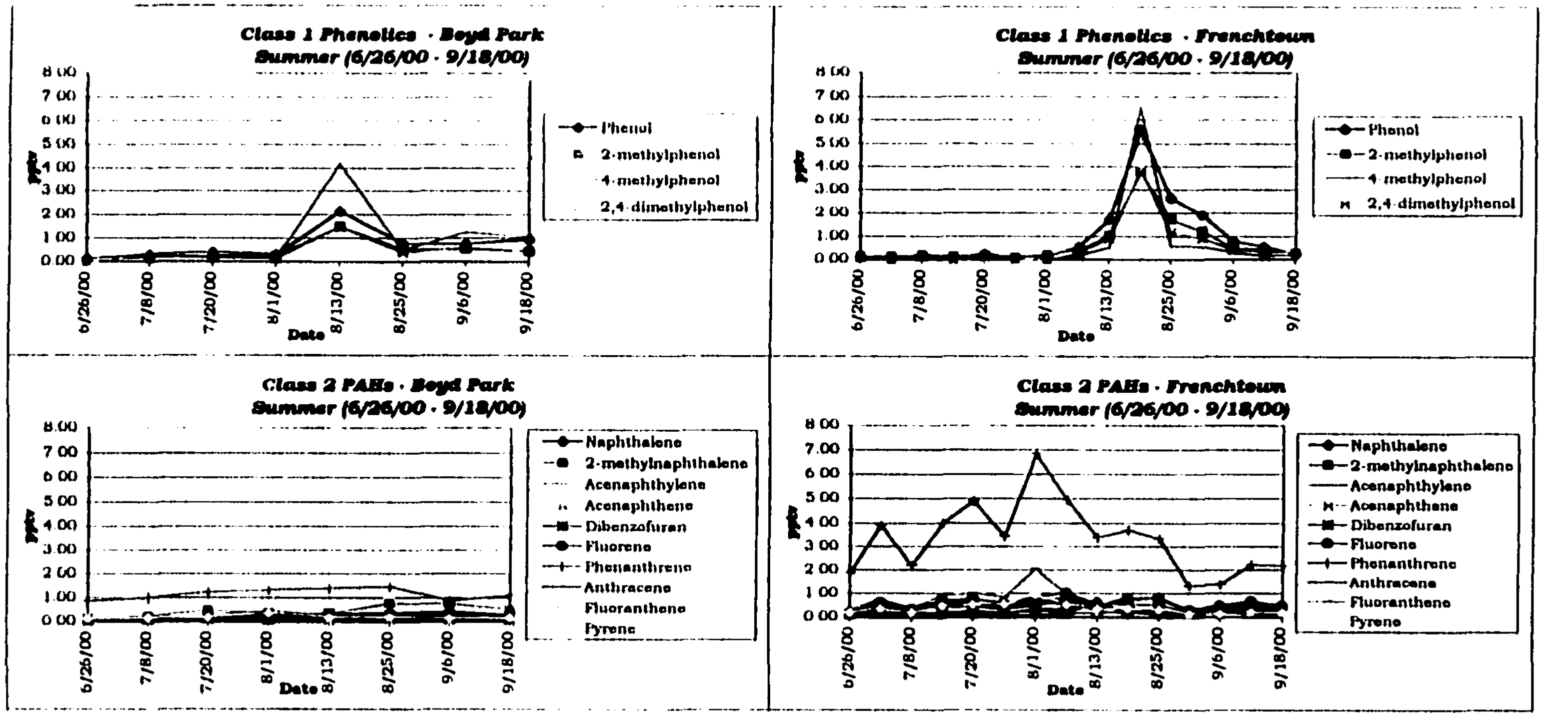
PAHs on wood soot can occur with reaction half-times of less than an hour (Kamens *et al.*, 1985; Kamens *et al.*, 1986). Other PAH degradation studies have shown a more rapid decay in a liquid mixture of methoxyphenols, an abundant class of compounds present in wood smoke, than in hexadecane, which is representative of aliphatic hydrocarbons abundant in diesel soot and automobile exhaust (McDow *et al.*, 1994). Particle associated PAHs from wood smoke have also been shown to decay rapidly in sunlight under some atmospheric conditions, but are generally stable at night. Their reactivity is strongly influenced by solar radiation intensity, temperature, and atmospheric concentrations of water, ozone, and nitrogen oxides (Kamens, *et al.*, 1988; Kamens *et al.*, 1994). Although the forest fires did not result in dramatic levels of PAHs in Missoula, bush fires are thought to be a significant source of PAHs to the Sydney, Australia population (Freeman and Cattell, 1990).

Table 13-5: SVOC averages (pptv) for Boyd Park and Frenchtown during the Summer (6/26/00 – 9/18/00).

Boyd Park	**Summer (6/26/00 – 9/18/00)**	**2000 Fire Season (8/13/00, 8/25/00)**	**Summer (Excluding Fire Season)**	**Frenchtown**	**Summer (6/26/00 – 9/18/00)**	**2000 Fire Season (8/13/00, 8/25/00)**	**Summer (Excluding Fire Season)**
Phenol^1	0.75	1.50	0.50		1.01	2.50	0.27
2-methylphenol^1	0.51	1.03	0.34		0.72	1.66	0.25
4-methylphenol^1	0.97	2.35	0.51		0.64	1.70	0.12
2,4-dimethylphenol^1	0.46	0.97	0.30		0.58	1.45	0.15
Napthalene^2	0.26	0.33	0.23		0.24	0.29	0.22
2-methylnapthalene^2	0.46	0.57	0.43		0.28	0.32	0.26
Aceanaphthylene^2	0.13	0.14	0.12		0.12	0.16	0.10
Acenaphthene^2	0.09	0.10	0.09		0.36	0.37	0.35
Dibenzofuran^2	0.17	0.32	0.12		0.51	0.65	0.44
Fluorene^2	0.22	0.27	0.21		0.63	0.70	0.59
Phenanthrene^2	1.17	1.44	1.07		3.33	3.36	3.31
Anthracene^2	0.17	0.17	0.17		0.37	0.36	0.38
Fluoranthene^2	0.26	0.29	0.26		0.70	0.60	0.74
Pyrene^2	0.21	0.22	0.21		0.40	0.38	0.41
Benzo[a]anthracene^3	0.00	0.00	0.00		0.02	0.05	0.00
Chrysene^3	0.00	0.00	0.00		0.00	0.00	0.00
Benzo[b]fluoranthene^3	0.00	0.00	0.00		0.00	0.01	0.00
Benzo[k]fluoranthene^3	0.00	0.00	0.00		0.01	0.02	0.00
Benzo[a]pyrene^3	0.00	0.00	0.00		0.00	0.00	0.00

1: Class 1 SVOCs.
2: Class 2 SVOCs.
3: Class 3 SVOCs.

Figure 13-7:



Class 1 Phenolics · Boyd Park
Summer (6/26/00 - 9/18/00)
ppb
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
6/26/00
7/8/00
7/20/00
8/1/00
8/13/00
8/25/00
9/6/00
9/18/00
Date
Phenol
2-methylphenol
4-methylphenol
2,4-dimethylphenol
Class 1 Phenolics · Frenchtown
Summer (6/26/00 - 9/18/00)
Class 2 PAHs · Boyd Park
Summer (6/26/00 - 9/18/00)
Class 2 PAHs · Frenchtown
Summer (6/26/00 - 9/18/00)
Naphthalene
2-methylnaphthalene
Acenaphthylene
Acenaphthene
Dibenzofuran
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene

13.6 VOCs

Class 1 VOCs showed measurable increases during the smoke season. 13 VOCs were tracked throughout the summer (6/26/00 – 9/18/00), and can be further broken down into two classes: automobile emission compounds (Class 1) and others (Class 2). The Class 1 emission compounds showed an increase during August at both sites, while the Class 2 VOCs did not show strong correlations evident with the incidence of active wildland fires. Although there was an increase in the Class 1 VOCs during the smoke season, this was probably caused by a reduction in convectional dispersion of automobile emissions in the smoke-impaired valley. While biomass combustion does lead to emission of benzene, toluene and xylene, their levels will be overwhelmed by that from fossil fuel sources. The peaks evident during the summer at Boyd Park were far below those seen in winter months when low sun angle and high reflectivity of snow cover also suppress dispersion processes. Summer levels for the Class 1 and Class 2 VOCs are presented for Boyd Park and Frenchtown in Figure 13-8, with the averages shown in Table 13-6.

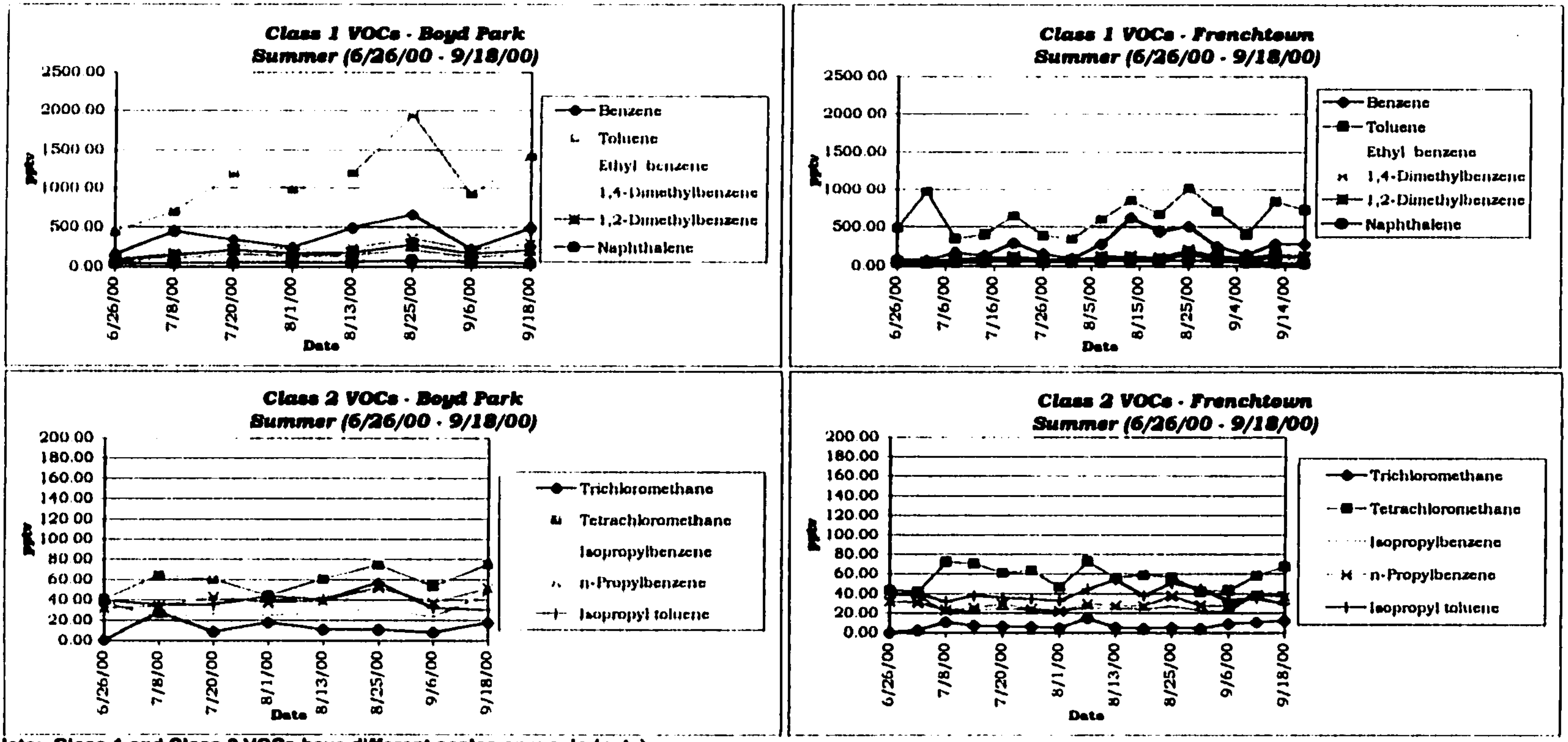
Table 13-6: VOC averages (pptv) for Boyd Park and Frenchtown during the Summer (6/26/00 – 9/18/00).

Boyd Park	**Summer (6/26/00 – 9/18/00)**	**2000 Fire Season (8/13/00 8/25/00)**	**Summer (Excluding Fire Season)**	**Frenchtown**	**Summer (6/26/00 9/18/00)**	**2000 Fire Season (8/13/00 8/25/00)**	**Summer (Excluding Fire Season)**
Trichloromethane[2]	13.18	11.42	13.77		7.33	7.13	7.43
Tetrachloromethane[2]	60.17	68.71	57.32		57.70	58.14	57.48
Benzene[1]	387.32	581.72	322.52		259.83	428.15	175.67
Toluene[1]	1114.93	1590.44	956.42		639.32	781.78	568.09
Ethyl Benzene[1]	137.28	181.28	122.61		76.24	102.34	63.20
1,4-Dimethylbenzene[1]	238.51	301.76	217.42		122.88	155.65	106.50
1,2-Dimethylbenzene[1]	181.15	230.02	164.85		98.83	122.23	87.12
Isopropylbenzene[2]	30.65	29.68	30.97		28.28	25.03	29.90
n-Propylbenzene[2]	41.77	46.61	40.15		30.17	30.89	29.80
1,3,5-Trimethylbenzene[2]	68.69	77.53	65.74		49.26	53.56	47.12
1,2,4-Trimethylbenzene[2]	158.73	183.60	150.44		96.50	114.15	87.67
Isopropyl Toluene[2]	39.78	49.36	36.58		39.74	47.12	36.05
Naphthalene[1]	60.71	77.09	55.25		60.99	75.38	53.80

1: Class 1 Automobile Emission VOCs.

2: Class 2 Other VOCs.

Figure 13-8:



Note: Class 1 and Class 2 VOCs have different scales on y-axis (pptv).

13.7 PM$_{2.5}$ CMB Source Apportionment Model

CMB Model 8.0 was used to apportion the sources of PM$_{2.5}$ during the summer of 2000. Average source contribution estimates (SCEs) for summer 2000, including the fire season (8/13/00 and 8/25/00), are presented in pie charts (% SCEs) in Figure 13-9 and graphs (μg/m^3) in Figure 13-10, while Table 13-7 gives a summary of the SCE information. During the smoky days of 8/13/00 and 8/25/00, the residential wood combustion source profile for Pocatello, Idaho gave a better fit for the forest fires than the Missoula source profile in the CMB model. Good statistical fits were also achieved using the smoldering slash burning profile (#42306) as well, but the Pocatello profile was used because it gave a better percent mass statistical fit with less total mass unexplained.

Table 13-7: Summary of the source contribution estimates (% and μg/m^3) for Boyd Park and Frenchtown during the Summer (6/26/00 – 9/18/00).

Boyd Park	**Summer (6/26/00 – 9/18/00)**	**2000 Fire Season (8/13/00, 8/25/00)**	**Summer (Excluding Fire Season)**
Wood Combustion (WC)	72% 10.7 μg/m^3	83% 32.5 μg/m^3	50% 3.4 μg/m^3
Diesel	13% 2.0 μg/m^3	10% 3.9 μg/m^3	19% 1.3 μg/m^3
Ammonium Nitrate (NH4NO3)	0% 0.0 μg/m^3	0% 0.0 μg/m^3	1% 0.1 μg/m^3
Kraft Recovery Boilers (KRB)	8% 1.3 μg/m^3	3% 1.2 μg/m^3	18% 1.3 μg/m^3
Hog Fuel Boilers (HFB)	4% 0.6 μg/m^3	3% 1.4 μg/m^3	5% 0.3 μg/m^3
Street Sand	3% 0.5 μg/m^3	1% 0.4 μg/m^3	7% 0.5 μg/m^3
Autos	0% 0.0 μg/m^3	0% 0.0 μg/m^3	0% 0.0 μg/m^3
Avg PM$_{2.5}$ Mass	15.0 μg/m^3	39.9 μg/m^3	6.7 μg/m^3
Frenchtown			
Wood Combustion (WC)	70% 10.4 μg/m^3	79% 33.6 μg/m^3	46% 2.6 μg/m^3
Diesel	13% 2.0 μg/m^3	11% 4.7 μg/m^3	19% 1.1 μg/m^3
Ammonium Nitrate (NH4NO3)	0% 0.0 μg/m^3	0% 0.0 μg/m^3	1% 0.1 μg/m^3
Kraft Recovery Boilers (KRB)	9% 1.3 μg/m^3	4% 1.7 μg/m^3	21% 1.2 μg/m^3
Hog Fuel Boilers (HFB)	1% 0.2 μg/m^3	1% 0.5 μg/m^3	1% 0.0 μg/m^3
Street Sand	7% 1.0 μg/m^3	5% 2.0 μg/m^3	12% 0.7 μg/m^3
Autos	0% 0.0 μg/m^3	0% 0.0 μg/m^3	0% 0.0 μg/m^3
Avg PM$_{2.5}$ Mass	14.7 μg/m^3	42.2 μg/m^3	5.6 μg/m^3

Figure 13-9: Source Contribution Estimates (%) for Boyd Park and Frenchtown.

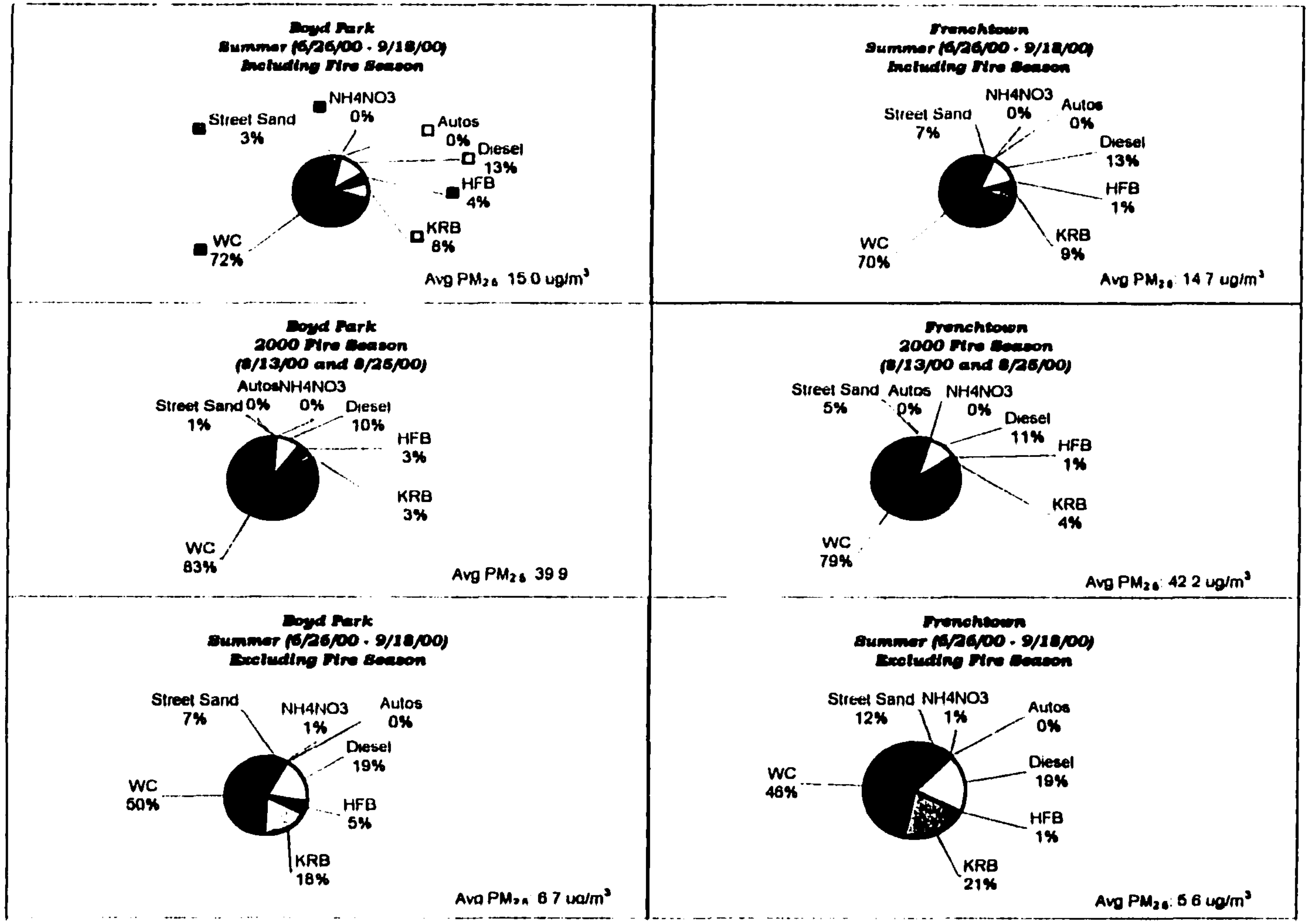
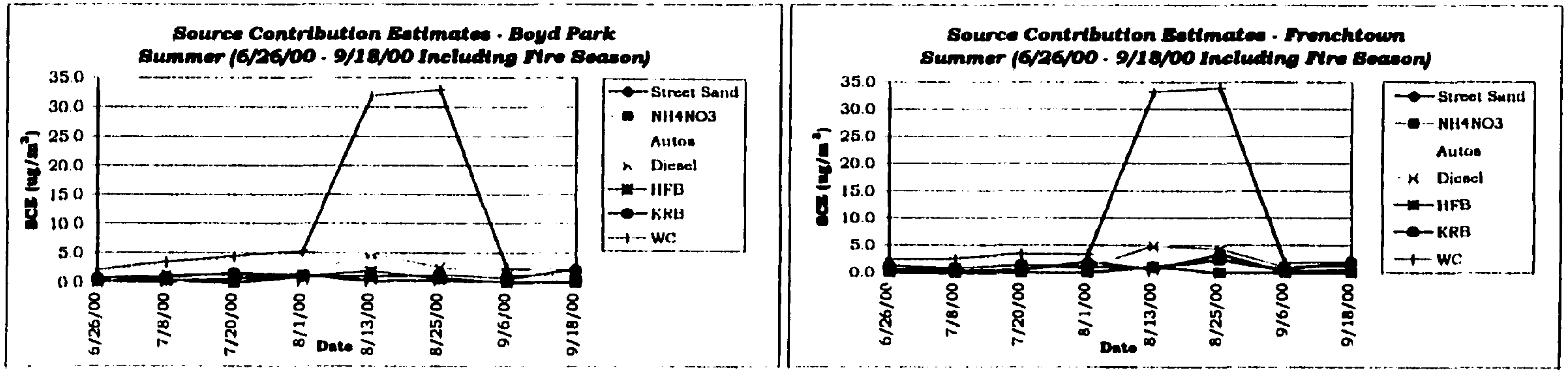


Figure 13-10: Source Contribution Estimates (ug/m^3) for Boyd Park and Frenchtown.



13.8 Fire Season 2000

The summer of 2000 was characterized by hot, dry, windy weather which resulted in widespread forest fires in Idaho and Montana. During August 13 and 25, 2000, $PM_{2.5}$ averaged 41.0 $\mu g/m^3$ in the Missoula Valley. CMB results from these days show that 81% of this $PM_{2.5}$ came from wood combustion (forest fires). Diesel was the second largest contributor at both sites, providing 10% (3.9 $\mu g/m^3$) at Boyd Park and 11% (4.7 $\mu g/m^3$) at Frenchtown to the fine fraction. Industrial sources (kraft recovery boiler and hog fuel boilers) contributed 6% (2.6 $\mu g/m^3$) at Boyd Park and 5% (2.2 $\mu g/m^3$) at Frenchtown to the fine fraction. Automobiles and ammonium nitrate were not detected during the warm summer months, despite there being an increase in both ammonium and nitrate detected on the quartz filter samples at both sites. Street sand at Frenchtown contributed more to the fine fraction (5%, 2.0 $\mu g/m^3$) than Boyd Park (1%, 0.4 $\mu g/m^3$), the result of unpaved areas around the Frenchtown Fire Department parking lot where the sampling station was located. During the fire season, the Frenchtown Fire Department was used as a staging area for fires on the west side of the Valley. Extra fire trucks and fire fighting crews were on standby, creating a lot of activity which could have resuspended street sand and crustaceous material around the samplers. This could also be the reason for the slightly elevated diesel contribution detected at Frenchtown during the fire season compared to Missoula.

Chapter 14 Conclusion

The 2000/2001 CMB Sampling Program data collected during the 2000 fire season suggest that the main health impacts to downwind populations reside in the fine particulate exposures, with an average of 81% of the Missoula Valley $PM_{2.5}$ collected on 8/13/00 and 8/25/00 resulting from forest fires. These results are consistent with a study conducted in 1994 by Babbitt *et al.* In that study, they concluded that particulate matter was a significant problem at both local and regional levels, but gas concentrations of CO were not high enough to violate national ambient air quality standards in downwind populations.

There also seems to be a fundamental difference in the airshed composition between the 2000 fire season and the winter, which is traditionally the worst air pollution season in the Missoula Valley. During the fire season, the samples that were collected showed high levels of $PM_{2.5}$ (~41 $\mu g/m^3$) which were composed of 45% OC and 14% EC. Since we performed solvent extracts on the particulates captured by the PUF samplers, we can assert that phenolics represent the most abundant organics among the suite of contaminants traveling with the particulates for which we analyzed. There was not a significant increase in the carcinogenic PAHs measured. During the winter, $PM_{2.5}$ levels were elevated (~29.5 $\mu g/m^3$) and levels of PAHs were measured at their highest concentrations of the entire sampling program. Winter levels of VOCs were also twice that measured during the fire season due to the lack of photochemical reactions which destroy the VOCs, and the stagnant conditions which are frequent during the Missoula winters which allow these contaminants to build up. This suggests that a Missoula resident can get a larger dose of hazardous air pollutants on an average winter day than they did during the extraordinary fire season of summer 2000.

Finally, potassium (both element and cation) and chlorine showed significant increases as a result of the forest fire smoke. Although there were increases in other compounds (fluoride, ammonia, nitrate, Class 2 PAHs, and Class 1 VOCs), this could be the result of the "smoke induced inversion" effect rather than the forest fire smoke itself.

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