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Source Apportionment of Ambient PM$_{2.5}$ in Urban Residential Areas

By

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ABSTRACT

This study undertook air sampling, subsequent elemental and morphological analysis, and source apportionment receptor modeling for $PM_{2.5}$ at four residential sites in Edmonton, Alberta over a five-month campaign (July to November 2004). The 24-hr average $PM_{2.5}$ levels ranged from about 0.6 to $28\mu g/m^3$ with the majority of concentrations falling between 0.9 and $20\mu g/m^3$. $PM_{2.5}$ samples from the two distinct sampling sites were analyzed by SEM-EDX to evaluate and compare chemical composition profiles. Elements detected at the two sites included: Si, Ca, Al, Mg, Fe, Na, K, Cl, S, Ti, Mn, Co, Pb, Cu, Cr, Cd, V, and Ba.

Four probable generic sources of $PM_{2.5}$ that combined to account for 86% of the original data set were identified at the two sites by utilizing principal component analysis (PCA). These included: re-suspended crustal material (37~ 44%), combustion (17 ~ 25%), transportation (12 ~ 14%), and regional sulphate (9 ~ 13%). Comparison of $PM_{2.5}$ profiles between the two sites suggested similar source profiles. Analysis of additional chemical species, including organic carbon, elemental carbon, and gas-phase pollutants, was recommended for future research to distinguish vehicular and industrial emissions for source apportionment.

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1. INTRODUCTION

1.1 Background

In recent years, people living in inner cities have become increasingly concerned about ambient air pollution and the associated health effects. Numerous epidemiological studies, for example, have reported a relationship between ambient air pollution and fetal development worldwide (Dockery *et al.*, 1993; Ha *et al.*, 2001; Loomis *et al.*, 1999; Bobak and Leon, 1999; Dejmek *et al.*, 1999; Woodruff *et al.*, 1997; Wang *et al.*, 1997). In the last decade, concern about the fine fraction of atmospheric particles (i.e., $PM_{2.5}$, particulate matter with aerodynamic diameter less than 2.5μm) has been raised because these particles contain a higher proportion of potentially harmful chemical species. These chemical species include acids, heavy metals, and PAHs (Polycyclic Aromatic Hydrocarbons). In addition, these small particles can be inhaled and retained by the respiratory system.

In urban areas of Canada, it has been reported that hospital admissions increase with increased levels of particulate matter, even at levels regularly experienced by the general population (Environment Canada, 1999). Thus, debate over evidence to identify an underlying cause linking airborne particulate matter to certain health effects has intensified. As a function of emission sources characteristics of mass, size, and chemical composition show inconsistencies between levels of particulate matter in urban air and health effects (Brauer *et al.*, 1995). With health effects varying for different particulate physical and chemical profiles, it becomes important to characterize and apportion sources using receptor modeling or source-to-receptor techniques (U.S.EPA, 1994).

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1.2 Problem Statement

Large industrial sources are often implicated as being substantial contributors to ambient $PM_{2.5}$ in urban areas and, therefore, are believed to be in need of stricter emission controls. Vehicle/household sources on the other hand, emit pollutants near ground level adjacent to/inside residences. As a result, local and near-filed sources in residential areas can contribute more to actual human exposure than their share in total emissions loads in an urban area would indicate. Epidemiological studies often use airborne particulate matter concentrations measured at centralized monitoring stations as surrogates of population exposure. The extent to which ambient particulate matter measurements at central monitoring station accurately reflect particulate matter exposure is a subject of considerable scientific debate.

In order to understand whether a relationship exists between prominent sources contributing to ambient $PM_{2.5}$ in urban areas (i.e., vehicles, oil refineries, coal-fired facilities, etc.) and health effects reported by others, source apportionment can be undertaken. Source apportionment – also called receptor modeling – can be employed to estimate the contributions of different sources to receptors in an airshed. The results of source apportionment can be used to evaluate emission reduction on ambient particulate matter levels, devise more efficient emission reduction strategies for industry and government, and to provide necessary information for the development of ambient particulate matter guidelines.

1.3 Study Objectives

The primary purpose of this study was to determine ambient levels and source origins of $PM_{2.5}$ in urban residential areas of the City of Edmonton and surrounding area.

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Specifically, this involved measuring ambient $PM_{2.5}$ mass concentrations, characterizing chemical composition and morphology, and undertaking source apportionment analysis for two residential areas. These two areas included:

- One with low traffic intensity

- One co-located at a central residential air monitoring station in Edmonton with intermediate traffic intensity

The goal of the study was to develop an enhanced foundation of information regarding the characteristics of fine particulate matter ($PM_{2.5}$) in Edmonton urban residential areas in order to lead to a better understanding about the source origins.

1.4 Thesis Organization

This thesis is divided into eight chapters. Chapter 2 provides an overview of relevant literature, including:

- Characteristics of particulate matter (physical and chemical properties, ambient levels, source identification, and the source elemental abundance profiles that they apply).

- Particulate matter measurements (types of filters and samplers, and particulate matter samplers used in Canada).

- Particulate matter trends (in Canada and Alberta).

- Impacts of particulate matter and relevant guidelines and regulations.

- Types of statistical study methods in use for source apportionment (chemical mass balances and factor analysis techniques).

- Current particulate matter management framework for Alberta, and a review of particulate matter studies done to date in Alberta.

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Chapter 3 presents an overview of the study scope and area (Edmonton), and background on air quality in the study area. Chapter 4 presents specific details of site selection and descriptions, sample protocols, instrument analysis, data analysis, and quality control and assessment as performed in this study. Chapter 5 presents the results and discussion, including: $PM_{2.5}$ mass levels, $PM_{2.5}$ chemical composition and morphology, and source apportionment. Seasonal differences, effects of meteorology, and a comparison of results to similar studies and current regulations are also reported in this chapter. Conclusions and recommendations are presented in Chapter 6 and references are listed in Chapter 7. The MiniVol Sampler calibration information used in the study along with detailed raw data are presented in Chapter 8 Appendices.

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2. LITERATURE REVIEW

2.1 Particulate Matter Characteristics

Characterization and measurement of ambient particles is a complex endeavor. The goal of this Chapter was to provide an overview of current particulate matter monitoring technologies and methodologies relevant to the present $PM_{2.5}$ study. Due to a wide variety of monitoring techniques and particulate matter monitoring objectives, it was beyond the scope of this study to provide a detailed discussion of all aspects of planning and implementing an ambient monitoring program.

2.1.1 Physical Properties

The dynamics of particulate matter in the atmosphere involve various physical and chemical processes under different time scales. To identify particulate matter sources, it is important to develop an understanding of particulate characteristics. The size of particulate matter is an important physical property and is typically related to mechanisms of production and removal that induce (Lurmann *et al.*, 1997; Turpin *et al.*, 1993; Lazaridis and Melas, 1998; Zannetti, 1990; Williams and Loyalka, 1991).

Based on size, ambient particles are typically categorized into fine particles (i.e., $PM_{2.5}$, mean aerodynamic diameter ≤ 2.5 μm), and coarse particles (i.e., PM_{10}, mean aerodynamic diameter between 2.5 μm and 10 μm). Since the size range of these particles can span over several orders of magnitude (0.01μm to >10μm) (Finlayson-Pitts and Pitts, 1986), it is best to characterize particulate matter in terms of size distribution. Based on particle count, volume, and surface area distributions, Figure 1 illustrates the three-modal volume size distribution of airborne particulates (Wison and Suh, 1997).

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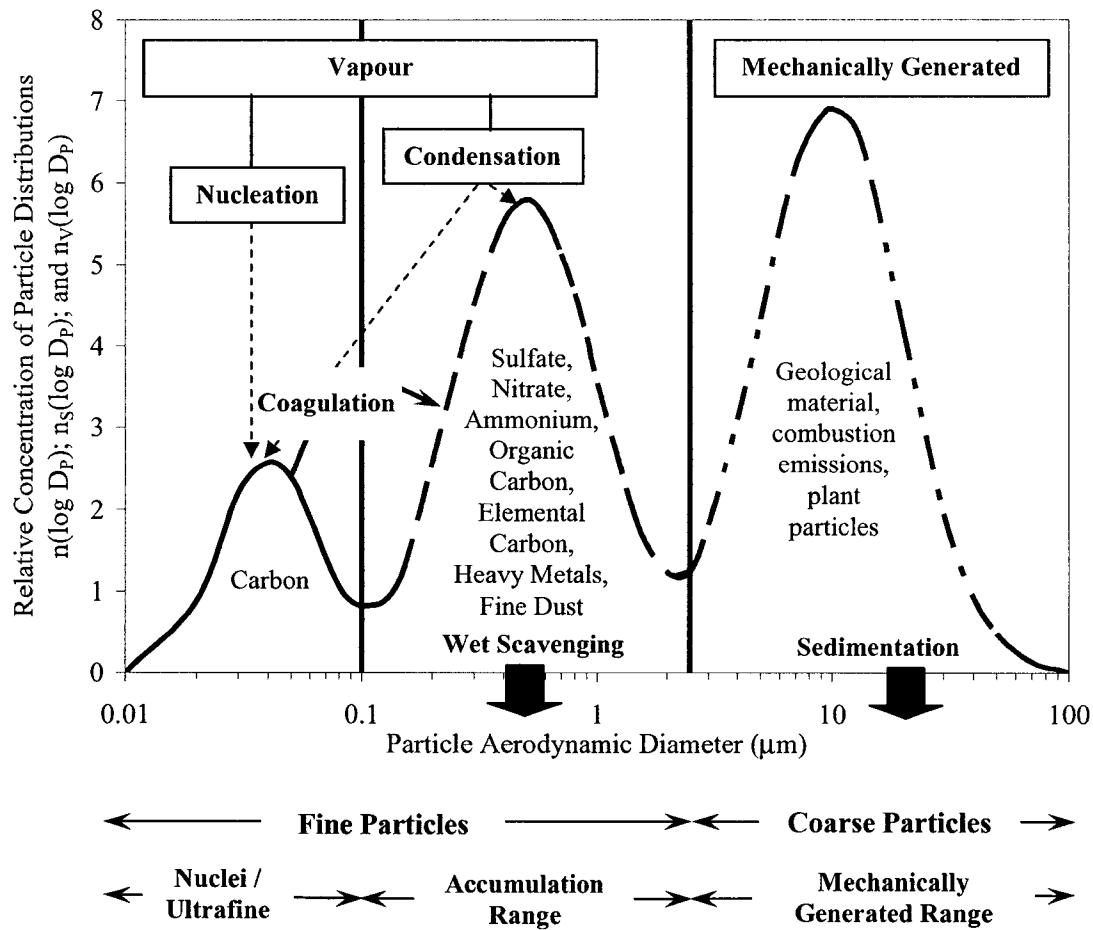
Figure 1   **Idealized distribution of particulate matter.**
(after Wilson and Suh, 1997; CEPA and FPAC; 1999; U.S.EPA, 1998; National Academy of Sciences, 1979).

The fine size fraction (aerodynamic diameter $\leq$2.5 μm) can be further broken into nuclei mode (<0.1 μm) and accumulation mode (0.1 to 1 μm) (Whitby, 1972). There have also been other classifications of particle size based on inhalation characteristics; these particles are classified as inhalable, thoracic, and respirable (U.S.EPA, 1996). Spektor (1998) indicated that the largest fraction of particles by count is in nucleation mode, with diameters less than 0.1 μm and a peak at 0.04 μm.

The mechanism of coagulation is very crucial for the development of the size distribution in the atmosphere (Friedlander, 1977). Aerosols in the atmosphere

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agglomerate due to Brownian motion or hydrodynamic, electrical, and/or gravitational forces. The collision of particles in the atmosphere is given by the *Smoluchowski Coagulation Equation*, which is normally expressed in terms of particle volume coordinates (Williams and Loyalka, 1991). The coagulation equation can be expressed in either continuous or discrete forms (Williams and Loyalka, 1991; Seinfeld and Pandis, 1998).

For the discrete forms, it is assumed that coagulation occurs from particles both removed and added to size bins as a result of coagulation between particles (Lazaridis and Koutrakis, 1997). More specifically, if two particles of masses m_1 and m_2 coagulate, the mass of the new formed particle is $m_3 = m_1 + m_2$, and the coagulation rate between particles of masses m_1 and m_2 is: $dn_1/dt = -K_{m1,m2} n_1 n_2$, $dn_2/dt = -K_{m1,m2} n_1 n_2$ and $dn_3/dt = K_{m1,m2} n_1 n_2$. There is a net loss of one particle per coagulation, but the total mass is conserved. The generalized equation for this situation is (Lazaridis and Koutrakis, 1997):

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{i+j=k} K(m_i, m_j) n_i n_j - n_k \sum_{i=1}^{\infty} K(m_i, m_k) n_i \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1)$$

Where, $i+j=k$ is the summation when coagulation has taken place over those grid points where $m_k = m_i + m_j$.

Sedimentation plays an important role for aerosols and gaseous species removal from the atmosphere. A common approach to characterize sedimentation is the concept of sedimentation velocity. There are two general approaches to determine the sedimentation velocity. One method is based on available experimental data from different aerosol and gaseous species. Seinfeld and Pandis (1998) defined the sedimentation velocity as the

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ratio of the deposition flux of the specified pollutant to the pollutant concentration. Another method is based on the transfer of material from the atmosphere to the earth's surface through different resistance mechanisms: aerodynamic resistance, surface resistance, and transfer resistance (Slinn and Slinn, 1980).

The particle sedimentation velocity with different particle size can be expressed using the following equation (Slinn, 1982):

$$v_d^i = \frac{1}{r_a + r_d^i + r_a r_d^i v_g} + v_g^i \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2)$$

Where the term, on the left hand side is the sedimentation velocity (m/s) of particles in the size bin i, r_a is the aerodynamic resistance (s/m), r_d is the deposition layer resistance (s/m) of particles in the size bin i, and v_g is the gravitational settling velocity (m/s) of particles in the size bin i.

The mechanism of dry sedimentation is not yet fully understand since the process is quite complex and involves many factors that cannot be readily accounted for in the field. These uncertainties include meteorological conditions, such as temporal and spatial characteristics of atmospheric turbulence, surface characteristics, and aerosol properties (Davidson and Wu, 1990).

Wet scavenging is another efficient mechanism for the removal of aerosols from the atmosphere. Hicks and Meyers (1989) found that aerosol scavenging rates within a cloud are about ten times larger than below a cloud's scavenging rate (i.e., approximately 3×10^{-5} s^{-1}). U.S.EPA (1996) also provides a detailed discussion for wet scavenging. Finalyson-Pitts and Pitts (1986) indicated that the wet sedimentation velocity can be expressed as the product of an average scavenging rate (Λ) and the vertical height

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h, where a uniform distribution of pollutant is assumed between the earth surface and height h.

Table 1   Source and dynamic/optical properties of particulate matter.
(after Seinfeld, 1975; Klemm and Gray, 1982; Beckett *et al.*, 1998)

Particle size	Sources / Origins	Dynamic properties	Properties
<0.1 μm Nuclei mode	Condensation, combustion, chemical reactions.	Brownian motion, coagulation with other particles.	Roughly obey the same laws of light scattering as molecules, but have little effect on visibility.
0.1to 2.5 μm Accumulation mode	Industrial dusts, fly ash from combustion, sea salt.	Combination of Brownian motion, coagulation and settling.	Particles are of the same order as visible wavelength, thus they are most effective in light scattering and visibility reduction.
2.5 to 10 μm Coarse mode	Erosion, grinding, spraying.	Settling, washout by rain, snow; impingement on surface.	Obey scattering laws of large bodies; not as effective in visibility as smaller particles.

Table 1 describes a breakdown of particles from different sources and dynamic properties as a function of size. In the nuclei mode, condensable aerosol can nucleate to form a new particle or can condense onto the surface of an existing particle (U.S.EPA, 1999a). Particles in this size range have a very short lifetime ($\leq$ hour) due to rapid condensation, and they are generally found close to an emission source. These particles are associated with combustion processes, such as vehicular, industrial processes, or vegetative material burning (Alberta Environment and Alberta Research Council, 1998; U.S.EPA, 1999a). Due to the rapid condensing and coagulation of ultra fine particles, these particles form larger particles in accumulation mode size range of 0.1 to 2.5 μm (U.S.EPA, 1998). For capturing these ambient particles, filters tend to have 2 μm pore

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sizes that are woven in an overlapping fashion which enable the entrainment of ultra fine particles (Whatman Inc., Clifton, NJ).

Unlike ultra fine particles, in accumulation mode, particles have a longer lifetime, lasting from several days to weeks in the atmosphere and traveling vast distances (Alberta Environment and Alberta Research Council, 1998). These particles are associated with combustion sources formed from gas to particle conversions and finely ground dust (U.S.EPA, 1999a). In coarse mode, the formation of coarse particles of aerodynamic diameter ranging from 2.5 µm to 10 µm, tends to be associated with mechanical processes, such as wind erosion and grinding operations. Coarse particles found in ambient air are generally dominated by biological material from pollen, spores, and decaying leaves, geological material from crustal erosion, and anthropogenic material from direct emissions, mechanically ground up trash, vehicular emissions, and agricultural emissions (U.S.EPA, 1999a; Chow, 1995).

2.1.2   Chemical Properties

The chemistry of ambient particles is dependent on a number of factors, including particle size and the source of particulate matter in the local environment. Despite the diversity of physical properties in different particulate matter samples, common constitute have been identified as including acid aerosols (sulfate and nitrate), elemental carbon (EC), various organic compounds, metal and other trace elements, and biological material.

Atmospheric chemical reactions, which usually involve a large number of reactive species on ppm (parts per million) or ppb (parts per billion) levels, not only depend on the background concentrations of the various chemical species from the emissions, but

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also on local meteorological conditions. Also due to the effect of turbulence, chemical reactions and stochastic mixing processes become more complex making the process of modeling the gaseous chemical reactions in the atmosphere a challenging task. Several simplifications are adopted in describing the gaseous phase chemical reactions in air quality models. Figure 2 presents a simplified schematic diagram of chemical reactions and processes associated with particulate matter.
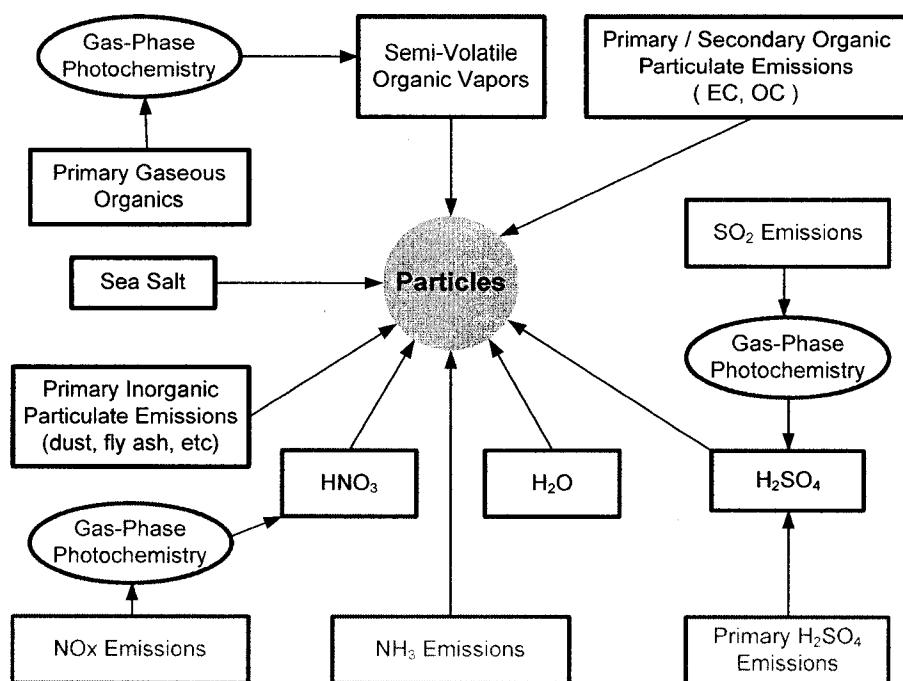
Figure 2   Schematic diagram of chemical reactions and processes associated with particulate matter.
(Meng and Seinfeld, 1996)

• **Acid Aerosols (sulfate and nitrate)**

Sioutas *et al.* (1995) defined aerosol acidity as acids and their precursors in aqueous phase residing in the atmosphere. Strong acidity refers mainly to sulfuric acid or partly neutralized acid particles, whereas weak acidity includes a number of inorganic (e.g. nitrous acid, hydrogen phosphates, hydrochloric acids) and organic species (e.g. phenols, carboxylic acids). Field studies indicate that spatial homogeneity in particle

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strong acidity over large geographical areas has occurred mainly during warmer periods and at similar times as photochemical smog episodes (Thurston *et al.*, 1992). Aerosol sulfuric acid is mainly produced through the photo oxidation of sulphur dioxide with hydroxyl radicals in the gaseous phase. Further neutralization of the aerosol particles occurs with the diffusion of ammonia (NH_3) in the liquid phase (Sioutas *et al.*, 1995). Nitric acid is mainly formed through the photo oxidation reaction between NO_2 and hydroxyl radicals in the gaseous phase. Nitric acid can be neutralized when it reacts with ammonia and forms particulate ammonium nitrate. Nitric acid can also react with the salts of chlorine or carbonate, and form particulate salt solutions.

- **Elemental Carbon**

Elemental carbon (EC) has a chemical structure similar to impure graphite, and is emitted as primary particles during incomplete combustion processes (wood-burning, diesel engines) (U.S.EPA, 1996; Burtscher, 1992; Hansen and Lacis, 1990). EC can absorb, and sscatter light, and thus contributes significantly to total light extinction (Finlayson-Pitts and Pitts, 1986). Much higher concentrations of EC are found in urban areas, compared to rural and remote locations. In rural and remote locations, the EC concentration can vary from 0.2 to $2.0\mu g/m^3$ (Clarke *et al.*, 1984; Pinnick *et al.*, 1993). In urban areas, the concentrations fall between 1.5 and $20\mu g/m^3$ (Heintzenberg and Winkler, 1984; Rau, 1989). The ratio of EC to total carbon ranges from 0.15 to 0.20 in rural areas, and 0.2 to 0.6 in urban areas (Wolff *et al.*, 1982; Chow *et al.*, 1993).

- **Organic Carbon**

Organic carbon is a complex mixture of thousands of different organic compounds (Turpin and Huntzicker, 1995; Grosjean, 1990; Odum *et al.*, 1997; Pandis *et*

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al., 1992) and a very small portion of it is characterized with regard to molecular structure/classification (around 10%). Due to difficulty in measuring organic compounds, our current knowledge about organic matter is limited and incomplete. Primary emission sources for organic carbon include combustion processes, and geological (fossil fuels) and biogenic sources.

- **Metals and other Trace Elements**

    Trace metals in atmospheric particulate matter are mainly from anthropogenic sources such as residential wood combustion, forest fires, combustion of coal and oil, waste incineration, and metal smelting (Chow *et al.*, 1992). In the fine particle size range, various trace metals have been found primarily including Pb, Zn, Cd, As, Sb, Ag, In, La, Mo, I, and Sm (U.S.EPA, 1996). In the coarse mode, mainly Ca, Al, Ti, Mg, Sc, La, Lu, Hf, and Th have been found (Klee, 1984; Bernstein and Rahn, 1979). Furthermore, in both the fine and coarse modes, Na, K, Fe, V, Cr, Co, Ni, Mn, Cu, Se, Ba, Cl, Ga, Cs, Eu, W, and Au have been found (U.S.EPA, 1996).

Table 2   **Concentrations of various trace elements in atmospheric particles.**
   (Schroeder *et al.*, 1987).

Elements	Remote (ng/m^3)	Rural (ng/m^3)	Urban (USA) (ng/m^3)
As	0.007 - 1.9	1.0 - 28.0	2.0 - 2,320
Cd	0.003 - 1.1	0.4 - 1,000	0.2 - 7,000
Ni	0.01 - 60.0	0.6 - 78.0	1.0 - 328
Pb	0.007 - 64.0	2.0 - 1,700	30 - 96,270
V	0.001 - 14.0	2.7 - 97.0	0.4 - 1,460
Zn	0.03 - 460.0	11.0 - 403	15 - 8,328
Co	0.001 - 0.9	0.08 - 10.1	0.2 - 83
Cr	0.005 - 11.2	1.1 - 44.0	2.2 - 124
Cu	0.029 - 12.0	3.0 - 280	3 - 5,140
Fe	0.62 - 4,160	55 - 14,530	130 - 13,800
Hg	0.005 - 1.3	0.05 - 160	0.58 - 458
Mn	0.01 - 16.7	3.7 - 99	4.0 - 488

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Emissions, meteorology, and photochemistry are all important factors that control the ambient concentration of trace species in the particulate phase (Finlayson-Pitts and Pitts, 1986). Table 2 gives a summary of the concentrations of trace species found in remote, rural, and urban sites in the USA.

- **Biological Aerosols**

Matthias-Maser *et al.* (1995) defined primary biological aerosol particles as follow: "primary biological aerosol particles (dead or alive) are solid particles that are or were derived from living organisms, including microorganisms and fragments of all varieties of living things". More specific, primary biological aerosol particles include viruses (0.005 to 0.25 µm), bacteria (≥0.2 µm), algae, and spores of lichen mosses, ferns and fungi (≥0.5 µm), pollen (≥5 µm), plant debris (e.g. leaf litter, part of insects), and human and animal epithelial cells (usually >1 µm) (Matthias-Maser *et al.*, 1995).

2.1.3 Source of Particulate Matter

A variety of suspended particles can be found in the atmosphere; however, there is surprising consistency regarding the major components of suspended particles (U.S.EPA, 1999a). Sources of particulate matter can be either primary (particles emitted directly into the atmosphere) and/or secondary (particles formed by chemical transformation of gaseous pollutants) in nature. Primary particles can further be distinguished between as coming from anthropogenic sources (human-caused, e.g. industrial, residential, and commercial sources, transportation and non-energy area sources, like road dust, construction, agricultural activities, etc.), or natural sources (e.g. forest fires, windblown soil, volcanic dust, sea spray, pollen, spores, and bacteria) depending on their origin. The ratio between anthropogenic and natural sources varies

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significantly by emission (Clean Air Strategic Alliance, 2002). For secondary particles, primary components are organics and ammonium sulfate and nitrate formed from gaseous emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) which react with ammonia (Section 2.1.2).

Table 3   Summary of particulate matter sources.
(Clean Air Strategic Alliance, 2002; Environment Canada and Health Canada, 2000; U.S.EPA, 1999a)

	Fine Particles ($PM_{2.5}$)		Coarse Particles (PM_{10})	
	Primary	Secondary	Primary	Secondary
Natural Source	Wildfires, sea salt spray, volcanic activity, viruses and bacteria.	Organic carbons from biogenic, VOCs, nitrate from natural NOx, natural NH3.	Windblown dust, sea salt spray, pollen and spores.	None.
Anthropogenic Source	Fossil fuel combustion, vehicle exhaust, industrial activates, wood combustion.	Organic carbons, NH3 from human activities, sulphates and nitrates from human sources of SO2 and NOx.	Construction, mining, soot, fly ash, road dust and agricultural soil.	None.

Table 3 presents a summary of the particulate matter in both fine and coarse modes. Generally, secondary particles are predominantly fine particles, although some may be larger. Because of the large number of sources, particulate matter may contain hundreds of different chemical species. Fine particles may contain substantial quantities of sulfate, ammonium, nitrate, elemental carbon, and condensed organic compounds. Carcinogenic compounds and trace metals such as arsenic, selenium, cadmium, and zinc

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are also concentrated in these particles. Coarse particles (e.g. soot, fly ash, road dust and soil) are composed primarily of minerals, including silicon, aluminum, potassium, iron, calcium, and other alkaline elements.

A recent study indicated that secondary $PM_{2.5}$ mass makes up more than half of the total $PM_{2.5}$ mass in eastern Canada and constitutes a substantial portion in the rest of the country (MSC, 2002). Amongst the precursor gases, SO_2, NO_X, and NH_3 were the most significant contributors to secondary particle formation in Canada.

Primary and secondary particles have long lifetimes in the atmosphere (days to weeks) and can travel long distances (hundreds to thousands of kilometers). They tend to be uniformly distributed over urban areas and larger regions. As a result, particles are not easily traced back to their original sources. The chemical composition of particulate matter in the atmosphere, however, can provide clues about its origins. Furthermore, the composition of individual particles can not only provide information regarding the formation and chemistry of these particles, but can also help to identify the source of the particles through the source apportionment technique (i.e., elemental fingerprinting).

In the most of source apportionment studies, source profiles are taken from the literature with recognition that these profiles do not necessarily represent the location (Alberta Environment and Alberta Research Council, 1998; Chow et al., 1995; Fraser et al., 2003; Glover et al., 1991; Yu et al., 2002). Table 4 illustrates commonly known sources of particulate matter and the elemental fingerprint of each based on a review of previous emission profile studies and source receptor studies. In addition, the U.S.EPA Speciate Database is a useful resource for particulate matter source apportionment studies (U.S.EPA, 2002).

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Table 4   Elemental profiles based on the source contributions.

Emission Source	Fine Particles Main (>1%) Trace (<1%)	Coarse Particles Main (>1%) Trace (<1%)
Road dust (paved and unpaved) [2, 6, 11, 13, 17, 19, 21, 24, 25, 29, 30]	**K, Ca, Fe, Si, (Na, Cl)*** S, Cl, Pb, Zn	**Al, Fe, Si, K, Ca** Cr, Sr, Pb, Cd, Zr, P, Zn, Ba, S, Cl, Mn, Ti, Na, V, Mg, Co, Sb, Ce, La, Sm, Th, Sc, Ni, Cu, Br
Crustal weathering (wind blown dust) [1, 2, 3, 4, 5, 7, 8, 9, 10, 11, 13, 14, 17, 18, 25, 26, 27, 28,]	**Si, Fe, Al, K, Ti** Pb, S, Ca, Fe, I	**Si, Al, Mg, K, Ca, Fe** Cr, Mn, Sr, Zn, Ba, P, S, Cl, Ti, Sb, Pb, Na, V, Cu
Agricultural soils [11, 25, 27]	**K, Cl, Si, S** Ca, Al, F, Na, Fe, Cu, Pb, Br	**Si, Al, K, Ca, Fe** Cr, Zn, Sr, S, Cl, Mn, Ba, Ti
Biomass-burning (wood burning) [4, 5, 10, 15, 22, 23, 25, 27,]	**Cl, K** S, Ca, Mn, Fe, Zn, Br, Rb, Pb, Cu, P	**K, Cl** As, Cd, Cr, Cu, S, Pb, Ca, Mn, Ni, Hg, Se, Zn, Fe, Sr, Na, Ba, Mg
Refuse incineration [1, 3, 6, 10, 14, 17, 25, 27, 28]	**Cl, Si, S, Ca, Fe, Br, La, Pb** Al, Ti, Zn, Hg, V, Mn, Cu, Ag, Sn, K, Cd	**Zn, Na, Al, Ag, In** Br, Fe, Sb, Cu
Motor vehicles [2, 3, 4, 5, 6, 8, 9, 10, 11, 14, 15, 18, 20, 22, 24, 25, 28, 29, 30]	**S, Ca, Fe, Zn, Na** Si, Cl, Al, P, Mn, Cr, Ni, Y, Sr, Ba, Ti, Cu, K	**Fe, Sb, Na, Ca** Br, S, Cl, Zn, Mn, Pb, Cd, Si, Al, Ti, K, Ni, Cu
Residual oil and heating [1, 4, 8, 9, 11, 14, 18, 19, 25, 29, 27, 28,]	**V, S, Ni** Zn, Fe, Si, Cl, Ti, Cr, Co, Ga, Se	**V, S, Ni, Na, Fe** Al, Si, Cl, K, Ti, Cr, Cu, Br, Al, Mn, Zn, Pb
Oil fired power plant [10, 14, 25, 27]	**S, Na, Ca, Pb** Al, Si, P, K, Zn, V, Ni, Se, As, Br, Ba	**V, Ni, Na, Cl, Ca** Al, Ba, Br, La, Sm, Mn
Coal fired power plant [1, 6, 10, 17, 25, 26, 27, 28]	**Si, Al, S, Ca, Fe** P, K, Ti, V, Ni, Zn, Sr, Ba, Pb, Cl, Cr, Mn, Ga, As, Se, Br, Rb, Zr	**Al, Fe, S, Si, Ca, Se** As, Na, K, Ti, V, Mn, Cu, Zn, Pb
Sulfates [3, 4, 5, 8, 9, 12, 25, 30]	**S, Pb, Fe, Si** Zn, Al	**S, Al, Fe** K, Pb, Mn
Construction [11, 14, 15, 25, 26, 28,]	**Si, Al, Fe, K, Ca** S, Ti, Mn, V, Zn, Cl, Cu, Rb, Mg	**Si, Al, K, Ca, Fe** Mn, Zn, Sr, Ba, S, Ti, Mg, Na, V, Cu, Ni, Br
Salts [5, 6, 8, 10, 11, 12, 14, 17, 25, 28]	**Na, Cl** Al, Si, K, Ca, Fe, Cu, Zn, Ba, La, Ti, V, Ni, Sr, Zr, Pb, Ag, Sn, Sb, Br	

[1] Alpert and Hopke, 1980; [2] Chang et al., 1988; [3] Alpert and Hopke, 1981; [4] Rojas et al., 1990; [5] Morales et al., 1990; [6] Van Borm et al., 1990; [7] Tuncel et al., 1985; [8] Pratsinis et al., 1988; [9] Stevens et al., 1984; [10] Chow, 1995; [11] Maenhaut and Cafmeyer, 1998; [12] Swietlicki et al., 1996; [13] Fung and Wong, 1995; [14] Huang et al., 1994; [15] Sexton et al., 1985; [16] Janssen et al., 1997; [17] Kowalczyk et al., 1982; [18] Cass and McRae, 1983; [19] Silva and Prather, 1997; [20] Fergusson and Ryan, 1984; [21] Liu et al., 1995; [22] Stevens, 1985; [23] Kulmala et al., 1986; [24] Linton et al., 1980; [25] Chow and Watson, 1998; [26] Cooper and Watson, 1980; [27] U.S.EPA, 2002; [28] Harrison et al., 1996; [29] Yassoglou et al., 1987; [30] Schneider, 1987. * de-icing salt.

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2.1.4 Ambient Levels of Particulate Matter

Ambient levels of particulate matter are affected by a number of factors, including local sources of particulate matter, long-range transport, and meteorological and topographical conditions (WGAQOG, 1998). As a result, particulate matter levels vary with season, time of day, and even within a city or region. As a general rule, elevated levels of particulate matter can be expected in situations where local sources are significant, where long-range transport is significant, and/or where meteorological and topographical conditions hinder the dispersion of air pollutants (WGAQOG, 1998).

Generally, particulate matter can be monitored in three different types of areas (U.S.EPA, 1996):

- Remote background (natural)
- Regional background and
- Urban (or industrial)

Remote background areas are considered to be influenced only by natural sources of particulate matter, and therefore to contain levels of particulate matter that would be detected in the absence of anthropogenic sources (U.S.EPA, 1996). Extreme examples of remote background areas include Antarctica, Greenland, or over an ocean. Since even remote areas can be impacted by the long-range transport of anthropogenic emissions, it is difficult to ascertain the exact magnitude of background concentrations of particulate matter. With this in mind, background concentrations of PM_{10} have been estimated to fall within the range of 4 to $12\mu g/m^3$ for a 24-hr average, and $PM_{2.5}$ concentrations are believed to fall within the range of 1 to $5\mu g/m^3$ for remote regions of North America (Environment Canada and Health Canada, 2000).

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Unlike remote background areas, regional background areas are influenced not only by natural sources, but also by anthropogenic sources (local and/or long-range transported emissions). Thus, the magnitude of particulate matter levels in regional background areas can vary dramatically from region to region. Urban (or industrial) areas include any region that is affected by all types of particulate matter emissions, including local industrial point sources; the levels of particulate matter in these areas can vary widely.

Little information exists on natural background levels of particulate matter in Canada since most monitoring occurs in urban centres. A study of six remote rural locations in Alberta showed PM_{10} concentrations ranging from 2.9 to $12\mu g/m^3$ with a mean value of $8.8\mu g/m^3$, and $PM_{2.5}$ concentrations between 1.7 to $3.8\mu g/m^3$ with an average of $3.2\mu g/m^3$ (Cheng et al., 2000). $PM_{2.5}$ concentrations measured at rural sites in eastern Canada while under northerly transport conditions ranged from $4.1\mu g/m^3$ at Egbert, Ontario to $6.1\mu g/m^3$ at St. Anicet, Quebec (Brook et al., 1997). In the western United States, natural background levels of 4 to $8\mu g/m^3$ have been reported for PM_{10} and 1 to $4\mu g/m^3$ for $PM_{2.5}$ (U.S.EPA, 1996). Data from the National Air Pollution Surveillance (NAPS) network from 1984 to 1995 show that most Canadian cities experience mean 24-hr PM_{10} concentrations in the range of 20 to $30\mu g/m^3$, and concentrations of 8 to $20\mu g/m^3$ for $PM_{2.5}$ (WGAQOG, 1998).

2.1.5   Meteorological Impacts

Particulate matter can be influenced by meteorology in several ways. Certain meteorological conditions have long been recognized as being associated with the worst air pollution episodes (Gong et al., 1998; Strader et al., 1999; Turpin and Huntzicker,

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1995). In general, four primary meteorological parameters are considered to affect particle formation, transport, and removal.

- **Temperature**

It has been demonstrated that temperature, in particular, plays a strongest role in dictating seasonal particulate matter patterns and varying particulate matter composition in summer and winter episodes (Lyons and Scott, 1990; Prandle *et al.*, 1997; Seinfeld and Pandis, 1998). Higher temperatures usually favour more reactive chemistry (i.e., faster oxidation and the production of condensable gases), higher OH^- concentrations, more SO_4^{2-} production, deeper vertical mixing, and higher emissions of VOCs from biogenic or anthropogenic evaporative sources. Higher temperatures also encourage the formation of sulphate aerosols. Lower temperatures are conducive to the condensation of some organic gases into the solids, or liquid phases, to the formation of nitrate aerosol, and to reduced vertical mixing (Prandle *et al.*, 1997; Ying and Kleeman, 2003).

In the summer, conditions of vertical stability, low wind speeds and high temperatures are usually met in high-pressure systems and have been associated with $PM_{2.5}$ mass episodes. In the winter, $PM_{2.5}$ mass episodes are associated with cold temperatures, which facilitate the formation of nitrate particle and stagnating air masses, which are conducive to the build-up of local precursor emissions. Moreover, during the winter and lower temperatures seasons, emissions from combustion due to heating and anthropogenic condensable gases will increase when compared to the summer.

- **Insolation**

Insolation refers to the amount of solar radiation incident on a horizontal surface at a specific level. The months of May through August are generally considered to have

high insolation in Alberta (Clean Air Strategic Alliance, 2003). High insolation favours the photochemical formation of secondary particulate matter. Peak insolation happens at the summer solstice, though the actual radiation received depends on cloud cover and atmospheric turbidity (Clean Air Strategic Alliance, 2003).

- **Wind Speed and Direction**

Lower wind speeds imply lower atmospheric mixing and thus less opportunity to allow primary particulate matter to accumulate along with precursors to secondary particulate matter. In addition, photochemical episodes are most likely to occur during low to moderate wind speeds. High wind speeds tend to disperse particulate matter and precursors, preventing the build-up of high particulate matter concentrations. Occasionally very strong winds may cause an elevation of $PM_{2.5}$ levels due to wind-blown dust (Clean Air Strategic Alliance, 2003).

Wind direction is the most useful data for determining the direction of atmospheric transport in the immediate environs of the monitoring site. An assessment of wind direction before and during an episode can indicate whether areas of significant anthropogenic emissions are contributing to the particulate matter measured at a given monitoring site. For longer-range transport assessment, back trajectories are considered as a more appropriate tool than local wind direction (Li, 2004; Snyder and Strawbridge, 2004; Stohl, 1996; White et al., 1994).

- **Mixing Height and Inversions**

Relatively higher mixing heights imply that air pollutants can be diluted by greater vertical mixing. Lower mixing heights mean that air pollutants tend to be mixed over a relatively thinner vertical layer near the surface of the earth, and thus can build-up

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to higher particulate matter concentrations (Clean Air Strategic Alliance, 2003). Mixing heights are also very seasonally dependent, being heavily influenced by local meteorological parameters. For example, in Alberta, the median mixing height at solar noon in the spring is 683 m; while in the summer, fall, and winter the mixing heights tend to decrease to about 659, 381, and 162 m, respectively (Myrick *et al.*, 1994).

An inversion is the most stable atmospheric condition, where the temperature of the atmosphere increases with increasing height. Stable atmospheric conditions therefore result in higher concentrations of precursor gases and more reactive chemistry (Ortiz *et al.*, 1993). Strong inversions often occur during the winter, or in high pressure systems and/or on clear nights throughout the year. These periods are conducive to increasing particulate matter levels. For example, on summer nights, strong inversions may lead to the accumulation of particulate matter precursors that contribute to the formation of secondary particulate matter formation on the following day.

2.2 Particulate Matter Measurement

Particulate matter measurement can be divided into the following procedures: (1) ambient particulate matter sampling; (2) mass measurement of particulate matter mass level; and (3) elemental and morphological analysis.

2.2.1 Ambient Particulate Matter Sampling

- **Types of Filter**

Filter sampling is the most common method for capturing PM_{10} and $PM_{2.5}$. Before discussing samplers that employ filters, it is important to identify an appropriate filter for analytical testing in receptor modeling studies. A number of factors, such as filter density, porosity, pH, and chemical and physical composition, play a crucial role in dictating a

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filter's performance (U.S.EPA, 1999a). Several other characteristics are also important in selecting a filter type; these include sampling efficiency, mechanical stability, chemical stability, temperature stability, blank concentrations, flow resistance and loading capacity, and cost and availability.

The most common filters used for ambient air quality studies are glass fibre filters due to their robustness, low moisture retention, and high collection efficiencies. If subsequent microscopic and/or chemical analysis is required, however, membrane filters are more suitable (Dzubay, 1991). Table 5 shows the compatibility of different filter media with sampling and analysis techniques.

Table 5 **Compatibility of filter media with sampling and analysis methods.**
(Dzubay, 1991)

	Ringed Teflon	Zefluor [1]	Quartz
Sampling			
PM_{10} Hi-Vol	None	fair	excellent
Dichotomous	excellent	excellent	excellent
Resistance to clogging	Fair	fair	excellent
Analysis			
Gravimetric	Good	good	fair-good [2]
XRF	excellent	poor-fair [3]	poor
PIXE	fair	poor	poor
INAA	excellent	excellent	difficult
ICP	excellent	excellent	good

[1] Zefluor® are registered Trade Marks of Gelman Sciences of Ann Arbor MI.
[2] Quartz is good for gravimetric analysis when the relative humidity is properly controlled.
[3] Zefluor is fair for XRF only if sample is collected on the membrane side.

Ringed Teflon is a thin Teflon (PTFE) filter pre-mounted on annular polymethylpentene, and Zefluor is a porous Teflon mat. Quartz filters are less prone to clogging than those of Teflon (Dzubay, 1991). PTFE filters are employed to obtain

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atmospheric particulate matter samples for the determination of mass concentration and for the subsequent measurement of a wide variety of trace elements and scanning electron microscopy (SEM). Pretreated quartz fiber filters are used to collect samples for the determination of atmospheric carbonaceous aerosol concentrations. Membrane filters are the best for sampling particulate matter. With SEM, the surface of a membrane filter is smooth enough for particles to be viewed easily, whereas fibre filters are far too rough and fibrous to allow particles to be viewed (IEA, 1998).

- **Types of Sampler**

Current techniques for particulate sampling have been selected, to some extent, to capture those particles that can penetrate the human lung. Sampling inlets are designed to have D_{50} cut-off points (the point where 50% of the particles pass the cut-off point and 50% do not) of either PM_{10} or $PM_{2.5}$ (or another point in between), as required. Conditions in the human lung and within sampling equipment, however, are incomparable. Therefore, the aim of sampling equipment is to trap all material below the required cut-off value and it is expected to provide as much data as possible on volume and, if possible, a viable sample for other analyses, such as individual particle morphological and chemical analysis (IEA, 1998). This will be important for such studies as source apportionment or toxicology.

There are a large number of sampling techniques and a wide variety of equipment available for PM_{10} and $PM_{2.5}$, each with its own advantages and disadvantages. In general, these are classified into two categories: (a) continuous (hourly) basis, and (b) intermittent (24-hr average) basis as described below:

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a)   Continuous Sampling

Due to the public need for near real-time air quality reporting and forecasting, continuous-based particulate matter monitoring technologies have been developed. The tapered element oscillating microbalance (TEOM), produced by Rupprecht & Patashnick Inc., USA, is one commercially available device for continuous real-time measurement of airborne particles. US EPA designates the TEOM as a federal equivalent method (FEM) for the 24-hr PM_{10} and $PM_{2.5}$ measurements (U.S.EPA, 1990).

The TEOM consists of a filter cartridge on top of a hollow tapered crystal element. It continuously draws an air sample through an inlet stream that aerodynamically separates particles of a specified diameter (e.g. 2.5 or 10 μm). A mass flow controller unit maintains constant flow through the system. The air sample then passes through a filter that is attached to a tapered element in a mass transducer. This tapered element vibrates at its natural frequency as particles are deposited onto the filter, the oscillating frequency changes in proportion to the amount of mass deposited (Rupprecht & Patashnick, 1996). To minimize thermal expansion of the tapered element, the working temperature is maintained at a constant value, typically 30°C or 50°C.

The heating results in a loss of volatile or semi-volatile compounds, thus the TEOM system often underestimates particulate matter concentrations when compared with manual gravimetric samplers (e.g. dichotomous samplers). At a number of locations in Canada, TEOMs are co-located with dichotomous samplers and ongoing comparisons of these two $PM_{2.5}$ measurement methods are being conducted. Preliminary data confirm the results of similar studies in Europe, the USA and western Canada, namely, that TEOM mass measurements are generally lower than mass values measured by other

gravimetric methods. This is due largely to the volatilization of semi-volatile compounds from the TEOMs (Mignacca and Stubbs, 1999; Soutar *et al.*, 1999).

b)   Intermittent Sampling

Two types of integrated gravimetric samplers, namely, high volume FRM (the US federal reference method) samplers and low volume personal or portable samplers, are commonly used for the collection of ambient particulate sample (Baldauf *et al.*, 2001). The most common types used for outdoor field studies of TSP (total suspended particulate, particulate matter of all size fractions), PM_{10}, or $PM_{2.5}$ are high volume FRM samplers. These two types of samplers use appropriate size selective inlets (SSI) for particle separation, with sampling flow rate as the primary difference. A FRM sampler typically draws approximately 17 liters per minute or greater in order to draw 24 m^3 of ambient air over a 24-hr period (Chow, 1995). Portable low volume samplers, however, have reduced sampling rates to as low as one to five litres per minute (Chow, 1995). One such low volume monitor is the MiniVol (Airmetrics, OR), a small and much more cost effective sampler than FRM samplers. The MiniVol sampler was co-developed by the Lane Regional Air Pollution Authority and the US Environmental Protection Agency (Airmetrics, 1998).

The MiniVol sampler does not require complicated siting, and can operate under a variety of climatic conditions (Airmetrics, 1998). This sampler has gained popularity in spatial and temporal gravimetric monitoring studies of PM_{10} and $PM_{2.5}$ (Baldauf *et al.*, 2001). A group of researchers used the MiniVol sampler to compare four other types of samplers in indoor air quality studies, and found good agreement between the samplers for 24-hr average PM_{10} mass measurements (Heal *et al.*, 2001). In a separate outdoor co-

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location study of PM_{10} and $PM_{2.5}$, statistically comparable findings were reported between MiniVols, a dichotomous Versatile Air Pollutant Sampler (VAPS), and a Tapered Elemental Oscillating Microbalance (TEOM) (Baldauf *et al.*, 2001).

The MiniVol is not a referenced method sampler. The method used in the MiniVol device is a modification of the standard particulate matter reference method as outlined in the Code of Federal Regulations (40 CFR 50, Appendix J) (U.S.EPA, 1999a). Recent research has demonstrated results that closely match reference methods (Tropp *et al.*, 1998). In addition, MiniVol samplers give good comparisons with equivalent method dichotomous samplers (Qones *et al.*, 1998). Environment Canada uses the MiniVol as a saturation sampler (i.e. many deployed in a given area), and they have been used extensively in several parts of Alberta under a variety of climatic conditions (Alberta Health, 1997).

2.2.2   Mass Measurement

Gravimetric analysis is the most common analytical technique for ambient particulate matter studies. The data are used to calculate particulate mass concentrations ($\mu g/m^3$) and/or chemical composition profiles (ng/m^3). The net particulate matter mass on a filter is determined by weighing the filter before and after sampling with a microbalance in an environment where temperature and relative humidity are controlled. Prior to gravimetric measurement, Teflon filters are conditioned for 24 hours at a constant relative humidity of $40\pm1\%$ and at a constant temperature of $22\pm3°C$. The minimum readability of the balance is 0.001 mg, the instrumental detection limit for mass collected on filters is 0.004 mg, and the corresponding method detection limit is about 0.02 mg (U.S.EPA, 1997).

2.2.3 Elemental and Morphological Analysis

Chemical speciation is a critical part of many ambient monitoring programs, but it is a complex process in its early stages of development. Currently, there is a variety of speciation monitors in use for ambient air monitoring and research programs, but there are no established reference methods for chemical speciation measurements (CCPA, 2001). Chemical speciation analysis can be broken into the three most common categories: elements, ions, and carbon. A comparison of analytical options for each of these categories is present in Table 6.

Table 6   Comparison of Canadian NAPS and U.S. PM$_{2.5}$ chemical speciation analytical technique.
(CCPA, 2001)

Filter Medium	Target Species	Canadian NAPS	Proposed U.S. PM2.5 Network
PTFE (Teflon®) filter	Elements: Al to Pb Mass: nitrate / sulphate, total carbon.	EDXRF Gravimetry IC	EDXRF (IO-3.3) Gravimetry
Nylon filter with nitric acid denuder	Anions: nitrate and sulphate Cations: ammonium, sodium, and potassium.		IC (Improve Method)
Pre-fired quartz fiber filter with gaseous organic denuder	Total Carbon (including organic, elemental, carbonate carbon).		TOA (NIOSH 5040)

For elemental analysis, Energy Dispersive X-ray Fluorescence (EDX) is utilized by NAPS and proposed for the U.S. chemical speciation network. Another option that is often utilized is proton induced X-ray emission (PIXE) spectroscopy. X-ray fluorescence (XRF) and proton induced X-ray emission (PIXE) spectroscopy quantify the

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concentrations of elements with atomic numbers ranging from 11 (sodium) to 92 (uranium). In addition to providing a large number of chemical concentrations, neither XRF nor PIXE require sample preparation or extensive operator time after being loaded into the analyzer. Filters remain intact after analysis and can be used for additional analyses by other methods.

Inductively coupled plasma (ICP) and instrumental neutron activation analysis (INAA) are not as commonly applied to aerosol samples as XRF and PIXE because these methods are more expensive. ICP requires the filter to be destroyed, and INAA wads up the filter and makes it radioactive. These analyses are useful in certain applications owing to lower detection limits for some species used in source apportionment studies. Atomic absorption spectrophotometry (AAS) is useful for a few elements, but it requires too great a dilution of the sample to be an effective technique when many different elements are to be measured (Chow, 1995).

2.2.4   Particulate Matter Measurements in Canada

In Canada, a national ambient air-monitoring network, called the National Air Pollution Surveillance (NAPS) network, was established jointly in 1969 by the federal, provincial, and municipal governments. Currently, NAPS network sites are equipped with dichotomous (often referred to as dichots) and TEOM samplers. Dichots are used to report both fine ($\leq$2.5 μm) and coarse (2.5 to 10 μm) mass, and samples are typically collected for 24 hours once every six days (Brook et al., 1997). Most dichotomous filter samples are analyzed by energy dispersive X-ray fluorescence (EDXRF) for approximately 50 elements and by high performance liquid chromatography (HPLC) for a number of anions and cations (Dann, 1994). TEOM real-time particle monitoring has

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been established to report hourly values of $PM_{2.5}$ mass (aerosol chemical composition is not measured with this instrument).

The addition of TEOM real-time particulate matter monitoring to NAPS has greatly increased the spatial and temporal resolution of the network. However, as with all methods for measuring the mass of particles or aerosols suspended in the air, there are uncertainties with TEOM measurements associated with the loss of semi-volatile chemical constituents. The co-located Canadian measurements provide a link between measurements of the spatial patterns of $PM_{2.5}$ using merged data from NAPS dichotomous samplers and TEOMs.

2.3   Particulate Matter Trends

2.3.1   Canada National Trends

In May 2004, Environment Canada released a report on air quality trend analysis from a limited number of urban sites for the period of 1990 to 2001 (Environment Canada, 2004a). The mean annual particulate matter concentrations from all urban sites in 2001 were 80% lower than in 1990. Data for missing years of data were calculated by linear interpolation from the surrounding years (Environment Canada, 2004a).

Annual mean concentrations of $PM_{2.5}$ decreased at all urban sites across Canada over the past decade, while annual mean concentrations of PM_{10} decreased at most urban sites (Environment Canada, 2004a). The mean annual $PM_{2.5}$ and PM_{10} concentrations in 2001 were 27% and 34% lower than in 1990, respectively. However, both total $PM_{2.5}$ and total PM_{10} emissions increased during this time, and increases of 7.7% and 11.3% were produced for total $PM_{2.5}$ and PM_{10} accordingly. Open sources (predominantly dust from unpaved roads), industrial sources (predominantly iron ore mining), and non-industrial

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fuel combustion accounted for the largest increase in particulate matter emissions during this time, while emissions from transportation sources decreased. The contrasting trends in annual mean $PM_{2.5}$ and PM_{10} concentrations and emissions data likely reflect the urban nature of the measuring sites (Environment Canada, 2004a).

Trends in inorganic concentrations varied considerably between compounds at urban sites in Canada during this period (Environment Canada, 2004a). The greatest change observed was in lead concentrations, which decreased at urban sites in response to regulations requiring the removal of lead from gasoline. Iron, manganese, zinc, sulphate, and total particulate mass decreased in concentration during the past decade, while chromium, copper, nickel, and vanadium showed little net change (Environment Canada, 2004a).

2.3.2   Alberta Trends

Cheng *et al.* (2000) summarized monitoring data from the Alberta Air Quality Network for the period of 1985 to 1995 in the two major cities of Edmonton and Calgary. Also, a recent review study revealed elemental trends in urban ambient particulate matter in downtown Edmonton and Calgary for the period from 1991 to 2002 (McCullum *et al.*, 2004). A statistically significant decrease in PM_{10} and $PM_{2.5}$ levels in both Edmonton and Calgary was noted in these studies.

$PM_{2.5}$ and PM_{10} levels in Edmonton and Calgary are similar to those measured in other urban areas of Canada. In Edmonton, higher coarse particulate levels are generally observed in the spring (March to May), primarily due to agricultural activities (i.e., spring ploughing, planting, etc.), and other sources of geological or crustal material (i.e., the suspension of road dust) (Cheng *et al.*, 2000). In Calgary, slightly higher PM_{10}

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concentrations are noted in winter (December to February), because warm Chinook winds that move in from the west cause snow to melt, thereby exposing surfaces to the entrainment of geological or crustal material by natural processes (i.e., wind erosion) (Cheng et al., 2000).

Although industrial sources have an impact on ambient PM_{10} and $PM_{2.5}$ levels in both Edmonton and Calgary, their influence is perceived to be relatively unimportant during seasonal peaks. Concentrations of $PM_{2.5}$, NO_3, and NH_3 are lower in Edmonton and Calgary than other urban and rural areas across Canada (Cheng et al., 2000). Table 7 presents the average annual median particulate matter concentrations in the cities of Edmonton and Calgary, as compared to some other sites in North America.

Table 7 **Average annual median $PM_{2.5}$ and PM_{10} concentrations ($\mu g/m^3$) in Edmonton and Calgary from 1985 to 1995, and comparison to other cities in North America.**
(Alberta Environmental Protection, 1998)

	$PM_{2.5}$	PM_{10}	$PM_{2.5}/PM_{10}$
Edmonton [1]	9	27	0.33
Calgary [1]	9	23	0.39
Winnipeg [2]	10.3	28.7	0.36
Toronto [2]	16.8	28.1	0.60
Montreal [2]	15.9-20. 9 [3]	27.8-44.6 [3]	0.47-0.57
Washington, DC [4]	26.5	34.9	0.76
St. Louis [5]	17.7-19.0	27.6-31.4	0.61-0.64

[1] Brook et al., 1997; [2] Measurements were made at two different sites; [3] Malm et al., 1994; [4] Spengler et al., 1983 and Dockery et al., 1992.

In addition, seasonal variations in volatile organic compounds (VOCs) concentrations were analyzed by Cheng et al. (1997) at downtown and industrial sites in Edmonton for the period from 1991 to 1993. For the downtown site, maximum values

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occurred in winter and minimum values in summer (Cheng *et al.*, 1997). This study also concluded that seasonal changes of VOC at the downtown site were primarily due to meteorology, while seasonal changes could not be detected at the industrial site owing to nearby industrial emissions which may have been higher in summer.

Recently, based on the regional allocation of source emissions, the Clean Air Strategic Alliance (Clean Air Strategic Alliance, 2002) issued a report on the forecast of common air contaminants (CAC) in Alberta for 1995 to 2020. Table 8 describes the total Alberta CAC emission projections. The focus of this report is on the growth of anthropogenic emissions from industrial sources in Alberta. Large natural sources were documented and included in total emissions, but these were kept constant at 1995 levels in the forecast period from 1995 to 2020.

Table 8   Total Alberta CAC emission projections.
(Clean Air Strategic Alliance, 2002)

Contaminant	1995	2000	2005	2010	2015	2020	1995 to 2010	1995 to 2020
PM_{total}	4993	5749	6368	6878	7358	8079	38%	62%
PM_{10}	1530	1722	1889	2032	2168	2366	33%	55%
$PM_{2.5}$	261	281	304	327	352	383	25%	46%
SO_x	609	515	519	561	561	562	-8%	-8%
$NO_{,}$	715	771	783	851	891	907	19%	27%
VOC	2051	2045	2098	2256	2296	2303	10%	12%
CO	1969	1728	1568	1508	1574	1614	-23%	-18%
NH_3	148	235	256	279	305	333	88%	125%

Note: emission in kilotonnes.

2.4 Particulate Matter Impacts and Related Regulations

2.4.1 Particulate Matter Impacts

From the perspective of human health, there is growing evidence that particulate matter present in the urban atmosphere can pose a health risk to a broad spectrum of the population (Environment Canada, 1998). This evidence comes from epidemiological studies and provides the basis for Canadian air quality standards and guidelines. The awareness of potential exposure to particulate matter has increased since the Government of Canada, under Environment Canada and Health Canada, released a priority substance list assessment report on "Respirable Particulate Matter Less than or Equal to 10 Microns" (Environment Canada and Health Canada, 2000).

Coarse particles tend to accumulate in the nose, throat, and airways of the lung and can potentially aggravate asthma (U.S.EPA, 1997; Chow and Watson, 1998). Fine particles have the greatest chance of reaching the furthest regions of the lung. Delicate tissues involved in the exchange of oxygen and carbon dioxide are present in this alveoli region (UK Department of the Environment, 1995; Farber and Wilson, 1961).

Inhaled particles can affect pulmonary functions either temporarily or permanently, which can potentially lead to the development of chronic bronchitis, aggravated bronchial asthma, pulmonary emphysema, and acute respiratory symptoms, including aggravated coughing, difficult or painful breathing, decreased lung function such as shortness of breath, and premature death (Health Canada, 1996; Health Canada and Ontario Ministry of Health, 1997; U.S.EPA, 1997; Brook et al., 1997; Tiittanen et al., 1999). Particles may also affect the body's defensive mechanisms; create scarring of

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the lung tissue, and cause eye and throat irritations, headaches and allergy problems (Rhebergen *et al.*, 1999).

In Canada, it has been reported that hospital admissions tend to increase with increased levels of particulate matter in urban areas, even at levels regularly experienced by the general population (Environment Canada; 1999, 1998). Those individuals at greatest risk from exposure to particulate matter are children, the elderly, and those with chronic respiratory problems (U.S.EPA, 1997; Health Canada and Ontario Ministry of Health, 1997). Children tend to be at the highest risk, as they breathe 50% more air per pound of body weight than adults and their respiratory systems are still developing (U.S.EPA, 1997). Thus, the debate over evidence to identify an underlying cause linking airborne particulate matter to certain health effects has intensified in the last decade. Uncertainties exist with respect to particle mass, size, and composition as a function of emission sources. With health effects varying for different particulate compounds, it becomes important to characterize and apportion sources using receptor modeling or source to receptor techniques (U.S.EPA, 1994).

The primary aesthetic effect of fine particulate matter is a potential visual impairment. To many in the general public, poor visibility is an indicator of poor air quality. It affects quality of life, poses transportation safety problems, and has direct economic costs associated with the potential loss of revenue from tourism (McNeill et al., 2001). In addition to visual impairment, there is a "soiling" effect of airborne particulate matter. When particles settle out of the atmosphere, they can accumulate on trees, crops, cars, homes, buildings, and statues, resulting in an irritating and unattractive environmental concern (Rhebergen *et al.*, 1999, U.S.EPA, 1997).

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2.4.2 Related Regulations

As evidence for the negative health effects of particulate matter grows, regulations on particulate matter are becoming increasingly stringent. Guidelines like the Canada Wide Standards (CWS) are currently being identified for PM_{10} and $PM_{2.5}$ (D'Innocenzio *et al.*, 1998). PM_{10} and $PM_{2.5}$ guidelines are typically based on health related studies, whereas guidelines for TSP are based on nuisance effects and the visual reduction of particulate matter (Myrick, 1996). A summary of the Alberta Guidelines is presented in Table 9. Other Provincial, National, and International guidelines and regulations are summarized in Appendix 8.1.

Table 9 **Alberta specific particulate matter guidelines.**

Location / Agency	Parameter	Guideline / Regulation
Alberta (Alberta Environment, 2000; Alberta Statutes and Regulations, 1997)	TSP	$100\ \mu g/m^3$ as a 24-hr average concentration $60\ \mu g/m^3$ as an annual geometric mean
	Dust fall	$53\ mg/100\ cm^2$ per 30 days in residential and recreation areas $158\ mg/100\ cm^2$ per 30 days in commercial and industrial areas
	Total Mass	$5\ mg/m^3$ of diatomaceous earth (8 hr occupational exposure) $10\ mg/m^3$ of nuisance particulate (8 hr occupational exposure)
	Respirable Mass	$2\ mg/m^3$ of diatomaceous earth (8 hr occupational exposure) $5\ mg/m^3$ of nuisance particulate (8 hr occupational exposure)

Alberta Environment developed a Particulate Matter and Ozone Management Framework in response to the endorsement of the Canada Wide Standards (CWS) for

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Particulate Matter and Ozone by the Canadian Council of Ministers of the Environment

(CCEM) (except Quebec). Figure 3 presents a simplified diagram of the particulate

matter management framework (ozone concentration is exclusive in this diagram).

CWS Exceedance Trigger
$PM_{2.5}$: $30\mu g/m^3$

Planning Trigger
$PM_{2.5}$: $20\mu g/m^3$

Surveillance Trigger
$PM_{2.5}$: $15\mu g/m^3$
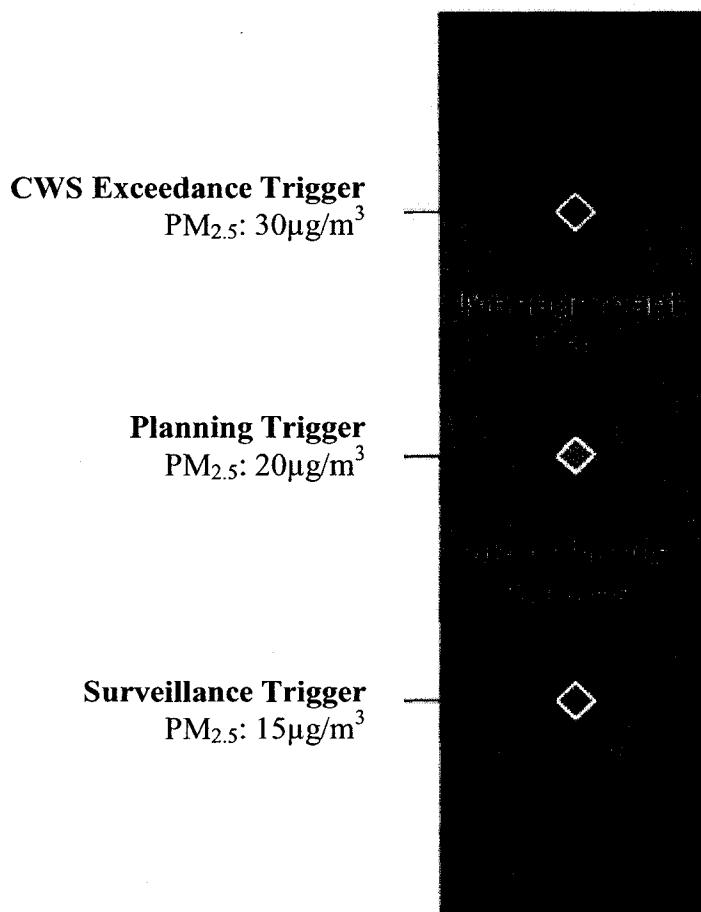
Figure 3   Alberta particulate matter management framework.
(after Alberta Environment, 2004)

Four action levels have been set out that represent a continuum of the analysis and

management activities that will be based on the measured ambient concentrations. This

framework meets and sometimes exceeds the provisions of the CWS and it recognizes

that implementation strategies may be different for different areas of the province. An

annual analysis of ambient particulate matter concentrations from Alberta's ambient air

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quality monitoring system determines the appropriate action level for each area of the province.

2.5 Statistical Study Methods

Over the last two decades, receptor models have been extensively used for the purpose of identifying and quantifying the impact of relevant sources on a measurement (receptor) site (Henry *et al.*, 1984). Receptor modeling techniques have become an important tool for estimating source to site influences at potential receptor locations. Current receptor models for ambient conditions involve measurements of chemical and/or elemental properties at a given (receptor) site. Linking contributions to various sources is based on source signatures, or elemental fingerprints. Monitoring sites are not directly located in the effluent stream of a source, rather the approach is to start from a measurement site and work back to the source(s) (Friedlander, 1981; Blanchard, 1999). The receptor modeling methodology was proposed by Hidy and Friedlander (1970), and includes the following assumptions:

- Source identities and their respective contributions to ambient pollutants can be inferred from the chemical composition of particulate matter collected at the receptor sites.

- Concentrations of airborne particulates measured at a receptor site are the sum of all the different source contributions impacting the site.

- Elemental compositions of source emissions are relatively constant in time and space.

- Source types can be identified (inferred) from characteristic elements or tracers.

There are two main types of receptor model approaches: chemical mass balance (CMB) and a multivariate "statistical" approach (Lioy and Daisey, 1987). CMB has been widely used for source apportionment studies in conjunction with FRM samplers (Kowalczyk et al., 1982; Chow et al., 1990; Lowenthal et al., 1997; Vega et al., 1997; Alberta Environment and Alberta Research Council, 1998; Chan et al., 1999). A disadvantage of this approach is that every potential source and source profile in the area of monitoring is required (Houck and Cooper, 1983). This is rarely practical in an urban setting; thus, a multivariate approach is often used.

A multivariate approach extracts source contribution information based on the variability of tracers, such as elements or chemical indicators of a source present on a set of filters. The advantage of this approach is that it allows for source contributions to be inferred without prior quantitative source composition data (Lioy and Daisey, 1987). A multivariate approach for source apportionment encompasses a wide range of statistical analysis methods, such as: Ordinary Weighted Least-Squares, Effective Variance Least Squares, Artificial Neural Networks, Partial Least Squares, Target Transformation Factor Analysis, Multiple Regression Analysis, Simulated Annealing, Genetic Algorithm, Factor Analysis / Multiple Regression, Positive Matrix Factorization, and Principle Component Analysis (Kleinman et al., 1980; Alpert and Hopke, 1981; Morandi et al., 1987; Chang et al., 1988; Pratsinis et al., 1988; Fung and Wong, 1995).

One of the most commonly used multivariate analysis methods in research is principle component analysis (PCA) (Buhr et al., 1992). The basic concept of PCA is to unravel seemingly unrelated data into source fingerprints or source profiles based on specific factors or elemental tracer data detected at a receptor location. PCA is a well-

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recognized form of multivariate analysis. It was introduced a century ago by Pearson (1901); however, the use of computers has facilitated the increased use of this technique. The use of PCA has been well demonstrated in source apportionment studies using FRM samplers (Cooper and Watson, 1980; Thurston and Spengler, 1985; Harrison *et al.*, 1997; Biegalski *et al.*, 1998; Pia *et al.*, 1998).

The basic principles of source apportionment start with the total particulate mass collected on a filter at a receptor-monitoring site (m), represented by (Friedlander, 1981):

$$m = \sum_{j=1}^{p} M_j \dotfill (3)$$

where; p sources (each labeled j) are emitting M_j mass of particles. This represents the total mass on a filter, however if the mass of a specific chemical or elemental species (m_i) is required then equation (3) can be re-written as:

$$m_i = \sum_{j=1}^{p} M_{ij} F_{ij} \dotfill (4)$$

where; M_{ij} is the mass of element i (i=1,...y) from source j (j=1,...n), and F_{ij} represents the source emission as a fraction of chemical species i emitted by source j; this is assuming that the mass of each individual chemical component is conserved. To determine a concentration, equation (4) is then divided by the total mass of deposited particulate matter, yielding:

$$C_i = \sum_{j=1}^{p} S_j F_{ij} \dotfill (5)$$

where; C_i is the concentration of chemical component i measured at a receptor-monitoring site (i.e. concentration collected on the filter), and S_j is the source

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contribution, that is the ratio of the mass contributed from source j to the total mass collected at the receptor monitoring site.

From these basic principles, PCA can then be applied in order to transform a large data set of interrelated concentration variables to reduce dimensionality to a small workable number of factors. These factors are then used to explain potential underlying relationships between data, such as elements related in source emissions. These underlying factors are generally representative of sources in the system.

The first step in PCA is to transform data into a dimensionless standardized form (normalization of parameters), referred to as a z-score. Standardization allows for the equalization of both large and small magnitude variables; otherwise the results will be influenced more by the variable with the greatest magnitude (Henry and Hidy, 1979; Gordon, 1988):

$$Z_{ik} = \frac{\left(C_{ik} - \overline{C_i}\right)}{\sigma_i} \dotfill (6)$$

where; Z_{ik} (z-score) is the standardized value of element i (i=1,...y) from observation (filter) k (k=1,...z), C_{ik} is the concentration of element i at observation k, $\overline{C_i}$ is the mean concentration of the ith element over all observations k and σ_i is the standard deviation of the ith element over all observations k. This leads to the principle component model (Henry and Hidy, 1979; Gordon, 1988):

$$Z_{ik} = \sum_{q=1}^{r} A_{iq} P_{qk} \dotfill (7)$$

where; A_{iq} is the loading matrix of the components, also known as eigenvectors or scoring coefficients, and P_{qk} is the qth (q=1,..r; number of underlying components

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influencing the data) component value for observation k. During the interpretation of scoring data, Table 10 can be used as a guide in terms of the value of A_{iq}.

Table 10   Interpretation of the PCA loadings.
(After Henry and Hidy, 1979)

Value of A_{iq}	Interpretation
-0.2 to +0.2	Almost no correlation to the factor
±0.2 to ±0.9	Proportionality towards a strong correlation to the factor
±0.9 to ±1	Strong correlation to the factor

In order to identify and delineate independent sources with PCA, there should be a large data set of samples. There should be many more observations than variables (i.e. k>q+50) if stable results are to be derived (Harrison *et al.*, 1997). In addition, this factor analysis can only distinguish approximately five to eight factors, occasionally with poor differentiation between closely related sources (i.e. vehicles and road dust) (Harrison *et al.*, 1996). The final factors ideally account for as much of the original total variance as possible and in turn, are uncorrelated with one another.

3. OVERVIEW OF STUDY AREA

3.1 Background of Study Area

The City of Edmonton and its surrounding area were selected as urban residential areas in this study. Edmonton, located at 53.5° N latitude and 113.5° W longitude, is the capital of Alberta, having a metropolitan population of ~900,000 in 2004. The Rocky Mountains, immediately to the west, prevent any sustained influence of the Pacific Ocean and lead to a continental climate with long, cold winters and short, warm summers (Cheng *et al.*, 1998).

Based on Canadian Climate Normals over the period of 1971 to 2000 (Environment Canada., 2004b), the general climate conditions in the city of Edmonton can be summarized as follows:

- The mean winter temperature is –8.7°C, and the mean summer temperature is 14.4°C.

- The mean annual precipitation is 412 mm. June, July, and August are the months of highest rainfall, totaling an average of just under 260 mm. The average annual snowfall is just over 1500 mm, varying from 300 to 2700 mm.

- The average wind speed is less than 14 km/h with little variation throughout the year. Prevailing upper level winds are west-northwesterly.

- The average bright sunshine per year is about 2,299 hours with extreme daily amounts ranging from 7.6 hours in the winter to 16.3 hours in the summer.

In addition, the city is surrounded by industry and satellite municipalities and is

the most northern major city in Canada. Early morning ground-based inversions are

frequent throughout the whole year (Myrick *et al.*, 1994).

As part of Environment Canada's NAPS network, the Alberta Department of

Environmental Protection has been routinely monitoring ambient concentrations of

particulate matter (PM_{10} and $PM_{2.5}$) using dichotomous samplers at downtown locations

in Edmonton since May 1984(Cheng *et al.*, 1998). Real-time TEOM samplers measuring

hourly concentrations of $PM_{2.5}$ and PM_{10} have been co-located in Edmonton since

November 1993 for the evaluation of particle measurement methods (Cheng *et al.*, 1998).
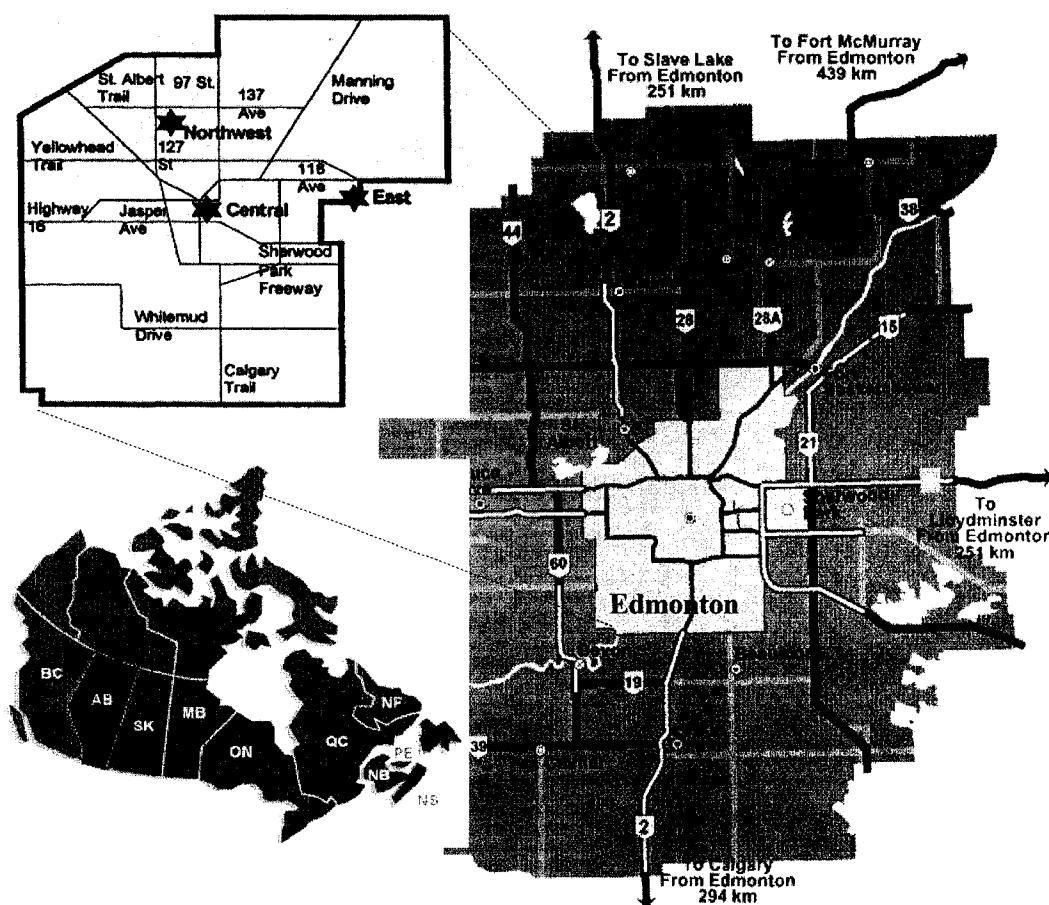
Figure 4   Map of city Edmonton and area.
(after City Edmonton, and Alberta Environment, 2003; Alberta
Environment, 1996)

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Figure 4 presents a map showing Edmonton and the surrounding area (City Edmonton, and Alberta Environment, 2003; Alberta Environment, 1996). Included in Figure 4 are the locations of three continuous air monitoring stations operated by Alberta Environment. Ambient air monitoring data and data reports form these stations are available online at the Clean Air Strategic Alliance - CASA Data Warehouse (Clean Air Strategic Alliance, 2004).

3.2 Particulate Matter Studies in Alberta

There have been remarkably few particulate matter source apportionment studies performed in Alberta, in contrast to the large body of receptor modeling development and application literature in the United States and elsewhere. An earlier source apportionment study conducted by Alberta Environment (1982) represents one of the first investigations of particulate matter in Alberta. The results indicated that most (95%) of Edmonton's TSP originates from lithophilic material. In particular, the elements silicon, aluminum, potassium, iron, and titanium were the main elements identified and these are essentially of crustal origin (Klemm et al., 1982). Small amounts of trace elements such as zinc and nickel and other aerosols such as regional sulphates, were also detected.

A comprehensive report by Cheng et al (1998) detailed the characteristics of inhalable particulate matter in Edmonton and Calgary from 1984 to 1994. More recent source apportionment studies reported on characteristics of particulate matter sampled in two small rural towns in Alberta: High Level, Alberta (McCullum and Kindzierski, 2001; Schulz and Kindzierski, 2001) and Devon, Alberta (McCullum and Kindzierski, 2001; Schulz and Kindzierski, 2001), and near a cement facility in Edmonton, Alberta (Schulz

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and Kindzierski, 2002). Table 11 and Table 12 provides the fact summary of these recent

studies in Alberta.

Table 11   Summary of the PM source apportionment studies in Alberta.

Location (Study Year)	Samplers (Chemical analysis)	PM level ($\mu g/m^3$)	Source Apportionment
			[Receptor Model] Results
Calgary, Alberta. (1984 to 1994)[1]	Dichotomous (EDXRF- IC).	Long-term median : $PM_{2.5} = 9$ $PM_{10} = 23$ $PM_{2.5}/PM_{10} = 0.39$	[CMB] for $PM_{2.5}$ • Wood Burning 27% • Transportation 21% • Asphalt Industry 11% • Paved Road Dust 4% • Cement Industry 5% • SO_4 by atmospheric reaction 4% • NO_3 by atmospheric reaction 2% • Other 27%
Edmonton, Alberta. (1984 to 1994)[1]	Dichotomous (EDXRF- IC).	Long-term median : $PM_{2.5} = 9$ $PM_{10} = 27$ $PM_{2.5}/PM_{10} = 0.33$	[CMB] for $PM_{2.5}$ • Transportation48% • Wood burning 27% • Paved Road Dust 12% • SO4 by atmospheric reaction 6% • Cement Industry 2% • NO3 by atmospheric reaction 1% • Other 4%
High Level, Alberta. (1999)[2]	TEOM MiniVols (SEM-EDX)	PM_{10} Spring: 20 Summer: 50 Fall: 12 Winter: 16	• [PCA] PM_{10} • Crustal Material 26% • Road Dust 13% • Road Salts 12% • Vehicle 11% • Residual Oil 10% • Sulfates 7% • Other 21%

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Table 12 Summary of the PM source apportionment studies in Alberta (continued).

Location (Study Year)	Samplers (Chemical analysis)	PM level ($\mu g/m^3$)	Source Apportionment	
			[Receptor Model] Results	
Devon, Alberta. (2000) [3]	TEOM MiniVols (SEM-EDX)	**PM_{10}** Aveg.: 13 (Aug to Oct, 2000)	[PCA] PM_{10} • Crustal Material 30% • Coal emissions 22% • Combustion 18% • Regional Sulphate 15% • Other 14%	
Lehigh Inland Cement Ltd, Edmonton, Alberta (2001-2002) [4]	TEOM MiniVols (SEM-EDX)	**PM_{10}** **$PM_{2.5}$** Annual 6 average: 11	[PCA] for $PM_{2.5}$ • Crustal Material 35% • Cement Particle 29% • Vehicle 11% • Fly ash 8% • Salt 6% • Other 12%	

[1] (Cheng et al., 1998); [2] (McCullum and Kindzierski, 2001); [3] (Schulz and Kindzierski, 2001); [4] (Schulz and Kindzierski, 2002).

3.3   Scope of Study

The scope of this study was to select residential sites, with one of them being co-located with an Air Monitoring (central) Station in order to identify and evaluate ambient $PM_{2.5}$ levels in these residential sites and between one selected residential site and the Air Monitoring Station site. An air sampling program was developed which involved an every second day sampling schedule by overlapping the NAPS network sampling schedule over two seasons (July to November of 2004). The Airmetrics Mini Volume Portable Air Samplers (MiniVol)® (Airmetrics, 1998) were used to collect 24-hr $PM_{2.5}$ filter samples. Laboratory work involved Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX) analysis to establish the elemental composition of $PM_{2.5}$ collected on filter samples. A receptor model utilizing principal component analysis (PCA) was performed to determine the most likely elemental profiles of the source.

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Comparisons were then made between the elemental profiles from one selected residential site and the central air monitoring station, and with previous studies, relevant literature and the U.S.EPA's Speciate 3.2 Particulate Matter Database (U.S.EPA, 2002).

4. EXPERIMENTAL PROGRAM

4.1 Particulate Matter Sample Collection

4.1.1 Intermittent PM$_{2.5}$ Sampling

A Method

The portable Mini volume Air Samplers (MiniVols)® (Airmetrics, Springfield, OR.) were used to collected intermittent 24-hr average PM$_{2.5}$ samples in this study. The MiniVols were used because of the advantages of their small, cost effectiveness, and easy siting capabilities in field (as discussed previously in Chapter 2).
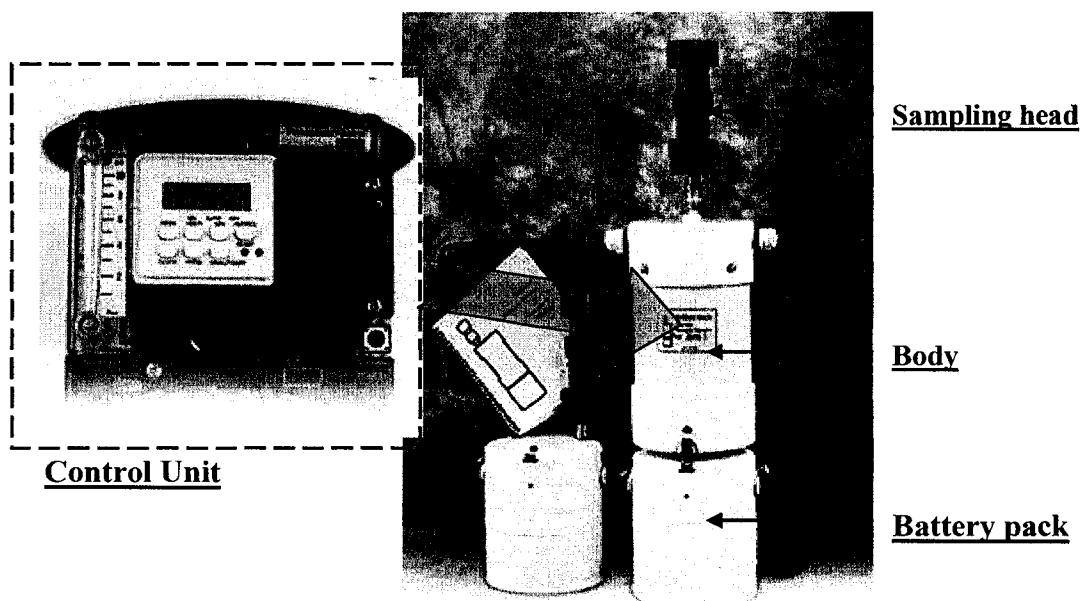
Figure 5   Photography of MiniVol portable air sampler.
(Airmetrics, 1998)

The MiniVol sampler contains a sampling head, body with control unit and battery pack (Figure 5). The control unit is equipped with timers for unattended start up and shut down.

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The MiniVols can be operated by either AC or DC supplies. In this study, all MiniVols were operated by AC supplies at flow rate 5 litre per minute (lpm) through sampling head with 2.5 μm aerodynamic diameter cutoff impactor. As considering subsequent elemental compositions analysis, the 47-mm Teflon ringed Teflon-membrane filters (Whatman, Clifton, NJ) were used in this study.

During operation of the MiniVol sampler, air was drawn through Teflon-membrane filters, leaving the entrained particles on the surface of the filter. Mass of the deposited material underwent gravimetric analysis to determine the $PM_{2.5}$ concentration, and the filter was subsequently submitted for elemental compositions analysis by using SEM-EDX technique. To ensure adequate operation of the MiniVol, they were re-calibrated prior to sampling with post flow checks performed for optimal performance. The MiniVol calibration graphs were presented in Appendix 8.2. In addition, the impactor heads were routinely greased according to the manual specifications to reduce the frequency of particle bounce and entrainment of larger particles (Airmetrics, 1998).

B Intermittent $PM_{2.5}$ Sampling Protocol

To avoid any contamination of samples during and after collection of the samples, particulate matter sampling collection by MiniVol adhered to the following procedure (McCullum and Kindzierski, 2001; Schulz and Kindzierski, 2001):

MiniVol Filters Preparation

- The filter was assembled into the MiniVol sampling impactor assembly in the laboratory before and after transportation to the sampling field.

- Filter retrieval was done under a fume-hood in the laboratory.

- The appropriate petri-slide was located.

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- The plastic bags were removed from the filter holder assembly.

- The preseparator assembly was removed.

- The filter was inspected for pinholes and cracks.

- The filter cassette was removed and placed in the cassette shoe. The top ring was removed.

- The filter was removed from the drain disk which rests on the filter support grid by using Teflon forceps (which were dipped in methanol and allowed to dry), with care taken not to shred or damage the edges of the filter and keeping it horizontal at all times.

- The filter was placed into the appropriate petri-slide.

- The petri-slide was capped and wrapped with a thin paraffin wax.

- The petri-slide was placed into a Tupperware® container and secured with bubble wrap for sample shipments.

- The old ID Tag from the Filter Holder Assembly was removed and discarded.

MiniVol Flow Rate Determination

- The weather data for each sampling day were obtained from two existing climatological stations: Environment Canada and a Weather Station at the University of Alberta. Temperature, atmospheric pressure, wind speed and direction, precipitation events, relative humidity and any other relevant information were recorded on the Air Sampling Field Log form for the day's filter.

- The flow setting was calculated via a Microsoft Excel spreadsheet following the directions in the MiniVol Operation Manual (Airmetrics, 1998).

- The desired flow was recorded on the Air Sampling Field Log form.

MiniVol Field Sample Collection

- For 24-hr mean PM2.5 sampling, the MiniVol control timer was set on 12:00 pm to 12:00 pm at all four sites. Sampling was performed every second day overlapping with the NAPS network schedule from July 22 to November 29 of 2004.

- All filters exchanges were taken place at 12:00 to 1:00 p.m.

- When conducting on-field sampling, before the MiniVol sampler was removed from the mounting cradle and set on a level surface, the filter assembly was placed on a firm level surface.

- The pump and timer assembly was lifted out in order to verify the setting time, elapsed time and dates on the LCD, and to check for any error conditions.

- The clock time, elapsed time and the ending flow rate were recorded on the appropriate Air Sample Field Log for that sample.

- The ending weather information was recorded on the Air Sampling Field Log for that sample.

- The MiniVol operating conditions and any other observations (i.e. potential sources) were recorded on the Air Sampling Field Log for that sample.

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4.1.2   Real-time PM$_{2.5}$ Sampling

TEOM has been operated at Edmonton Northwest Air Quality Station for continuously monitoring PM$_{10}$ and PM$_{2.5}$ since 1993 (Sandhu, 1998). However, only till January of 1988 and thereafter, over 95% of time the instrument was in operation (Clean Air Strategic Alliance, 2004). The TEOM has been tested by the USEPA and has been designed as being equivalent method to the reference method for the determination of 24-hr mean PM$_{2.5}$ concentrations in ambient air for compliance purpose (U.S.EPA., 1990). Real-time technology is well suited to receptor based monitoring approaches because it can detect changes in particulate matter concentration over the short term. These changes tend to be more representative of particulate concentrations in settings where humans spend time (U.S.EPA, 1996; Wallace, 1996), and they are more representative of exposure conditions.

In this study, intermittent-based sampler - MiniVol was co-monitoring with continuous-based sampler - TEOM at Edmonton Northwest Station to verify correlation between type of samplers for the purpose to evaluate accuracy and precision and data validation of PM$_{2.5}$ sampling by MiniVol. More details for co-location and co-monitoring at Northwest Station were presented in Section 4.2.2.

4.2   Site Selection and Description

4.2.1   Selection Criteria

Several sites were inspected in order to determine the experimental sites. Factors judgmentally considered included:

- The location should be representative of the prevailing conditions in the selected residential area.

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- The types of neighbor were minimal or light local anthropogenic point source so that no point source could unduly affect particulate matter levels.

- The traffic characteristic of nearest roadway was expected to represent minor traffic intensity.

- The sites were in relatively open areas, free from overhead obstructions, and away from the influence of tall buildings.

- The distance of selected sites was far enough so as to assess the spatial variability of particulate matter levels.

- The central air monitoring station, Edmonton Northwest Station, was selected as the co-location and co-monitoring site in order to identify and compare particulate matter levels and elemental compositions profiles with the selected residential sites.

- The sampling sites offered an electricity supply and security for the sampling equipment.

In conclusion, the selected sampling sites that were to be representative of prevailing residential sites in urban had minimal local anthropogenic (human related) point emissions source of particulate matter (i.e., industrial, commercial source, etc.). These sites, however, would still be under the influence of local and/or near-field open and natural sources, and in addition to regional sources from industrial activities surrounding.

4.2.2 Sampling Site Descriptions

- **Site A**

Site A was located on the east side of 122 Street, between 51 Avenue and 71 Avenue in Edmonton, Alberta, with relatively larger open field surrounding and least traffic intensity (Figure 6). As shown in Figure 6, this site was adjacent to residences from north, east and west within 500 m. This location is property of the University of Alberta experimental farm. Site access was permitted by the Department of Agricultural, Food and Nutritional Science, Edmonton Research Station, University of Alberta for the entire sampling period. The MiniVol filter sampler was set on a tripod stand in the field. The height of sampling inlet above the ground was 2.0 m, which was intend to collect air samples within the human breathing zone. $PM_{2.5}$ samples collected at site A were subject to only $PM_{2.5}$ levels measurements.

Figure 6   Aerial photography of site A.

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- **Sites B**

The site B was located on the east side of 127 Street, between 132 and 135 Avenue in Edmonton, Alberta (Figure7). At this site, MiniVol sampler was co-located and monitoring with Edmonton Northwest Station. Portable MiniVol filter sampler was mounted at a height of 1.5 m above the ground of the Station. This site is much closed to 127 Street (<50 m) with highest traffic intensity during weekdays through entire sampling periods. Moreover, a number of commercial activities (e.g. restaurant, gas station, shopping centre, garage, etc.) surrounded site B within 200 m. Higher $PM_{2.5}$ levels as near-field source emissions were suspected. The site was secure, had a power supply, and access was granted by the AENV for the entire sampling period.

As Northwest Station (Figure7) is a part of Canada NAPS network, it collects $PM_{2.5}$ samples using continuous-based sampler - TEOM. Northwest Station was intended to be a reference method sampling site in this study. Height of Northwest Station is 2.5 m, height of TEOM sample inlet above the ground was 3.5m. Table 13 lists the continuously monitored parameters start date at Northeast Station.

Table 13   Ambient PM parameters monitored at Northwest Station.
(after Clean Air Strategic Alliance, 2004)

Collection Type	Parameter Name	Sampler	Start Date
Continuous particulate matter mass	PM_{10} Mass (81102)	TEOM	29-Aug-97[1]
	$PM_{2.5}$ Mass (81104)	TEOM	1-Apr-98[1]

[1] indicates over 95% of time the instrument has been in operation since then (Clean Air Strategic Alliance, 2004).

It was noted that the former name of Northwest Station was Edmonton Residential Monitoring Unit (ERMU) (Alberta Environment., 1981). As its former name

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implied, this station is intended to monitor and represent the air quality of Edmonton residential areas. Ambient air monitoring data and data reports form the Northwest Station are available online at the Clean Air Strategic Alliance Data Warehouse (Clean Air Strategic Alliance, 2004). $PM_{2.5}$ samples collected at site B were subject to both $PM_{2.5}$ levels and subsequent elemental compositions by SEM/EDX and then $PM_{2.5}$ source apportionment by PCA approach.

Figure 7   **Aerial photography of site B.**
(Co-located with Northwest Air Quality Station)

- **Site C**

The site C was located on the east side of 127 Street, between 158 Avenue and 160 Avenue in Edmonton, Alberta (Figure 8). Site C was about 3.0 km north from site B (Figure 7). This location is a property of EPCOR which is used as drinking water storage

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reservoir adjacent to larger open field (Figure 8). Both electricity supply and security requirements were met, and access was granted by the EPCOR for the entire sampling period. This location is intended to be representative of the prevailing conditions of residential area in that: no local point sources, far from traffic road, and relatively open field. $PM_{2.5}$ samples collected at site C were subject to both $PM_{2.5}$ levels and subsequent elemental compositions by SEM/EDX, and then $PM_{2.5}$ source apportionment by PCA approach.

Figure 8   Aerial photography of site C.

- **Site D**

Site D is located at the backyard of a private residence on the southwest of St Albert (Figure 9). This location is representative of the prevailing conditions in the selected residential area: no point sources, low to minor traffic intensity, relatively open field; and both electricity supply and security requirements were met. The MiniVol was set on a metal stand. The height of sampling inlet above the ground was 2.0 m. $PM_{2.5}$

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samples collected at site D was intended for comparison purpose to identify and evaluate

spatial variability in urban residential areas in the Edmonton area. $PM_{2.5}$ samples

collected at site D were subject to only $PM_{2.5}$ levels measurements.
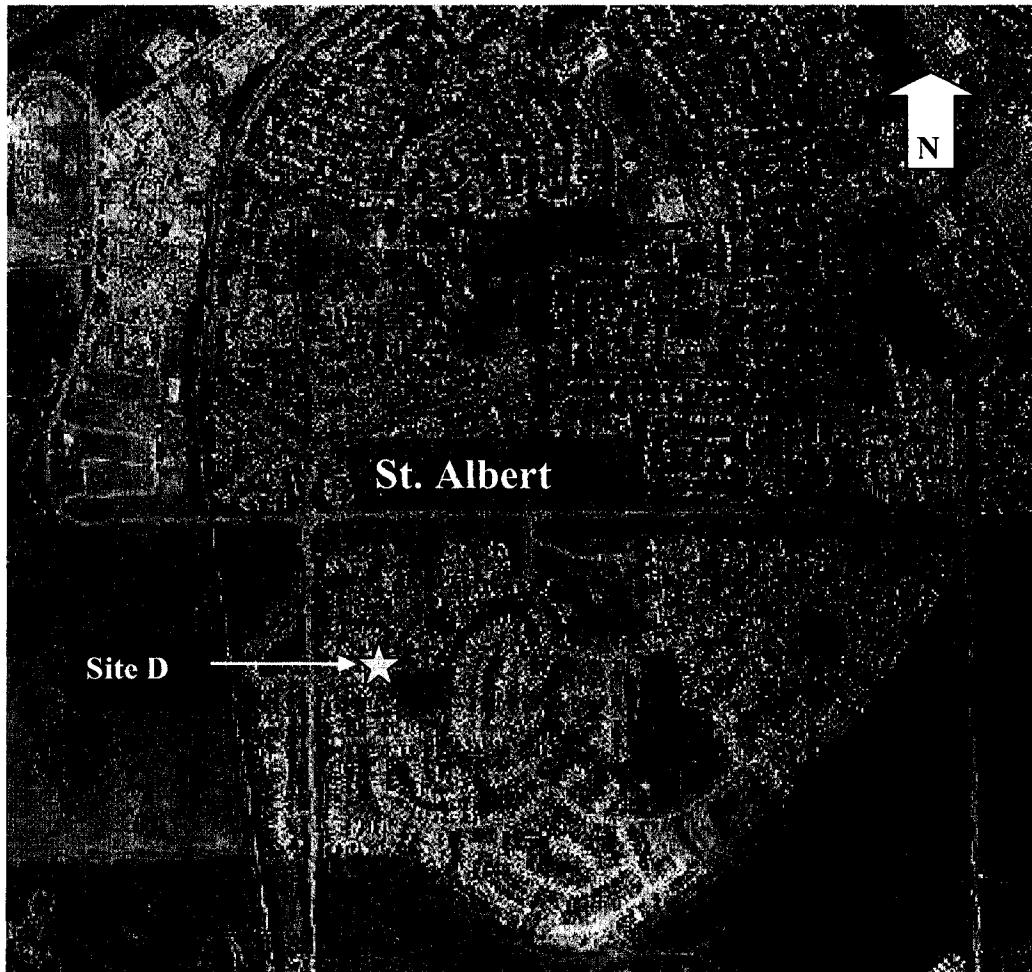
Figure 9   Aerial photography of site D.

4.3   Sampling Schedule

With the sampling equipment and sampling location identified, a schedule was

developed that would account for sampling during two seasons in 2004 (summer and fall).

The purpose was to sample and monitor $PM_{2.5}$ at the four selected representative sites in

Edmonton and area for a total of sixty sampling days in the fashion of every second day

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(Table 14). In this way, daily and monthly temporal variability would be accounted for over two seasons.

Table 14   Ambient PM$_{2.5}$ sampling program in Edmonton and area.

	MiniVols (This Study)				TEOM (Ref.)
	Site A (UA Farm)	Site B [1] (Northwest Stn.)	Site C (Epcor Site)	Site D (St Alberta)	Northwest Station.
Method	24-hr intermittent basis (every second day)				1-hour continuous basis
Period	July 22, 2004 to November 29, 2004				1998 [2]
Sampling	(12:00 pm to 12:00 pm local time)				n/a

[1] co-located with Edmonton Northwest Air Quality Station.
[2] indicates 95.11% of percentage of time the instrument has been in operation since January of 1998 (Clean Air Strategic Alliance, 2004).

The seasonal sampling schedule is shown in Table 15. This sampling schedule provided sixty MiniVol 24-hr filter samples at each selected site for two seasons for a total of the two-hundred-forty samples. Samples, blanks, and replicates were taken according to protocols outlined in Section 4.1 and 4.7 and stored until required for subsequent laboratory analysis.

Table 15   MiniVol ambient PM$_{2.5}$. seasonal sampling schedule.

Season	Start		End	
Summer	July 22, 2004	Thu	July 30, 2004	Fri
	Aug 1, 2004	Sun	August 31, 2004	Tue
Fall	September 2, 2004	Thu	September 30, 2004	Thu
	October 2, 2004	Sat	October 30, 2004	Sat
	November 1, 2004	Mon	November 29, 2004	Mon

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4.4 Meteorological Data

Meteorological data (i.e., temperature, atmospheric pressure, wind speed and direction, precipitation events, relative humidity) were obtained from two existing climatological stations as follows:

- Environmental Canada Environment Canada 5 Day Forecast. Data are available online at http://weatheroffice.ec.gc.ca/city/pages/ab-50_metric_e.html

- Weather Station and Conditions 24/7 basis form The University of Alberta's Department of Earth & Atmospheric Sciences. Data are available online at http://www.uofaweb.ualberta.ca/weather

4.5 Laboratory Analysis

4.5.1 Gravimetric Analysis

Gravimetric analysis is the most common analytical technique for ambient particulate matter studies. The data is used to calculate the particulate mass concentration ($\mu g/m^3$). For the $PM_{2.5}$ gravimetric analysis in this study, a Mettler semi-microbalance (precision ± 10 μg, Mettler AE166 Delta Range, Mettler Instrumente, Zurich, Switzerland) and Sartorius microbalance (precision ± 1 μg, Santorius, ISO9001, Mississauga, ON) were used for weighing. Filter conditioning was performed in accordance to U.S.EPA guidelines in which the filter was pre-conditioned and post-conditioned for 24-hr at 20°C and 30% relative humidity (U.S.EPA, 1997). In this study, all $PM_{2.5}$ samples were gravimetrically analyzed by the Environmental Monitoring Business Unit of Albert Research Council (ARC) at Vegreville, Alberta.

4.5.2 Chemical Compositions and Morphology Analysis

A. Method

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To assist in determining probable source contributing to the $PM_{2.5}$ detected at the residential site (i.e. source apportionment), knowledge of the chemical composition and morphology of the $PM_{2.5}$ is essential. An SEM-JEOL-6301F scanning electron microscope (Field Emission SEM) with a Light Element Energy Dispersive X-Ray Analysis (EDX) attachment was used in the present study for analysis of $PM_{2.5}$.

Scanning Electron Microscopy with Energy Dispersive X-Ray spectrometry or SEM-EDX uses a computer controlled scanning electron microscope equipped with image analysis software to determine the size and shape of a moderate number of particles and EDX to provide qualitative and a moderately sensitive quantitative elemental concentration in a particle of >0.1%(Henry et al., 1984). SEM-EDX represents a powerful tool for the identification and classification of airborne particles.

The primary advantage of the SEM-EDX technique is the ability to characterize individual particle both chemically and physically, and thus reduce problem of compositional co-linearity between contributing sources. Another benefit of using SEM is that it can provide an estimate of the contribution of carbonaceous particles to particulate matter levels (Hamilton et al., 1994). Particles containing light elements (i.e. carbon, hydrogen, nitrogen and oxygen) cannot be analyzed with normal analytical techniques because their X-rays emitted cannot be easily detected. These types of particles can include pollen, spore, bacteria, and charred plant and wood debris from residential burning, forest fires and agriculture burning.

In addition, the most important types of carbonaceous particle that cannot be correctly analyzed are those from vehicle emissions, which generally contain over 98% carbon. Since the mass contribution of carbonaceous particles to the total particulate

matter concentration in an area can be substantial, they must be accounted for in some manner. The SEM is able to do this by providing a means to identify and characterize these particles based on their morphology (size and shape). This particular benefit was found to be very useful in this study.

The disadvantages of the SEM-EDX technique include poor quantitative sensitivity (Linton *et al.*, 1980) and practical difficulties such as excessive time for a representative analysis and the occurrence of both particle damage and compositional changes during analysis (Post and Buseck, 1984). In addition, the EDX method can normally only analyze individual particles >0.4 μm in size (Braybrook, 2004). This becomes a problem because the contribution from $PM_{2.5}$ from ultra-fine particles can be substantial, and therefore may not be fully accounted for in receptor modeling.

B. SEM-EDX Protocols

General Rules for SEM-EDX Analysis

- When a sample was prepared for the SEM-EDX analysis, filter preparation was performed in a laminar-flow hood to prevent dust fall on the filter.

- The 47 mm Teflon filters were mounted on a 13 mm metal plate with carbon tape on top, with the excess filter cut out, leaving approximately 13 mm of exposed filter surface. For QA/QC purposes, the filter was cut into half: one half piece of filter for SEM-EDX analysis, and another half as duplicate in case of first piece of sample's failure. In the interest of consistency, only the center of each piece of filter was used to represent the entire filter.

- The filters were pre-coated with gold for better transmission and imagery.

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- When analyzing a filter, particles were chosen at random by an outside party for quantification analysis. The purpose of this was to reduce bias when selecting particles to represent the entire filter.

- Laboratory control blanks and field blanks were analyzed in the same way as the other filters, and SEM photographs were taken of all blanks. Any particles discovered on the blanks suggested procedural or equipment error

Procedure for Inert Particle Analysis

- All particles except biological particles or particles with primary carbonaceous compositions were candidate particles for analysis regardless of size, shape, or composition. Because EDX is incapable of accurately analyzing biological or primarily carbonaceous (i.e. oil droplet) particles.

- Each filter was divided into four quadrants.

- Multiple random areas were chosen for each quadrant. After selecting a random area, the SEM was set at full magnification and then slowly reduced.

- The first recognizable particle was analyzed and a new area was then chosen.

- A maximum of three particles from each quadrant were analyzed.

- A total of ten particles for each filter were analyzed. The purpose of this was to save time and money while at the same time still analyzing enough particles on each filter to adequately represent the entire filter.

Procedure for Biological or Carbonaceous Particles

This procedure was only used to account for biological or primarily carbonaceous particles:

- A particle was identified as biological or carbonaceous (i.e. oil droplets) when it was either visually recognized as such or when it was analyzed using the EDX and the only elemental spectral peak was gold. If the gold peak is the only one present, it can be assumed that the particle consists solely of carbon or other light elements, but in insufficient quantities to be noticed above background (Hopke, 1985).

- The number of biological or carbonaceous particles encountered while analyzing the 10 required inert particles for each filter was noted.

- The amount of biological and/or carbonaceous particles on each filter was presented as a ratio between the number of biological and/or carbonaceous particles and the number of analyzed inert particles (i.e. 10).

- A large ratio would indicate a large amount of biological or carbonaceous particles present on that filter and a small ratio would indicate a small amount of biological or carbonaceous particles present on that filter.

Procedure for SEM-EDX Documentation

For each new classified inert particle analyzed, a description of the particle, inert particle SEM photo, elemental spectra, and elemental abundance table generated by EDX quantitative process were recorded on Analysis Data Log. For each sampling season, the following were recorded on an SEM-EDX Analysis Data Log:

- SEM photograph of overview of one filter

- SEM photographs of every particle analyzed on one filter

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- SEM photographs, elemental abundance tables, and elemental spectral graphs of every different type of particle encountered during entire analysis procedure (including biological particles)

Elemental Abundance (%) Determination

- Elemental composition (abundance percentage) for each filter was determined by averaging the elemental compositions of all 10 inert particles analyzed on each filter.

- This number of particles was used as a standard minimum because it could ensure an adequate statistical population (when budget and time constraints were considered) to represent conditions at the time the sample was taken.

- The same number of particles was analyzed on each filter to ensure that an equal population represented every filter.

- Replicates were analyzed in the same manner as their counterpart samples. If the replicate and the corresponding sample represented the same timeframe, they were analyzed for statistical similarity. The elemental composition of the replicate and the corresponding sample were then averaged and used to represent the sampling period. If the timeframes were different for the sample and replicate, the one that was closest to 24 hours was used to represent that sampling day.

4.6   Statistical Analysis

4.6.1   Method

This study employed a multivariate receptor modeling technique using the available elemental data provided by the SEM-EDX analysis to apportion the $PM_{2.5}$

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found at the receptor location the residential monitoring sites among probable sources. Specifically, the multivariate receptor modeling technique used is known as principle component analysis (PCA).

PCA takes a large data set of interrelated variables and reduces the dimensionality to a small workable number of independent variables that are then used to explain the potential underlying relationship between the data. To achieve this, factors or principle components are constructed according to a linear combination of the original variables, so that the newly formed factors are uncorrelated and are constructed with decreasing degree of importance. The factors obtained in this way embody the linear independent variance present in the data of the original variables and are generally representative of the sources in the system.

When applied in particulate matter source apportionment studies, the basic concept of PCA is to unravel the seemingly unrelated elemental data to reveal a new related data set based on the variations in abundances of elements detected at a receptor location over time. This related data set could then be used to find statistically independent source tracers that can identify the nature of each source category. The data used in any PCA are composed of the elemental concentrations of many samples acquired under different circumstances. In this study, the elemental concentrations measured for samples at site B (Figure 7) and site C (Figure 8) determined by the SEM-EDX analysis were used.

Following the application of a PCA, interactions of the various elements with the factors can be investigated to determine probable emission sources. Interpretation of the underlying origin of the factors has been traditionally limited to inspection of factor

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loadings only. Since the factor loadings are correlation coefficients between the original variables and the factors, they provide key information as to the nature of the factor.

Elements that have high or moderate loadings (i.e., PCA loading ≥0.8) for a particular factor can be used to construct an elemental profile for a probable source. This profile or tracer can then be compared with those similar studies, relevant literature, and particulate matter databases to label each factor as a specific source or a source category. It is usually the case that as many as five to eight individual source types can be identified with this method (Harrison *et al.*, 1996).

4.6.2 Procedure for the PCA

The specific procedure for the PCA employed in this study was as follows:

- Mass concentrations ($\mu g/m^3$) for the PM2.5 MiniVol filter samples were determined gravimetrically.

- The resulting mass concentrations ($\mu g/m^3$) were multiplied by the average elemental abundances (%) determined by the SEM-EDX for the same time periods resulting in average elemental mass concentrations (ng/m^3).

- The average elemental mass concentrations (ng/m^3) for each filter sample were converted into z-scores (Equation 6). This procedure standardizes the data prior to PCA, which tends to equalize the opportunity of both large and small magnitude variables to influence the analysis.

- The z-score data matrix was then subjected to principle component analysis (PCA) utilizing the commercial statistic software SYSTAT Version 10.0® using a varimax rotation (SPSS, 2002).

- The elements were eliminated and PCA was repeated until all conditions described in the Section 2.5 (Receptor Models for Regional Background Studies) were met.

- The results of the PCA were compared to the previous studies, relevant literature, and the U.S. EPA's Speciate Database) (U.S.EPA, 2002) to identify and categorize the most likely sources of $PM_{2.5}$ at the receptor locations.

4.7   Quality Control and Quality Assurance

The precision, accuracy, and validity of measured values can be established under quality control (QC). Quality control is intended to prevent, identify, correct, and define the consequences of difficulties that might affect the precision and accuracy, and/or validity of measurements. Quality assurance (QA) integrates quality control, measurement method validation, and sample validation into the measurement process.

To ensure proper QA/QC, the laboratory control blanks, field blanks and replicates were all routinely taken and analyzed along with the sample filters. All laboratory control blanks, field blanks and replicates were analyzed by the gravimetric method and subsequently the SEM-EDX in an exactly identical manner as the other samples. The information provide by these measurements was used to help deduce the quality of the data by indicating the amount of sample contamination and reproducibility. Specific procedures for QA/QC are described as below:

Laboratory Control Blanks

- One control blank was performed for each sampling season, for a total of two control blanks. These control blanks were taken at the start of each sampling season.

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- Control blanks also followed a rule based on each batch of filters. This was done by simply selecting the first filter for each sampling season or each batch of filters, and marking it as a control blank. The filter was not taken out of the petri-slide but was instead stored in a Tupperware® container in the laboratory room until needed for analysis.

Field Blanks

- For each sampling site, field blanks were performed during each sampling month. A total of twenty field blanks were collected at the four sampling sites.

- Days that field blank sampling was to be performed were randomly decided before each sampling month.

- Procedures for field blanks were exactly the same as for other samples except that no actual sampling took place. All handling, transporting, and assembling procedures were followed, but the MiniVol was not turned on. Instead, the filter was removed from the MiniVol and transported, retrieved and stored according to normal procedures.

Replicates

- For sampling site C, three replicate samples were taken during each sampling month for a total of twelve.

- Days that replicate sampling was to be performed were the first, middle, and end of each sampling month.

- Procedures for replicates were exactly the same as for other samples except that sampling was conducted using a second MiniVol that was co-located beside the first MiniVol.

5. RESULTS AND DISCUSSIONS

5.1 Particulate Matter Level Results

5.1.1 Ambient $PM_{2.5}$ Mass Levels

Intermittent ambient air monitoring was performed using MiniVol samplers at four sites in the Edmonton area for the period July 22 to November 29, 2004. The sampling schedule was every second day and overlapping with the NAPS network sampling schedule (every sixth day) for the entire sampling period. A total of 240 $PM_{2.5}$ samples were obtained at the four sites. The monitoring adhered to techniques and protocols outlined in Section 4.1. The 24-hr average $PM_{2.5}$ concentration, temperature, and precipitation data are presented in detail in Appendix 8.3.

Results for the 24-hr average $PM_{2.5}$ levels from all four sites are presented in Figure 10 to Figure 13. The 24-hr average $PM_{2.5}$ levels exhibited very similar behavior across the sites:

- Site A – University Experimental Farm

- Site B – Edmonton Northwest Station co-monitoring location

- Site C – EPCOR Reservoir site

- Site D – residential site in St Albert

Figure 11 shows that 24-hr average $PM_{2.5}$ levels at the Edmonton Northwest Station (site B) – which was also continuously monitored with a TEOM (and converted into 24-hr average concentrations accordingly) – illustrated a good agreement with $PM_{2.5}$ levels measured by the MiniVol method. The TEOM method is considered a reference method. The agreement observed between MiniVol and TEOM $PM_{2.5}$ levels at site B (Figure 11) suggested that all measurements by MiniVols of this study were valid

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observations. More discussion of the comparison of simultaneous MiniVol versus TEOM levels at site B is given in Section 5.1.3.

It was observed that 24-hr average $PM_{2.5}$ levels from all monitoring locations were lower than the Alberta Environment surveillance trigger concentration (i.e. <15 $\mu g/m^3$) for most sampling periods(Clean Air Strategic Alliance, 2003). However, a number of peaks did occur on several occasions and there were times of sustained elevated levels, especially during the August sampling month (August 10 to August 20 2004). These elevated levels were consistently reflected through Figure 10 to Figure 13. Depending on local meteorological conditions, short-term fluctuations of $PM_{2.5}$ levels from the monitoring locations can be generally attributed by the near-field sources and/or regional sources under prevailing winds. For instance, at the site B (Figure 11), the elevated levels observed during the periods August 10 to August 20, October 28, and November 11 to November 13 of 2004 were most likely attributed by the near-field sources. Roadwork construction occurred in very close proximity to site B (i.e. <50 m away). The maximum 24-hr $PM_{2.5}$ level observed during the entire sampling period at site B was 27.7$\mu g/m^3$ on day of October 28, 2004. Similarly on July 22, 2004 at the site A (Figure 10), the elevated level of $PM_{2.5}$ was most likely attributed by the near-field sources. Agricultural events (i.e., field ploughing) occurred during that time in very close proximity (i.e. <100 m).

Whereas the prolonged durations of low 24-hr average $PM_{2.5}$ levels can be partially explained by influences from precipitation events and snow cover on the ground. Precipitation creates a wet- scavenging effect that removes aerosols and particulates from the atmosphere and snow cover prevents re-suspension of particulate material:

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- Low levels observed from all monitoring locations from July 24 to July 31, and August 21 to September 30 of 2004 appeared to be related to precipitation events observed during that time.

- Low levels of $PM_{2.5}$ observed for October 14 to October 16 and November 15 to November 27 of 2004) are likely explained by presence of snow cover.

Compared to the 24-hr Canada-wide Standard (CWS) benchmark concentration of 30 $\mu g/m^3$ (CCME, 2000), 24-hr $PM_{2.5}$ levels were not exceeded in any samples collected from the four sites during the sampling period.

Descriptive statistics for all valid observations of the 24-hr average $PM_{2.5}$ levels from the four sites are included in Table 16. $PM_{2.5}$ levels from the four residential sites ranged from about 0.6 to 28$\mu g/m^3$ with a majority of the concentrations between 0.9 and 20$\mu g/m^3$. The arithmetic average concentrations of $PM_{2.5}$ ranged from 6.3 at the site D (residence at St. Albert) to 9.3 at site B (Edmonton Northwest Station), and the arithmetic standard deviation ranged from 5.2 to 6.6$\mu g/m^3$.
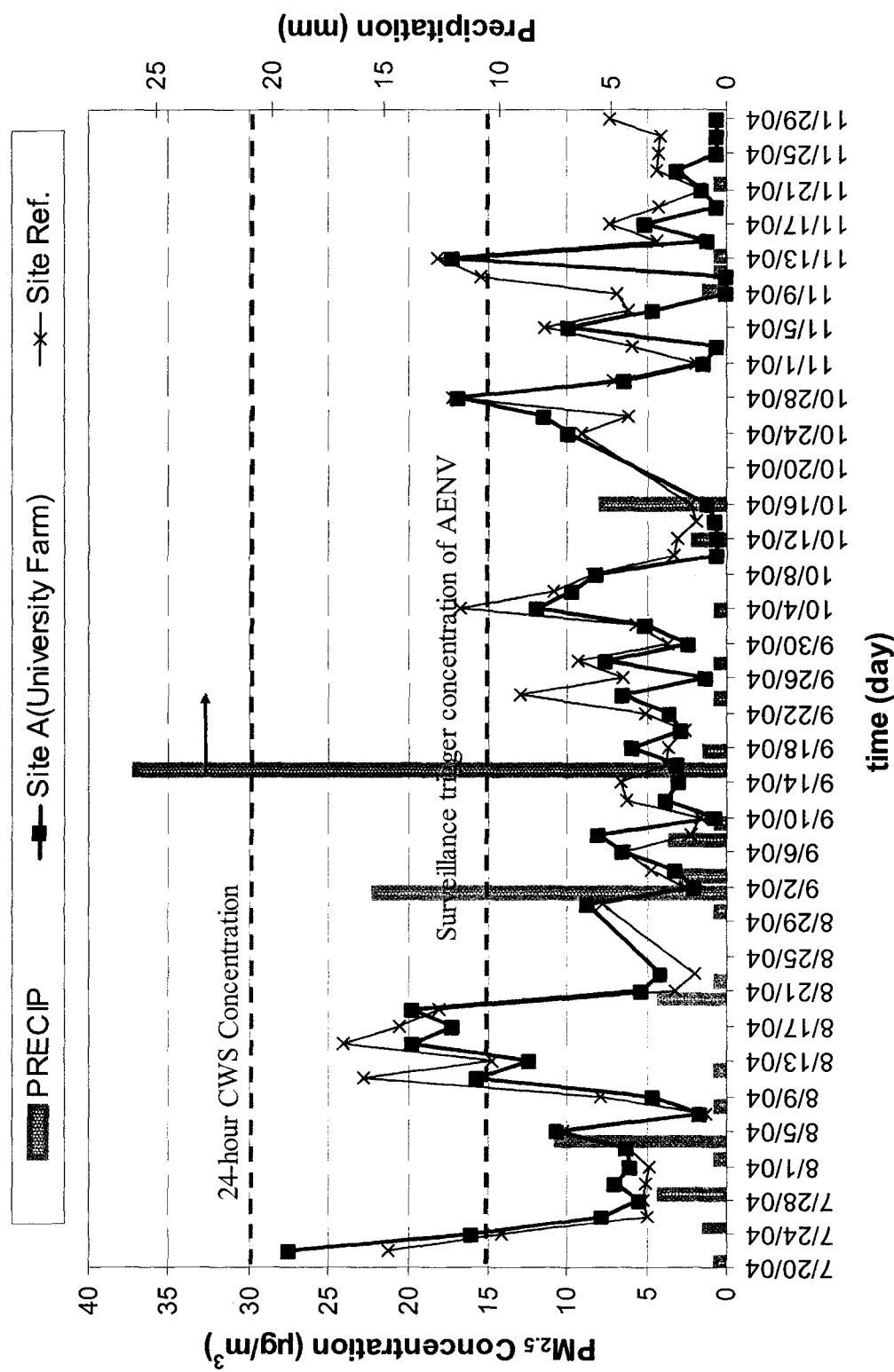
Figure 10   24-hr average PM$_{2.5}$ concentrations ($\mu g/m^3$) at site A.

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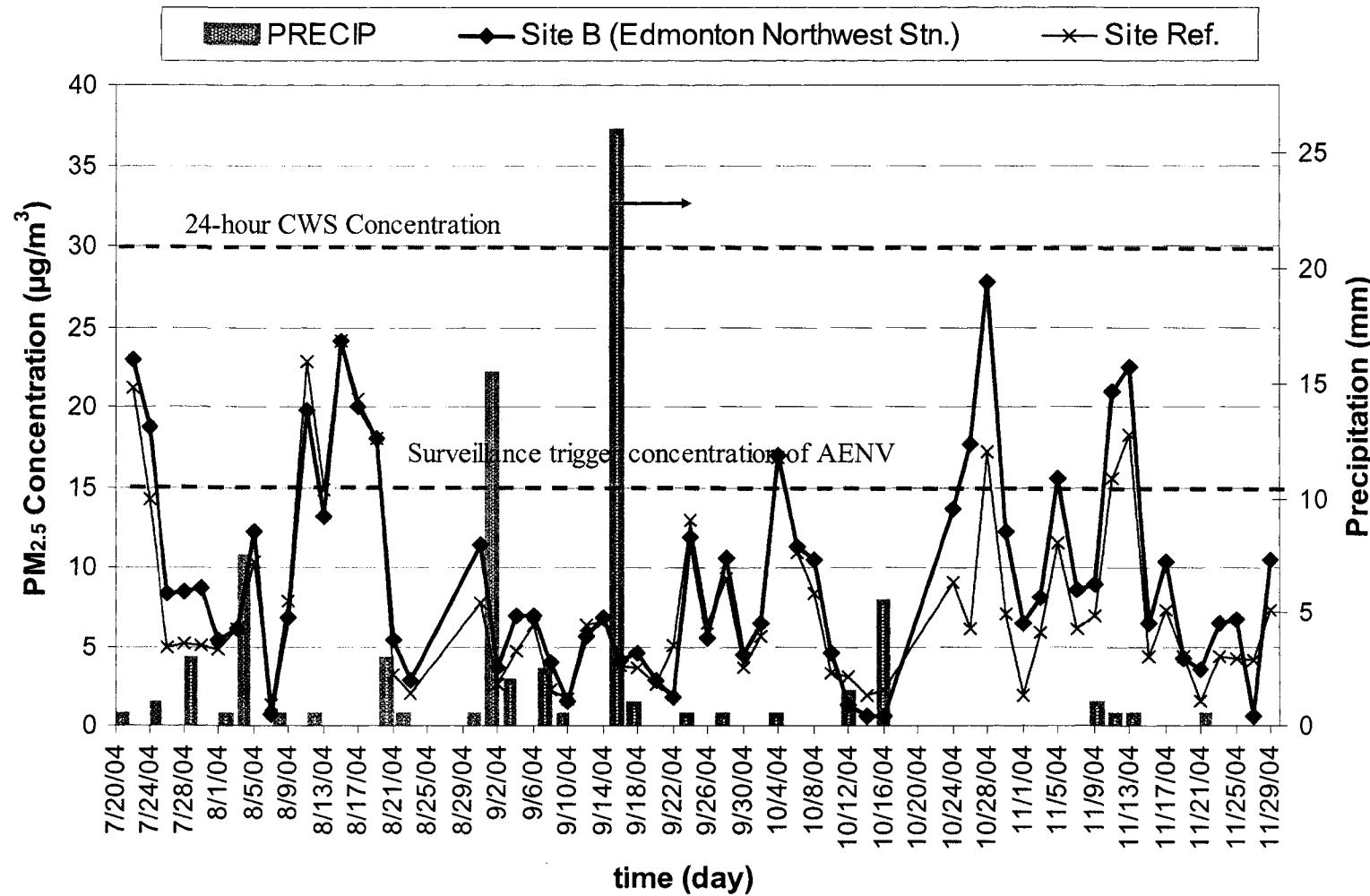
Figure 11   **24-hr average PM$_{2.5}$ concentrations (μg/m^3) at site B.**
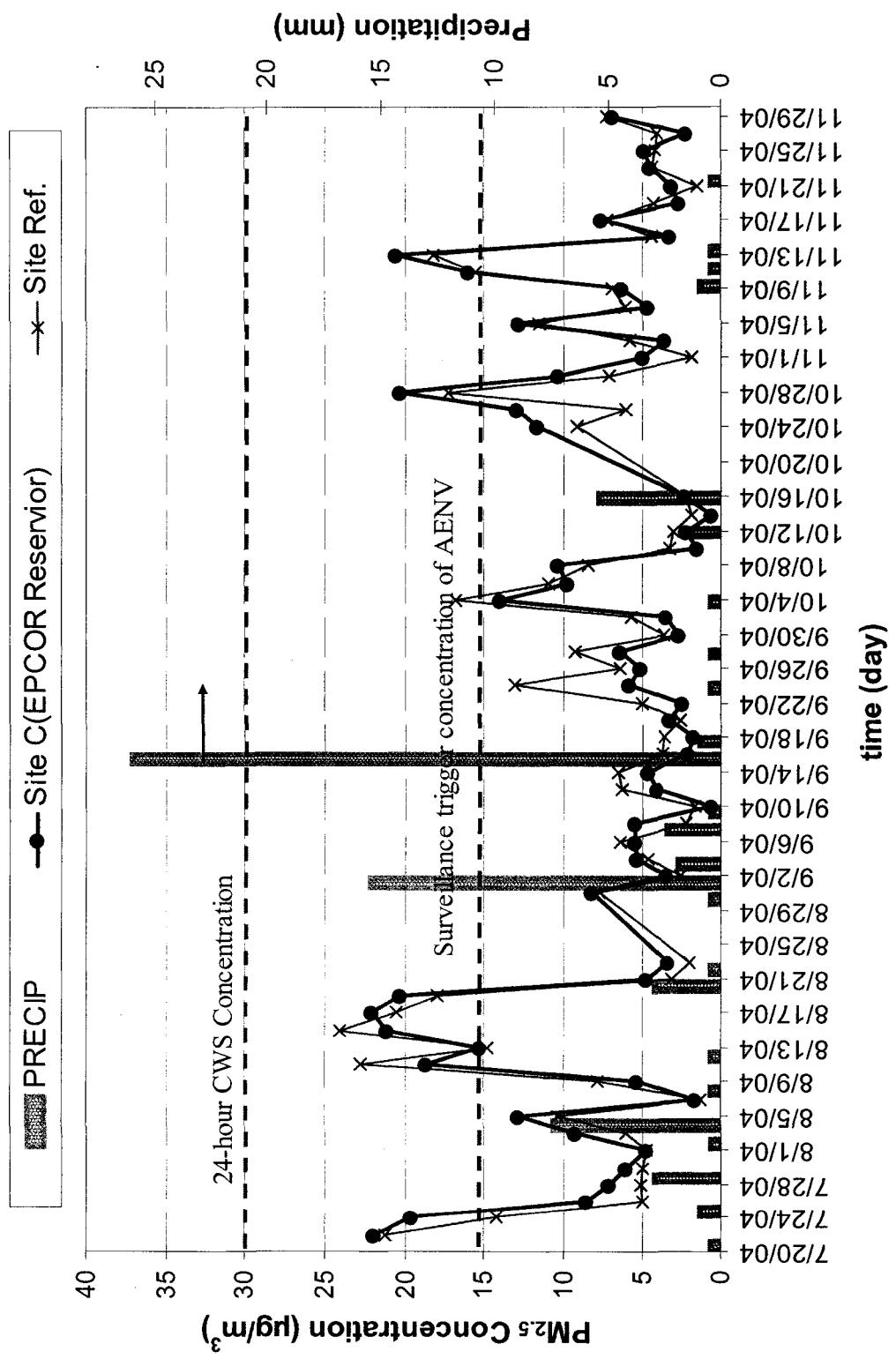
Figure 12   24-hr average PM$_{2.5}$ concentrations (μg/m^3) at site C.

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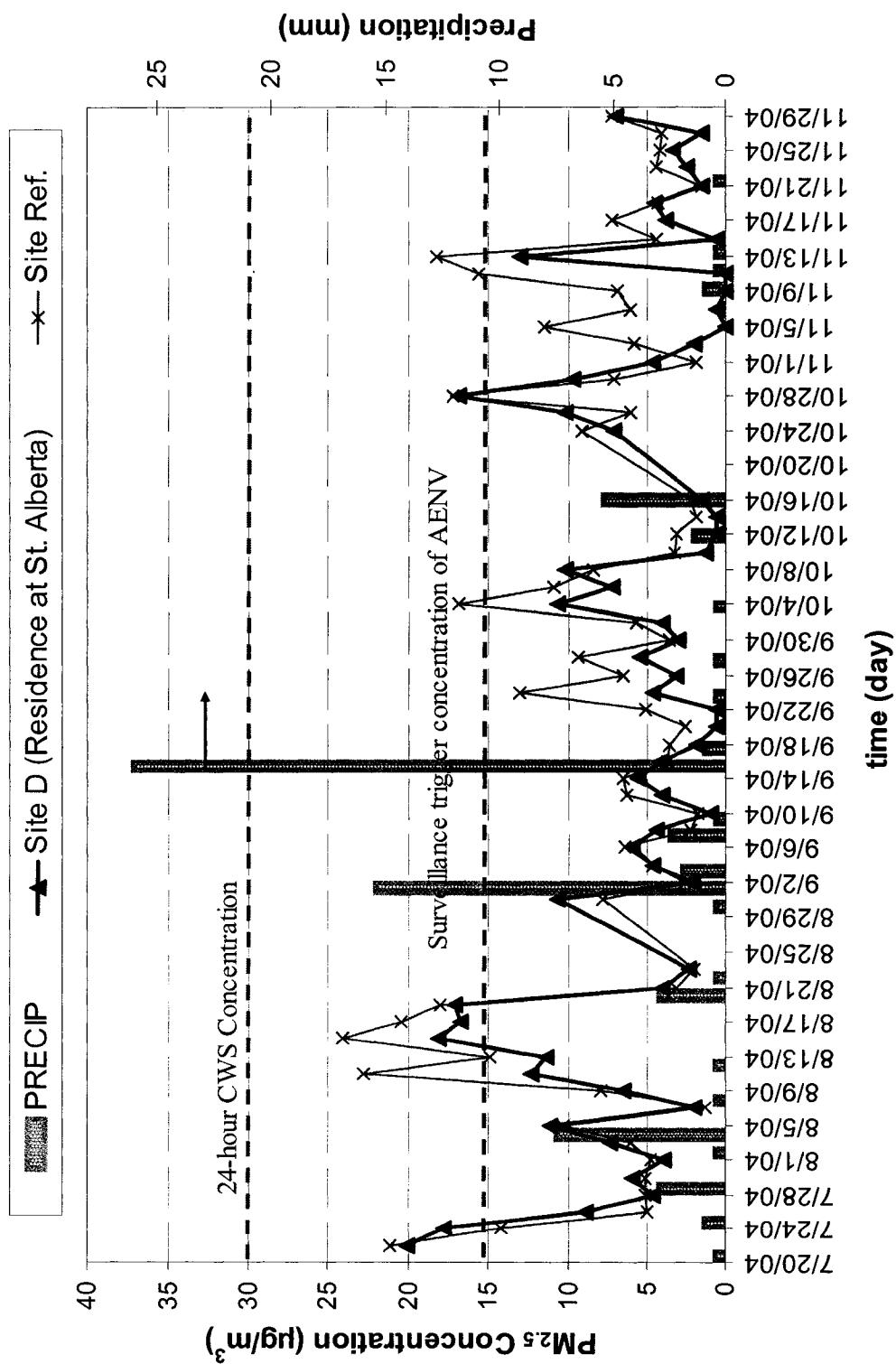
Figure 13   24-hr average $PM_{2.5}$ concentrations ($\mu g/m^3$) at sites D.

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Table 16 Summary statistics of the 24 hour average $PM_{2.5}$ concentration ($\mu g/m^3$) at four sites by MiniVols sampler.

(for the periods from July 22 to November 29 of 2004)

	Site A (University Farm)	Site B (Co-located w/ site Ref.)	Site C (EPCOR Reservoir)	Site D (Residence at St. Alberta)	Site Ref. (Edmonton N.W. Stn.) [1]
Sample Size	58	60	60	57	60
5th Percentile	0.6	0.7	1.6	0.6	1.9
25th Percentile	1.7	4.6	3.4	2.1	3.8
50th Percentile	5.2	6.9	5.5	4.7	6.1
75th Percentile	9.5	12.2	10.6	9.7	9.6
95th Percentile	17.6	22.5	20.6	17.2	20.5
Minimum	0.6 [2]	0.6	0.6	0.6	1.3
Mean	6.6	9.3	7.9	6.3	7.8
Maximum	27.5	27.7	22.1	20.1	24.1
Standard Deviation	6.0	6.6	6.2	5.2	5.8

[1] monitored by TEOM; [2] detection limit of MiniVol.

5.1.2 Temporal and Spatial Variation

Meteorological conditions play an important role in influencing ambient air quality. Variation (daily, monthly, or seasonal) in source emission rates can influence ambient particulate levels, however variation in meteorological conditions tend to have a greater effect relative to emission variations. More specifically, meteorological parameters of major importance are wind speed, precipitation, and temperature (Colls, 1997; Keith, 1991). Temperature and precipitation observed during sampling periods are given in detail in Appendix 8.3 (Environment Canada, 2004c).
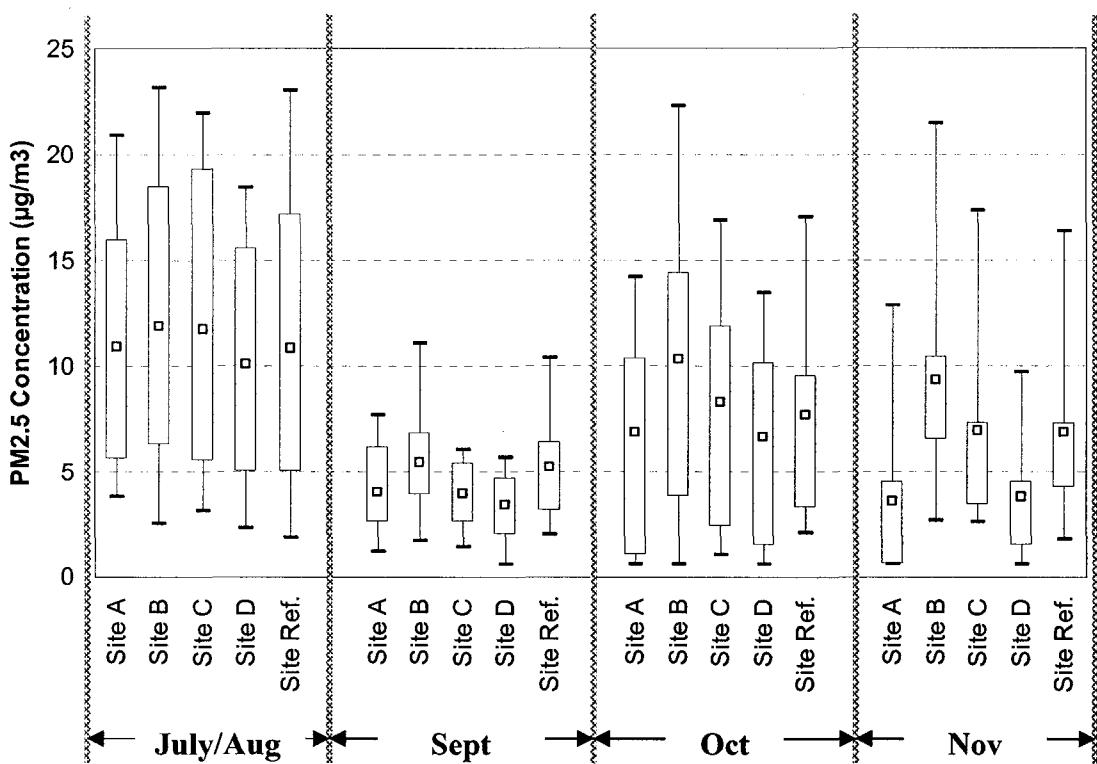
Figure 14 **Comparison of monthly distribution of the 24-hr average PM$_{2.5}$ mass (μg/m^3) at four sites.**
(The box plots indicate the mean 24-hr PM$_{2.5}$ concentration and the 5th, 25th, 75th, and 95th percentiles over the sampling month.)

Figure 14 compares the monthly distribution of 24-hr average PM$_{2.5}$ mass (μg/m^3) at the four sampling sites. During the warmer months of July and August the mean temperature was 17°C and the mean PM$_{2.5}$ mass concentration from the four sites was higher at ~11μg/m^3 compared to other months. Whereas during cooler months (October and November) the mean temperature was lower (~6°C in October and ~1°C in November) and the mean PM$_{2.5}$ mass concentrations from the four sites was lower at 5 to 8μg/m^3. Snowfall that occasionally occurred in October and November in Edmonton may have contributed to the lower PM$_{2.5}$ concentrations (as discussed earlier).

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Table 17 describes relevant descriptive statistic for seasonal variation of 24-hr average $PM_{2.5}$ mass for the four sites over the entire sampling period. The median 24-hr average $PM_{2.5}$ mass from all sampling sites in the summer season was 8 to 10 $\mu g/m^3$ (standard deviation 7 $\mu g/m^3$). The median of 24-hr average $PM_{2.5}$ mass in the fall season was 3 to 7$\mu g/m^3$ (standard deviation 5$\mu g/m^3$). Compared to similar studies conducted in Alberta (Cheng *et al.*, 1998 and 2000), seasonal variations observed in the present were quite similar.

Table 17 **Summary seasonal variation of the 24-hr average $PM_{2.5}$ concentrations ($\mu g/m^3$) at four sites.**

	Summer [1] (June to August)					Fall [2] (September to November)				
	Site A	Site B	Site C	Site D	Site Ref.[3]	Site A	Site B	Site C	Site D	Site Ref.
Mean	10.9	11.9	11.7	10.1	10.8	4.7	8.2	6.3	4.5	6.5
Min	1.6	0.7	1.6	1.9	1.3	0.6	0.6	0.6	0.6	1.5
Median	8.3	10.1	9.0	9.8	7.9	3.2	6.6	4.8	4.1	5.8
Max.	27.5	24.1	22.1	20.1	24.1	17.2	27.7	20.5	16.9	18.2
Std. Dev.	7.0	7.2	7.2	5.9	7.7	4.4	6.2	4.9	3.8	4.4
N	18	18	18	18	18	40	42	42	39	42

[1] samples were collected starting on July 22, 2004 and ending on August 31, 2004.
[2] samples were collected starting on September 1, 2004 and ending on November 30, 2004.
[3] Ref. site is refer to Alberta Environment (AENV) Northwest Air Station using real-time TEOM.

5.1.3 Quality Assurance and Control

- **MiniVol Sampler Duplicate Test**

Duplicate ambient 24-hr average $PM_{2.5}$ samples were collected based on the sampling program at site C (EPCOR Reservoir Site). Samples were collected at this site to fulfill internal Quality Assurance/Quality Control objectives, aid in understanding of source influences at the location, and to the further test MiniVol sampling and SEM-EDX

analysis protocols. From these tests, a total of twenty filters were collected, and two additional blank samples were also collected – one from each sampler.

Mass concentrations from the ten 24-hr average $PM_{2.5}$ samples collected by two MiniVol samplers at site C are compared in Table 18. Figure 15 shows the relative agreement with 24-hr average $PM_{2.5}$ mass concentrations for these two MiniVol samplers. Regression analysis was undertaken to compare the 24-hr average $PM_{2.5}$ mass concentration data collected from both samplers based on ten field tests. The result is provided in Table18. The relative degree fit between the two samplers – as measured by the coefficient of determination (R^2) – was excellent based on a R^2-value of 0.90. This result indicates good agreement among each sampler for measuring 24-hr average $PM_{2.5}$ mass concentrations.

Table 18   **$PM_{2.5}$ mass concentration ($\mu g/m^3$) of duplicate MiniVols at site C.** (EPCOR Reservoir Site)

Sample Date	Minivol #2326	Minivol #2324 (Dup)
July 22, 2004	21.9	20.8
August 1, 2004	4.8	3.1
August 9, 2004	5.3	7.0
September 2, 2004	3.5	4.2
September 16, 2004	2.1	5.3
October 2, 2004	3.6	5.2
October 16, 2004	2.4	0.8
October 30, 2004	10.3	7.7
November 15, 2004	3.2	4.5
November 29, 2004	6.9	6.6

This was further confirmed by performing a paired t-test of measured 24-hr average $PM_{2.5}$ mass concentrations determined from each sampler for all ten field sample results. Results shown in Table19 indicated no statistical difference in the collection ability of each sampler ($P \leq 0.05$).

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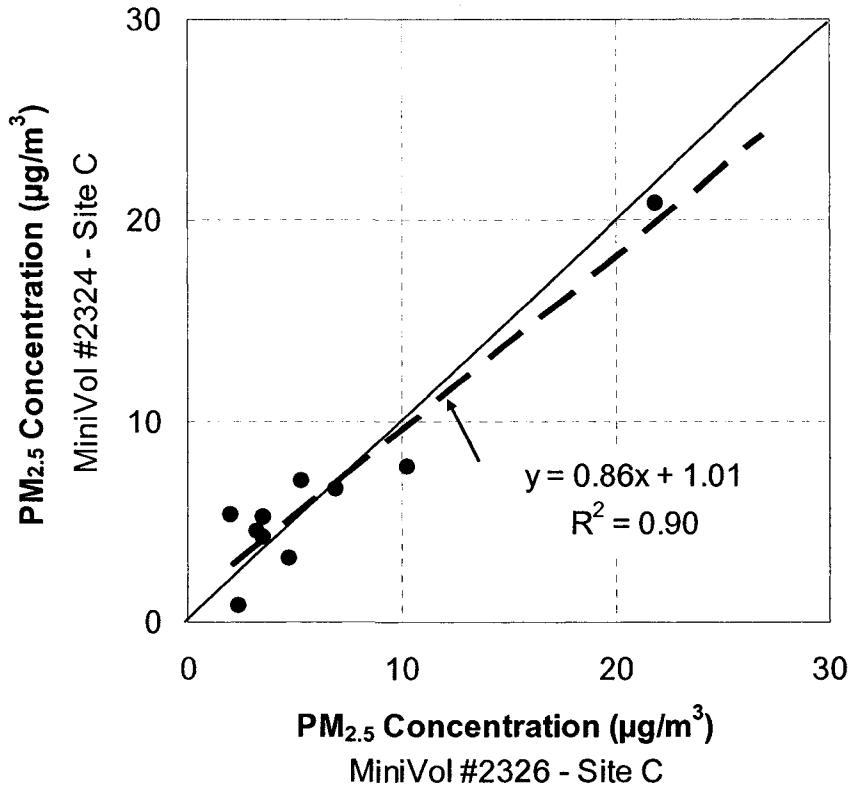
Figure 15 **Comparison of PM₂.₅ mass concentrations for duplicated samplers at site C.**

(EPCOR Reservoir Site, sample size=10)

Table 19 **Regression and paired *t*-test for duplicated MiniVols at site C.**

(EPCOR Reservoir Site)

Samples (n=10)		Y = mX + b		R^2	Paired t-test (P ≤0.05)
X	Y	m (±SE)	b (±SE)		H_o: The means are equal
					H_a: The means are unequal
					reject if: $\|t_{stat}\| > t$ Critical two-tail
MiniVol #2326	MiniVol #2324	0.86 (±0.10)	1.01 (±0.84)	0.90	|0.19| < 2.26 do not reject the hypothesis

- **MiniVol versus TEOM Test**

One MiniVol sampler was co-located and co-monitoring with the reference method sampler (TEOM) at site B during the entire sampling period. A comparison of results between these two types of sampling methods was made in order to estimate the precision of the MiniVol's measurements. The 1-hr average $PM_{2.5}$ concentrations observed by the TEOM at the Northwest Station were converted into the 24-hr average concentrations accordingly so that the comparison can be made between these two types of samplers. In this study, a total of 60 matched pairs of the 24-hr average $PM_{2.5}$ results, and four additional blank and field sample results were obtained. The 24-hr average $PM_{2.5}$ concentrations for these two types of sampler are provided in detail in Appendix 8.3.

As expected, due to the heating of inlet air in the TEOM sample column, $PM_{2.5}$ levels measured by the continuous TEOM sampler were lower than levels reported by MiniVol sampler as shown in Figure 16. Heating of the inlet air above ambient temperatures (30 to 50°C) during operation has been reported by others to cause volatilization of semi-volatile particulate material, and potentially result in lower measurement of PM (Allen *et al.*, 1997; Ayers et al., 1999; Soutar *et al.*, 1999).

Regression analysis was undertaken to compare the 24-hr average $PM_{2.5}$ mass concentration data collected from both MiniVol and TEOM samplers based on 60 samples through the entire sampling period. A coefficient of determination (R^2) value shown in from this comparison was 0.83. Figure 16 suggests a good agreement between the two types of method through the measurements of the 24-hr average $PM_{2.5}$ mass concentrations.
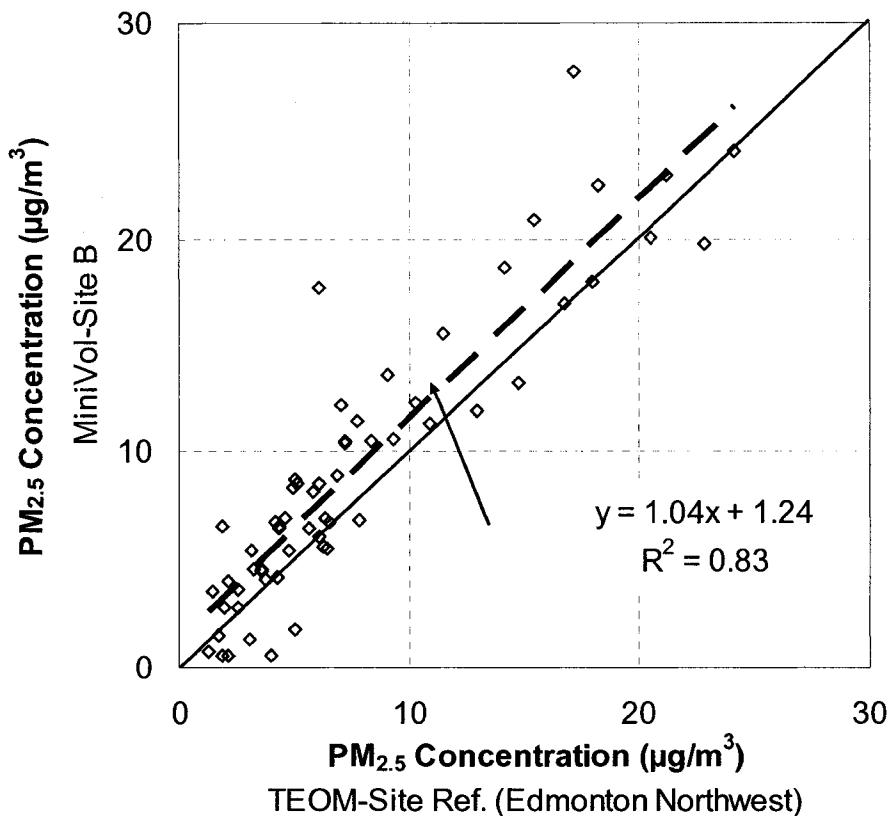
Figure 16 **Comparison of PM$_{2.5}$ mass concentrations for MiniVol versus TEOM Sampler at site B.**
(Edmonton Northwest Station, sample size=60)

5.2 Particulate Matter Elemental Composition and Morphology

Chemical speciation is a critical part of many ambient monitoring programs. In order to assist in determining probable source contributing to the PM$_{2.5}$ measured at the four residential sites (i.e. source apportionment), knowledge of the chemical composition and morphology of the PM$_{2.5}$ is essential. The intermittent 24-hr average PM$_{2.5}$ samples collected by MiniVol over the period of July to November 2004 were analyzed by Scanning Electron Microscopy with Energy Dispersive X-ray spectrometry or SEM-

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EDX. This analysis provided the chemical composition and morphology of the $PM_{2.5}$ at the four residential sites and assisted in determination of probable sources.

5.2.1 Chemical Composition Results

Results from the MiniVol filter samples were used to evaluate and compare the chemical composition profiles between two sites – site B (the centralized Northwest Station, Figure 7) and site C (EPCOR Reservoir Site, Figure 8). A total of 120 filter samples, twelve replicates, and four field blanks and lab control blanks were collected; and subsequently analyzed by SEM-EDX. These samples were representative of ambient $PM_{2.5}$ at sites B and C over the period July to November 2004.

The SEM-EDX analysis adhered to techniques and protocols outlined in Section 4.5. A total of eighteen elements were detected including: Si, Ca, Al, Mg, Fe, Na, K, Cl, S, Ti, Mn, Co, Pb, Cu, Cr, Cd, V, and Ba. A major limitation of the SEM-EDX technique is its inability to elementally analyze small, carbonaceous particles. As the majority of particles indicative of vehicle emissions are both small and carbonaceous, the contributions of vehicle emission were greatly underestimated in this analysis. This underestimation, however, can be properly addressed and accounted for in the morphology analysis (discussed in next Section 5.2.2). In addition, PCA source apportionment (discussed in Section 5.3) can also provide another interpretation of the importance of particle origins in ambient air at these two sites.

Complete data for samples descriptions, elemental abundance (%) and elemental concentrations (ng/m^3) for the entire sampling periods are presented in detailed in Appendix 8.4. Results of the SEM-EDX analysis for total $PM_{2.5}$ elemental composition at site B are presented in Figure 17. Similarly, Figure 18 describes results of the SEM-EDX

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analysis for the total $PM_{2.5}$ elemental composition at the residential site C (EPCOR Reservoir Site). The elemental composition is presented as a percent relative abundance of the total composition using a logarithmic scale.

The chemical composition results exhibited a distinct distribution between those elements that were found to be highly abundant (defined as <1% mass fraction) and those that were found only in trace amount ($\leq$1% mass fraction). For both sites, elements that were highly abundant contributed to a majority (i.e. ~97%) of the total elements mass fraction of the $PM_{2.5}$ samples. These highly abundant elements included: Si, Ca, Al, Fe, K, Na, Mg, and Cl. Whereas, elements present in trace amounts contributed to the rest (i.e. ~ 3%) of the total mass fraction of $PM_{2.5}$ samples. These trace elements included S, Ti, Mn, Cr, Cu, Ni, Pb, V, Co, and Ba.

The first detail noted from Figure 17 and Figure 18 was that crustal materials probably are the dominant sources of $PM_{2.5}$ particles for both site B and C. Typically, crustal materials contain clay particles that can be comprised of elements including: primary Si, Ca, Al, Mg, Fe, K, and trace elements Ti and Mn. They could be associated with crustal sources such as agricultural activities, crustal weathering (wind blown soil), road dust (paved and unpaved), constructions, and others (Stevens, 1985; Beceiro-Gonzalez et al., 1997). These elements, however, can also indicate the presence of fly ash particles due to similar elements compositions as crustal materials (Chow, 1995).

Crustal materials are likely to retain chemical and elemental characteristics over a long time period (Chow et al., 1995). The results show that the primary elements Si, Ca, Al associated with crustal material exhibit very slight variations within individual element throughout sampling periods. It suggests that $PM_{2.5}$ in the centralized air station,

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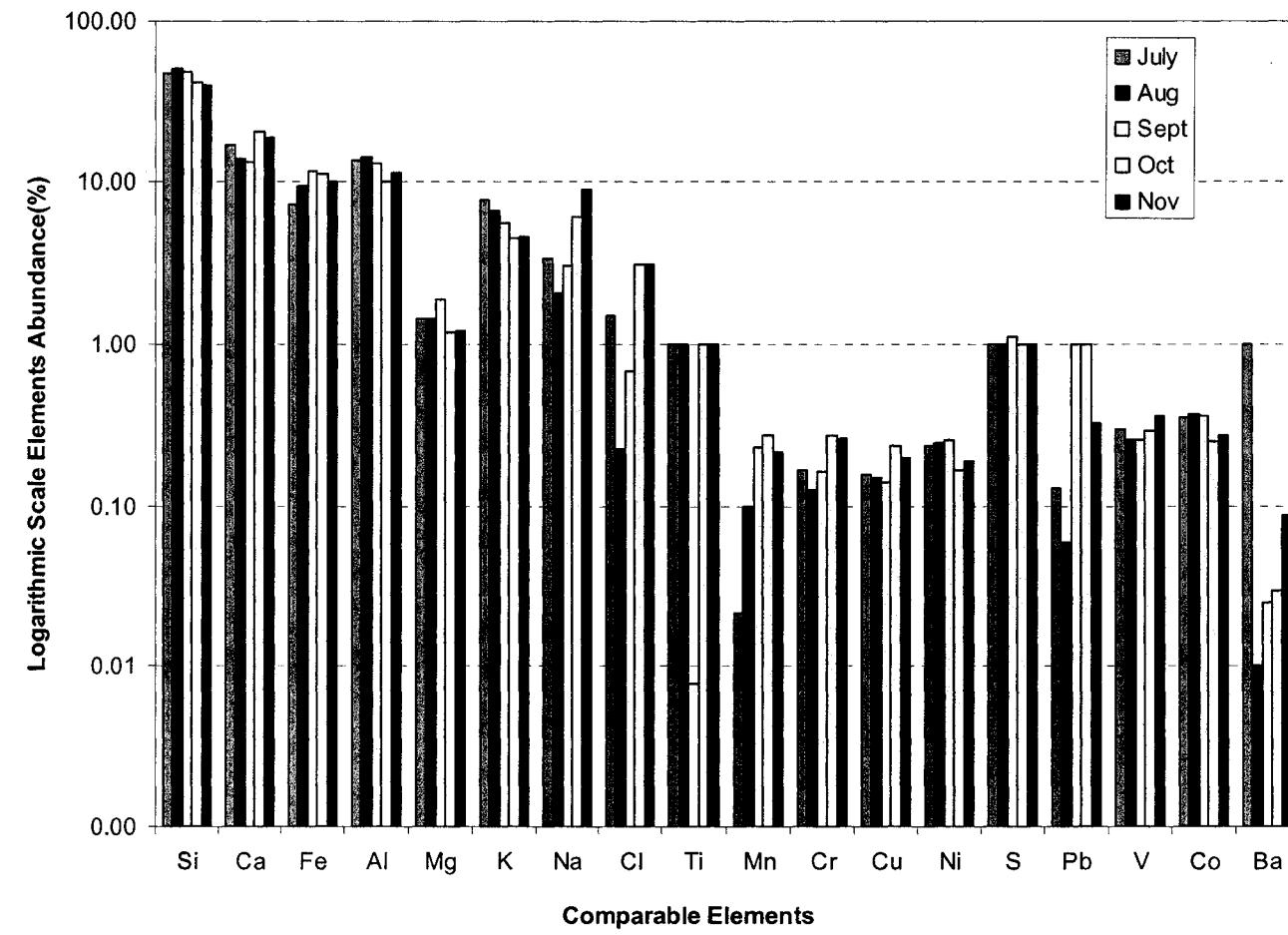
Figure 17   Variation of PM$_{2.5}$ chemical composition at site B.
(co-located with Northwest Station, more traffic)
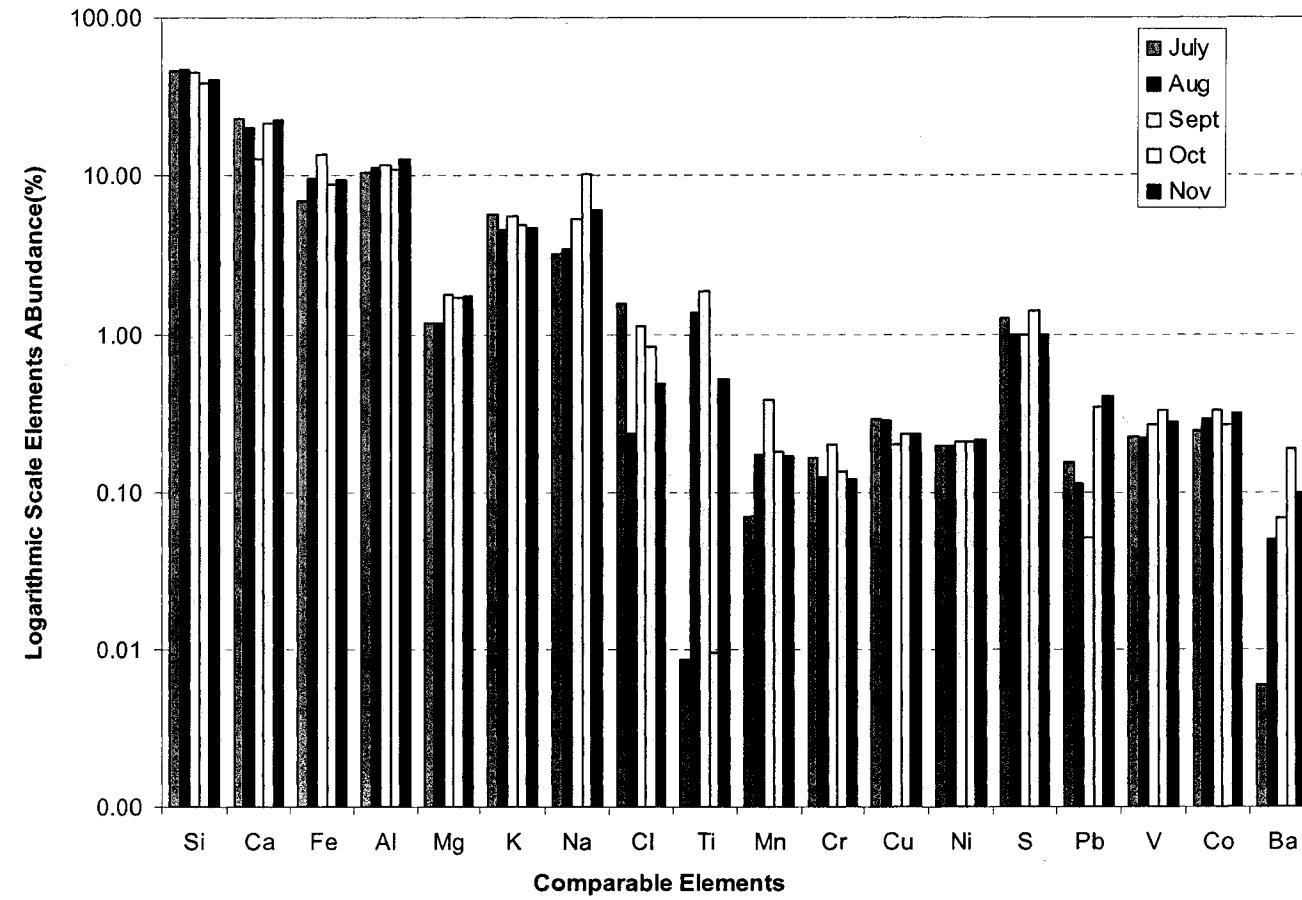
Figure 18   Variation of PM$_{2.5}$ chemical composition at site C.
(Epcor Reservoir Site, less traffic than site B)

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site B, and the residential Site C may originate essentially from similar dominant (crustal) sources, despite the distinct different character of locations.

The second detail noted in these two figures was that roadside dust may be important in vicinity of traffic road. The majority of road dusts in the $PM_{2.5}$ fraction are associated with the direct vehicle emissions (CEPA and FPAC, 1999), and they can include: worn tire flakes, brake and clutch lining particles, sand, salts, and deposited atmospheric particles (CEPA and FPAC, 1999; Al-Chalabi and Hawker, 2000; Lamoree and Turner, 1999; Miguel et al., 1999; Glovsky et al., 1997). Primary and trace elements associated with road dust include Si, Ca, Fe, K, Na, Cl, and trace elements S and Pb.

The abundant elements Na and Cl are very indicative of salt aerosols such as those found in road salt (Marcazzan, 1998; US EPA, 1993). Salt is found more prevalent after de-icing materials are applied (U.S.EPA, 1999). Several snowfalls occurred in the time frame through the middle of October as well as November 2004. Due to close proximity to intensive traffic road at site B (<50 m), salts aerosols may have been present. Results for site B (Figure 17) indicate that mass fraction levels of elements Na and Cl tended to increase from the warmer months (July to September) to the cooler months (October to November). Moreover, the abundant trace element Pb is also very indicative of road dust. The results suggest that the mass fraction levels of trace element Pb at site B (in close proximity to traffic road) are greater than levels at site C during the sampling period.

The last detail noted in these two figures is that occurrence of the abundant trace element S from both sites is normally indicative of oil combustion and regional sulphates (Tuncel et al., 1985; Marcazzan, 1998). Besides the element S, the primary element Cl

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and trace elements V and Ni also are associated with oil combustions (Kitto, 1993; Gao *et al.*, 1996). In addition, flyash associated with coal combustion has the primary elemental signature of Pb (Parekh and Husain, 1981; Fung and Wong, 1995; Alves *et al.*, 1998). The chemical composition at the both site B (Figure 17) and site C (Figure 18) show that the mass fraction levels of trace elements S, V, and Ni exhibited small variation during the sampling period. The results suggest that those trace elements may be indicative of surrounding industrial and other anthropogenic activities.

5.2.2 Morphological Results

By supplementing quantitative EDX analysis with scanning electron microscopy (SEM), particle morphology can aid in characterizing individual particles through identification of size, shape, and surface texture. This information can be used in combination with elements detected by the EDX analysis to further specify the source of $PM_{2.5}$ sampled at the sites.

A total of 1,200 particles were inspected and analyzed and hundreds more were observed individually by SEM from 120, 24-hr $PM_{2.5}$ filters collected at site B and C. Use of SEM enabled classification of individual particles based on their morphology and provided some insight into possible sources and contributions which otherwise might not have been apparent. Examples of each type of particles are presented in Figures 19 to 34 (shape and surface texture) and Tables 20 to 31 (weight % of elements). In general, the majority of particles randomly selected on the sample filers could be classified as one of four particle types based on their morphology and their distinctive elements. These four particle types included: crustal, industrial/vehicular exhaust, biological, and unknown.

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Overall, particle classification results for site B and C are summarized in Table 32 and Table 33, respectively. Similar to previous studies (Schulz and Kindzierski, 2001; McCullum and Kindzierski, 2004), it was noted that on some filters from site B that oil droplets covered a vast majority of the filter, and would contribute substantially to the total number of particles present on the filter. In addition, it was found that there were more biological particles observed at site C during the warmer sampling month.

Figure 19   SEM image of a crustal clay particle – primary Si.

Table 20   Corresponding EDX elemental scan of a crustal clay particle – primary Si.

Library Standard: /imix/spectra/system standard (LDL 0.1%)

| Accelerating Voltage | 20KeV |
| Takeoff Angle | 56.8 degrees |

Elements	wt %
Na	9.62
Mg	0.13
Si	53.46
K	2.10
Ca	9.77
Fe	5.15
Cu	0.56
Al	15.11
Ba	4.02

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Figure 20   SEM image of a crustal clay particle – primary Ca.
(scale bar=1 μm)

Table 21   Corresponding EDX elemental scan of a crustal clay particle – primary Ca.

Library Standard: /imix/spectra/system standard (LDL 0.1%)

Accelerating Voltage	20KeV
Takeoff Angle	56.8 degrees

Elements	wt %
Mg	0.64
Si	24.80
K	1.15
Ca	67.15
V	0.87
Cr	0.34
Fe	1.41
Co	0.41
Al	0.20
Cl	2.04
Ni	0.99

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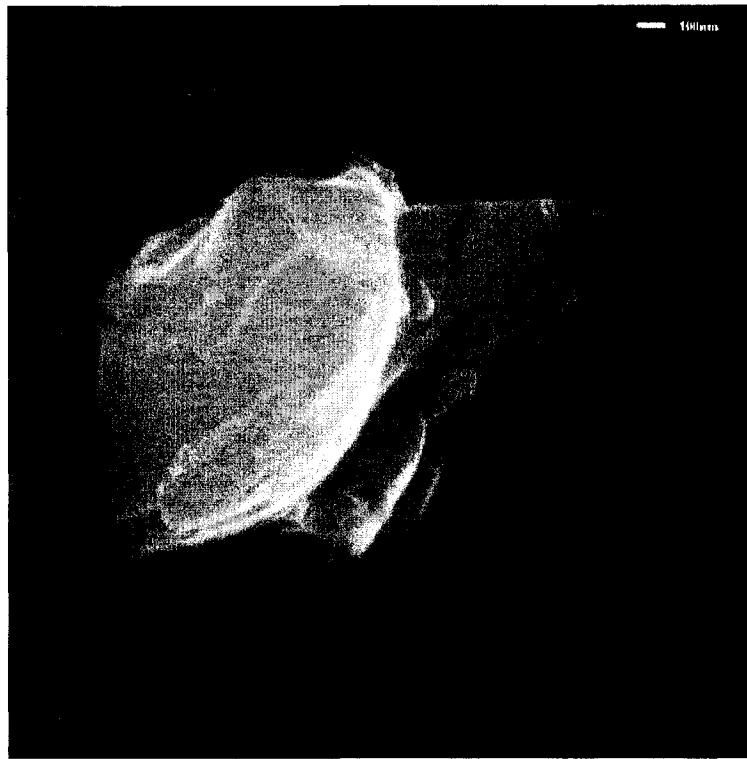
Figure 21   SEM image of a crustal silica particle.
(scale bar=100nm)

Table 22   Corresponding EDX elemental scan of a crustal silica particle.

Library Standard: /imix/spectra/system standard (LDL 0.1%)

Accelerating Voltage	20KeV
Takeoff Angle	56.8 degrees

Elements	wt %
Na	1.51
Mg	1.00
Si	74.95
K	4.67
V	0.37
Cr	0.51
Fe	9.14
Co	1.35
Al	5.88
Ni	0.62

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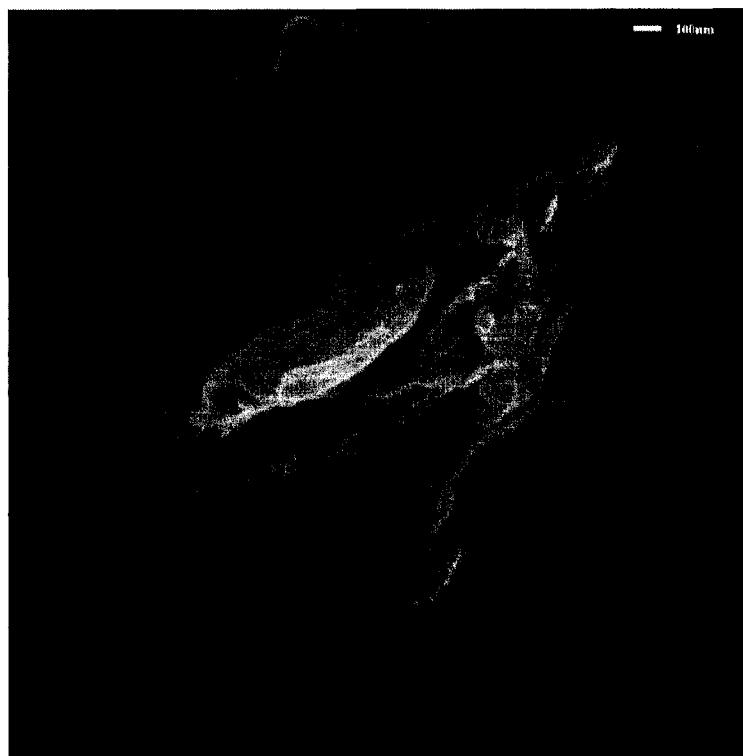
Figure 22   SEM image of a calcium particle.
(scale bar=100nm)

Table 23   Corresponding EDX elemental scan of a calcium particle.

Library Standard: /imix/spectra/system standard (LDL 0.1%)

Accelerating Voltage	20KeV
Takeoff Angle	56.8 degrees

Elements	wt %
Mg	0.63
Si	0.90
K	0.19
Ca	95.54
Fe	1.20
Cu	0.83
Al	0.10
Cl	0.61

95
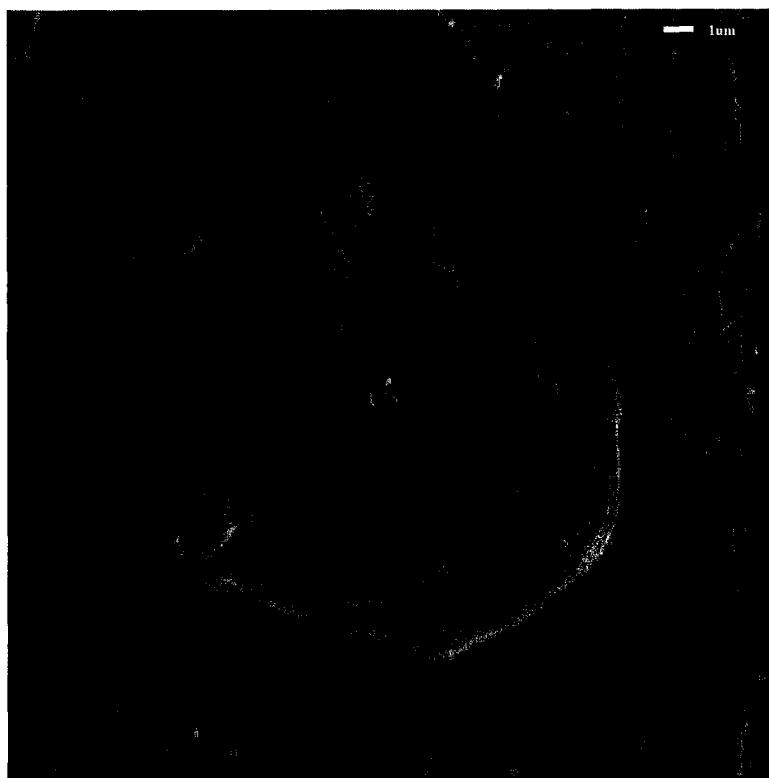
Figure 23   SEM image of a salt particle.
(Salt particle mixed with silica, primarily comprised of Na and Cl with varying amounts of other crustal elements, scale bar=1 μm)

Table 24   Corresponding EDX elemental scan of a salt particle.

Library Standard: /imix/spectra/system standard (LDL 0.1%)

Accelerating Voltage	20KeV
Takeoff Angle	56.8 degrees

Elements	wt %
Na	46.64
Mg	1.16
Si	7.44
K	3.98
Cl	35.12
Fe	2.55
V	1.40
Cr	1.71

96
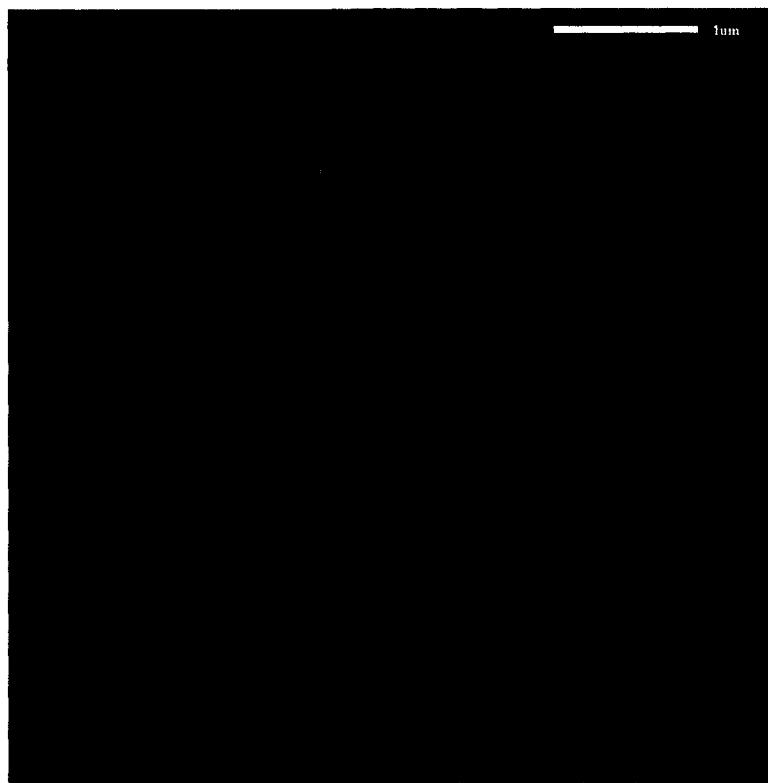
Figure 24 **SEM image of a titanium particle.**
(scale bar=1 μm)

Table 25 **Corresponding EDX elemental scan of a titanium particle.**

Library Standard: /imix/spectra/system standard (LDL 0.1%)

| Accelerating Voltage | 20KeV |
| Takeoff Angle | 56.8 degrees |

Elements	wt %
Al	1.05
Si	5.66
Cl	0.54
Fe	1.82
Ti	87.60
V	0.10
Cu	0.50
Co	1.72
Ni	0.86
Cr	0.15

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Figure 25   **SEM image of industrial exhaust – flyash.**
(scale bar=100nm)

Table 26   **Corresponding EDX elemental scan of industrial exhaust – flyash.**

Library Standard: /imix/spectra/system standard (LDL 0.1%)

Accelerating Voltage	20KeV
Takeoff Angle	56.8 degrees

Elements	wt %
Na	6.13
Mg	2.00
Si	39.45
K	2.18
Ca	3.36
Fe	3.68
Co	0.19
Al	35.20
Cl	0.31
Ni	0.15
Pb	7.35

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Figure 26 **SEM image of an exhaust particle – primary S.**
(scale bar=100nm)

Table 27 **Corresponding EDX elemental scan of an exhaust particle –
primary S.**

Library Standard: /imix/spectra/system standard (LDL 0.1%)

| Accelerating Voltage | 20KeV |
| Takeoff Angle | 56.8 degrees |

Elements	wt %
Ca	1.37
K	2.91
Fe	3.85
S	89.09
Ti	0.60
V	2.18

99
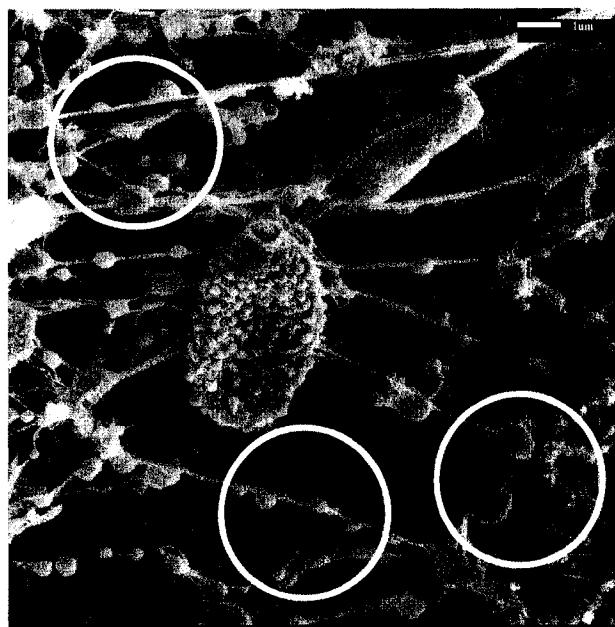
Figure 27   **SEM image of oil droplet particles at site B during a typical weekday.**
(Oil droplets, be circled in figure, with small and smooth appearance are easily identified. These particles, however, are extremely difficult to scan with EDX because of their size and they deform when analyzed, scale bar=1 μm)
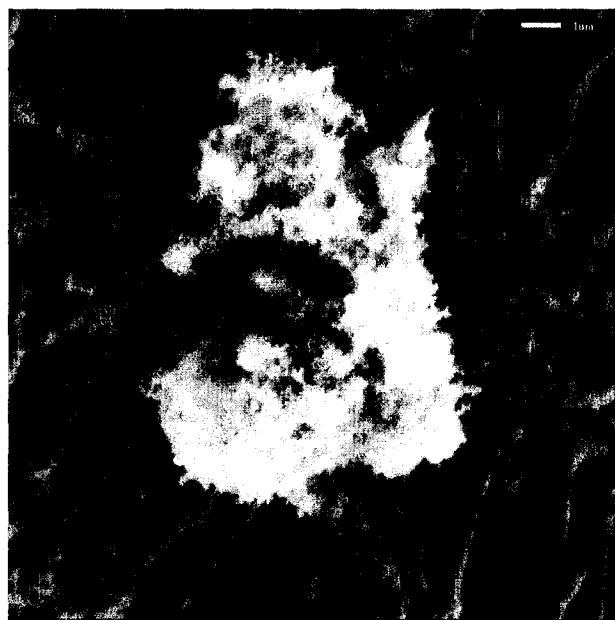
Figure 28   **SEM image of a typical combustion particle.**
(Combustion particles with small loose porous structures, which are difficult to with EDX due to composition of carbon element and porous structure, scale bar=1 μm)

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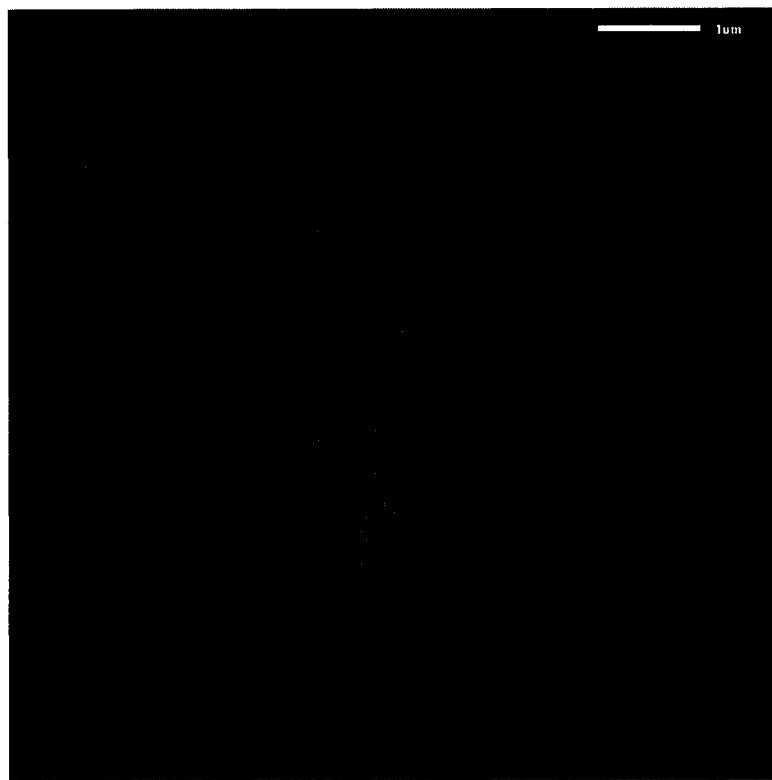
Figure 29   SEM image of a rust particle – primary Fe.
(Most common type of particle classified as "other" found at site B was
rust particles that are comprised primary of Fe, scale bar=1μm)

Table 28   Corresponding EDX elemental scan of a rust particle – primary Fe.

Library Standard: /imix/spectra/system standard (LDL 0.1%)

Accelerating Voltage	20KeV
Takeoff Angle	56.8 degrees

Elements	wt %
Fe	74.62
Mg	0.22
Al	0.91
Si	3.26
K	0.30
Ca	0.32
Na	15.54
Ba	0.42
Cr	0.60
Mn	3.81

101
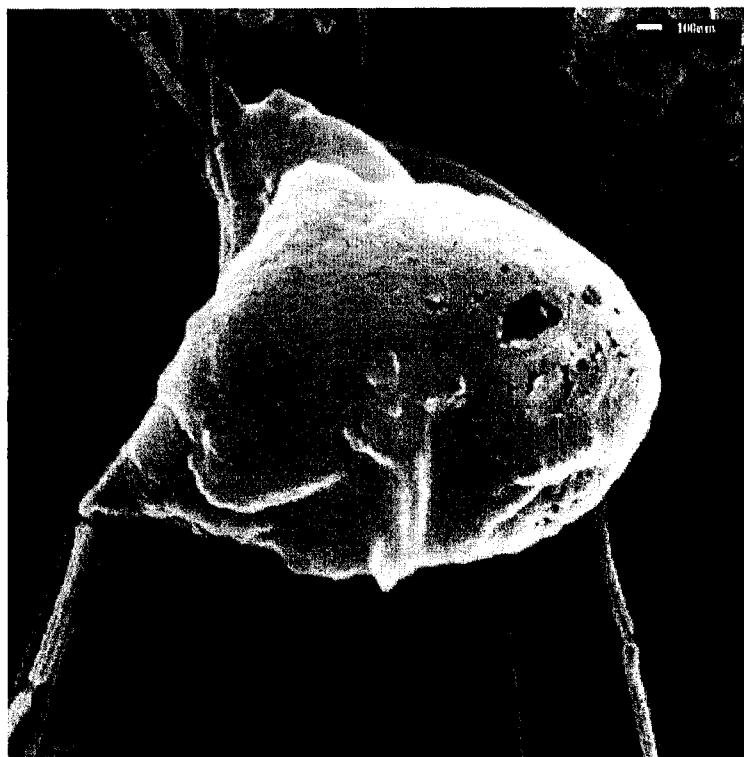
Figure 30   **SEM image of an unclassified particle – primary Na.**
(scale bar=100nm)

Table 29   **Corresponding EDX elemental scan of an unclassified particle –
primary Na.**

Library Standard: /imix/spectra/system standard (LDL 0.1%)

Accelerating Voltage	20KeV
Takeoff Angle	56.8 degrees

Elements	wt %
Na	93.70
Si	0.25
Ca	2.22
Ba	2.19
V	1.64

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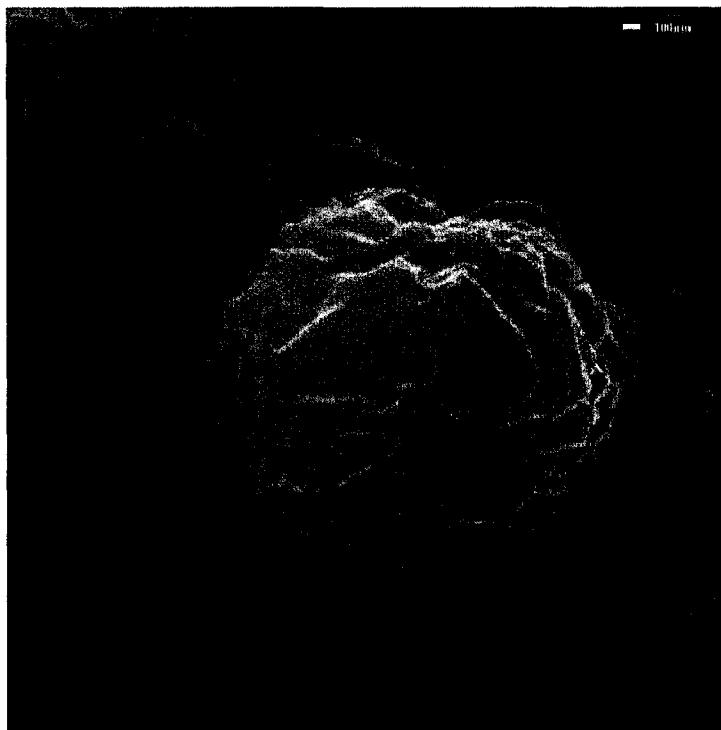
Figure 31   SEM image of an unclassified particle – primary Mg.
(scale bar=100nm)

Table 30   Corresponding EDX elemental scan of an unclassified particle –
primary Mg.

Library Standard: /imix/spectra/system standard (LDL 0.1%)

Accelerating Voltage	20KeV
Takeoff Angle	56.8 degrees

Elements	wt %
Si	0.42
Ca	3.13
Fe	1.40
Mg	84.81
Cl	6.11
K	1.60
Co	2.21
Cr	0.32
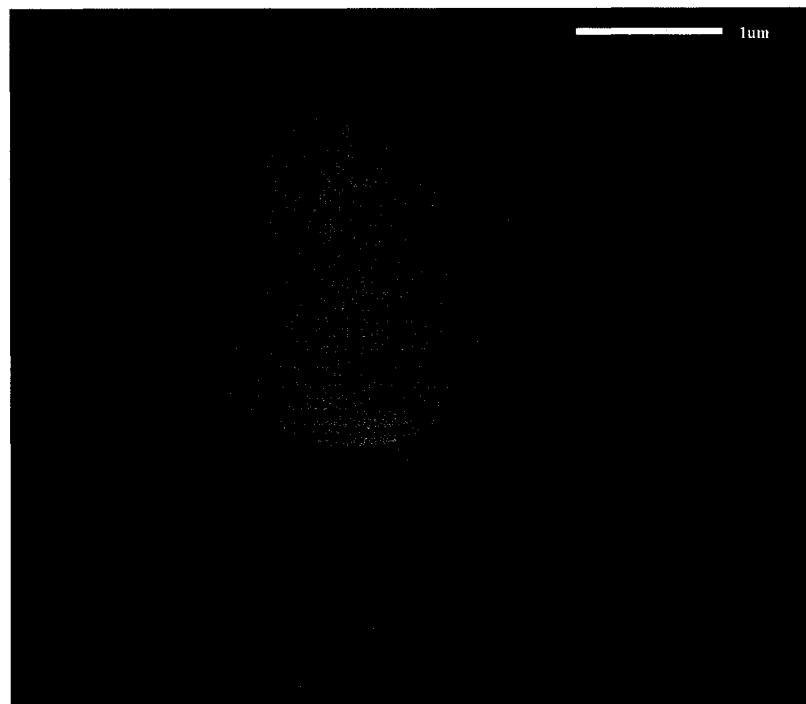
Figure 32   **SEM image of an unclassified particle – primary K.**
(scale bar=1 μm)

Table 31   **Corresponding EDX elemental scan of an unclassified particle –
primary K.**

Library Standard: /imix/spectra/system standard (LDL 0.1%)

Accelerating Voltage	20KeV
Takeoff Angle	56.8 degrees

Elements	wt %
Mg	2.13
K	96.78
Mn	1.09

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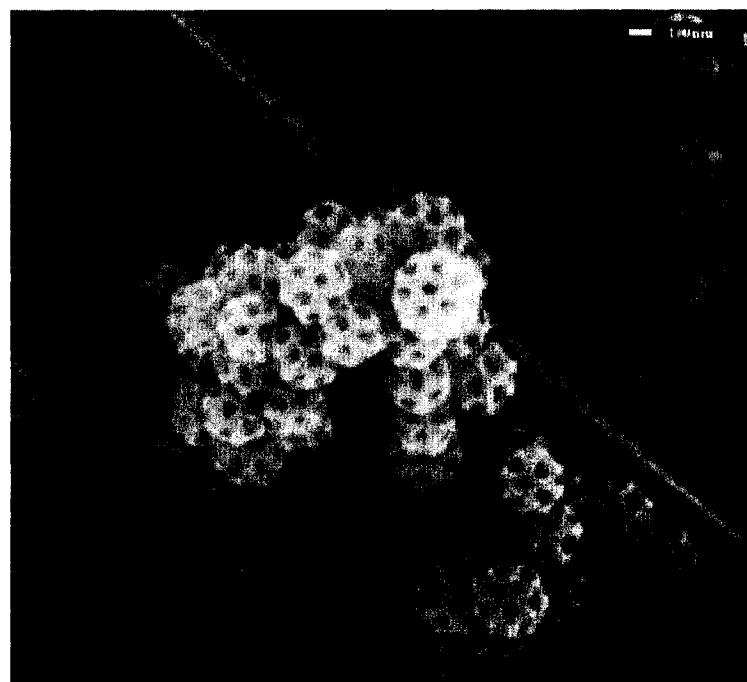
Figure 33   SEM image of organic particles.
(Organic particles are identifiable from their distinct sharp and form. EDX scan of organic particles appear with the same spectrum as the filter background, scale bar =100 nm)
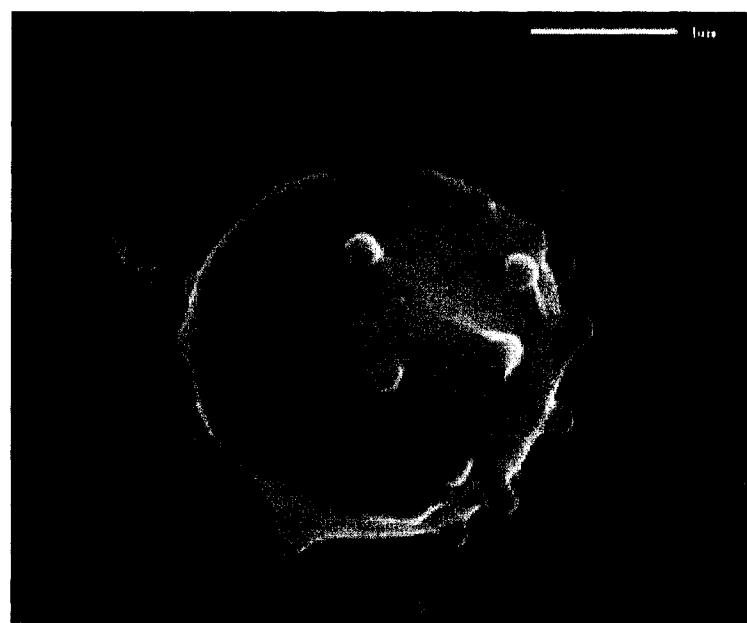
Figure 34   SEM image of an organic particle.
(scale bar=1 μm)

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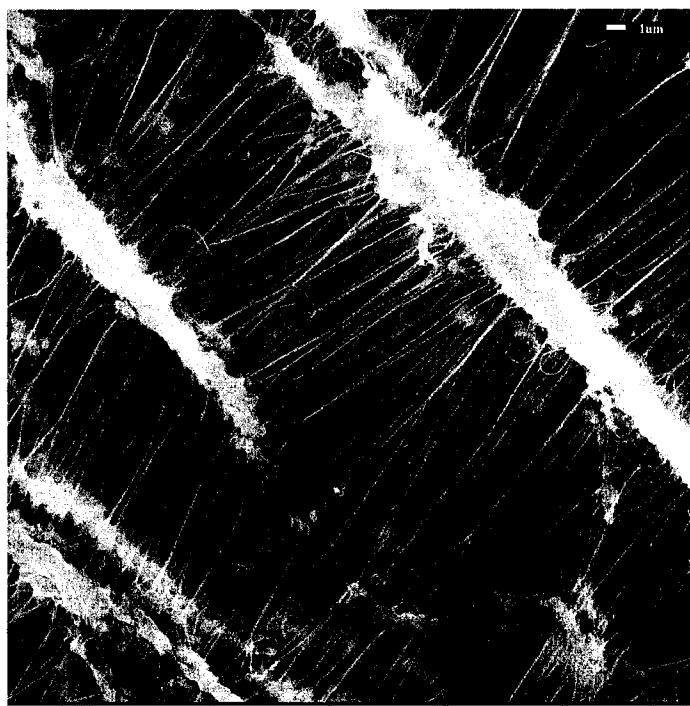
Figure 35   SEM image of a laboratory blank.
(scale bar=1 µm)
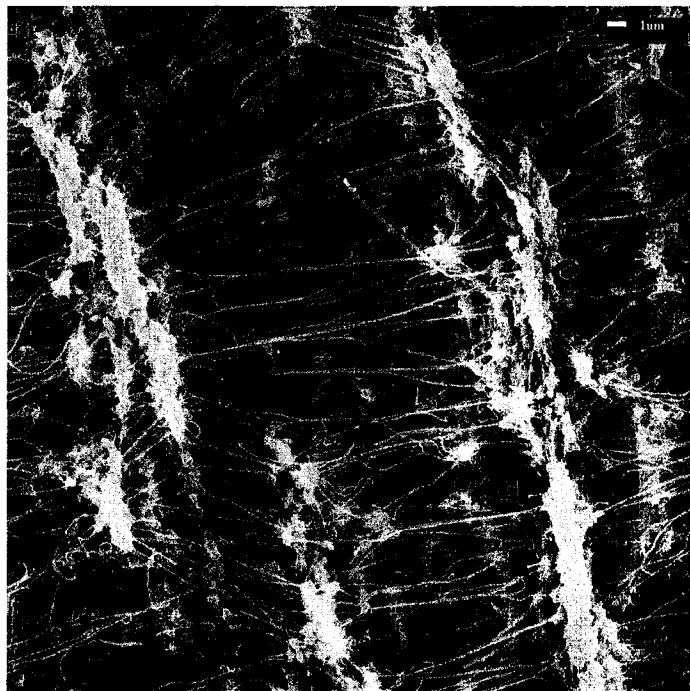
Figure 36   SEM image of a field blank.
(In gravimetric analysis, the net mass of filter <0.004 mg for 24-hr
sampling period, scale bar=1 µm.)

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Table 32   **Summary of classifications of particle counts at site B.**
(based on 60 PM$_{2.5}$ filters SEM-EDX analysis)

Particles Type	Descriptive properties	July	Aug	Sept	Oct	Nov
Biological	Pollen	3	24	14	0	0
	Fibrous	2	0	2	0	0
	Other	27	47	51	27	8
Crustal	Clay	36	94	110	63	85
	Silica	9	27	33	26	26
	Calcium	3	3	4	16	18
	Salts	2	0	2	9	14
Exhaust (Vehicular /industrial)	Fly ash	1	1	0	0	7
	Combustion	8	15	27	31	46
	Oil droplets	30	135	90	35	45
	Sulphur	0	0	2	0	0
Other	Sodium	0	0	0	0	5
	Potassium	1	1	0	0	0
	Rust	0	3	10	9	9
	Magnesium	0	0	1	0	0
Total						

Table 33   **Summary of classifications of particle counts at site C.**
(based on 60 PM$_{2.5}$ filters SEM-EDX analysis)

Particles Type	Descriptive properties	July	Aug	Sept	Oct	Nov
Biological	Pollen	1	25	23	8	0
	Fibrous	0	0	2	3	0
	Other	11	67	102	35	26
Crustal	Clay	26	71	89	61	93
	Silica	14	34	32	22	23
	Calcium	9	16	5	18	22
	Salts	2	0	4	2	1
	Titanium	0	2	3	0	1
Exhaust (Vehicular /industrial)	Fly ash	1	2	1	6	9
	Combustion	5	15	27	31	46
	Oil droplets	7	30	28	16	12
	Sulphur	1	0	0	2	0
Other	Sodium	0	2	2	9	6
	Potassium	1	0	1	1	0
	Rust	1	6	15	6	8
	Magnesium	0	0	1	1	1
Total						

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The first detail noted from Tables 32 and 33 was that crustal particles were the most abundant type of particles. These particles accounted for ~45% of particles identified at site B and ~48% at site C, respectively over the sampling period. The amount of these crustal particles was found to be relatively higher during the warmer sampling months (July to September) than the colder months (October to November). This suggests that originating sources for these types of particles (i.e. open fields, road dust) were more established during warmer months. During the colder months, snow cover and precipitation inhibit re-suspension of crustal particles into air. Relative to site C, a greater amount salt particles at site B in colder months was likely a result of localized sanding (including salt) material being placed on roadways in the vicinity of sampling site B.

The second detail noted in Tables 32 and 33 was the amount of exhaust-related particles (i.e. fly ash, combustion, and oil droplets). These particles accounted for ~36% of particles were detected at site B and about 21% at site C, respectively over the sampling period. A greater number of combustion particles was observed in the colder months (September to November) compared to warmer months (July an August) at site B.

Another detail noted was large oil droplets counts observed in August 2004 at site B. It is suspected that this result is from 127th Street roadwork in vicinity of the monitoring station. In addition, it was quite apparent that oil droplets counts on the filters were much higher on weekday samples compared to weekend samples at site B over the entire sampling period. This can be observed in Figures 37 and Figure 38. After further investigation with site personnel, this trend was concluded to be related to a greater frequency of localized traffic during weekdays compared to weekends.

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The last detail noted was biological particles accounted for ~16% of particles identified at site B and ~26% at site C. The higher count of biological particles found at site C is primarily a result of its proximity to a large open-field. During sampling in warmer months (July to September), higher biological counts were found. This is indicative of open-field sources (i.e. pollen, plant fragments and debris) being important during warmer months. This is an expected finding as other previous study has also found that during warmer periods a large fraction of particulate matter sampled is comprised of biological particles (Schulz and Kindzierski, 2001).

Figure 37 **Comparison of SEM image of oil droplets at site B during weekdays and weekends.**

(Sampling periods from July 22 to November 30, 2004, scale bar=1 μm)

Weekdays	**Weekends**

July to August

September

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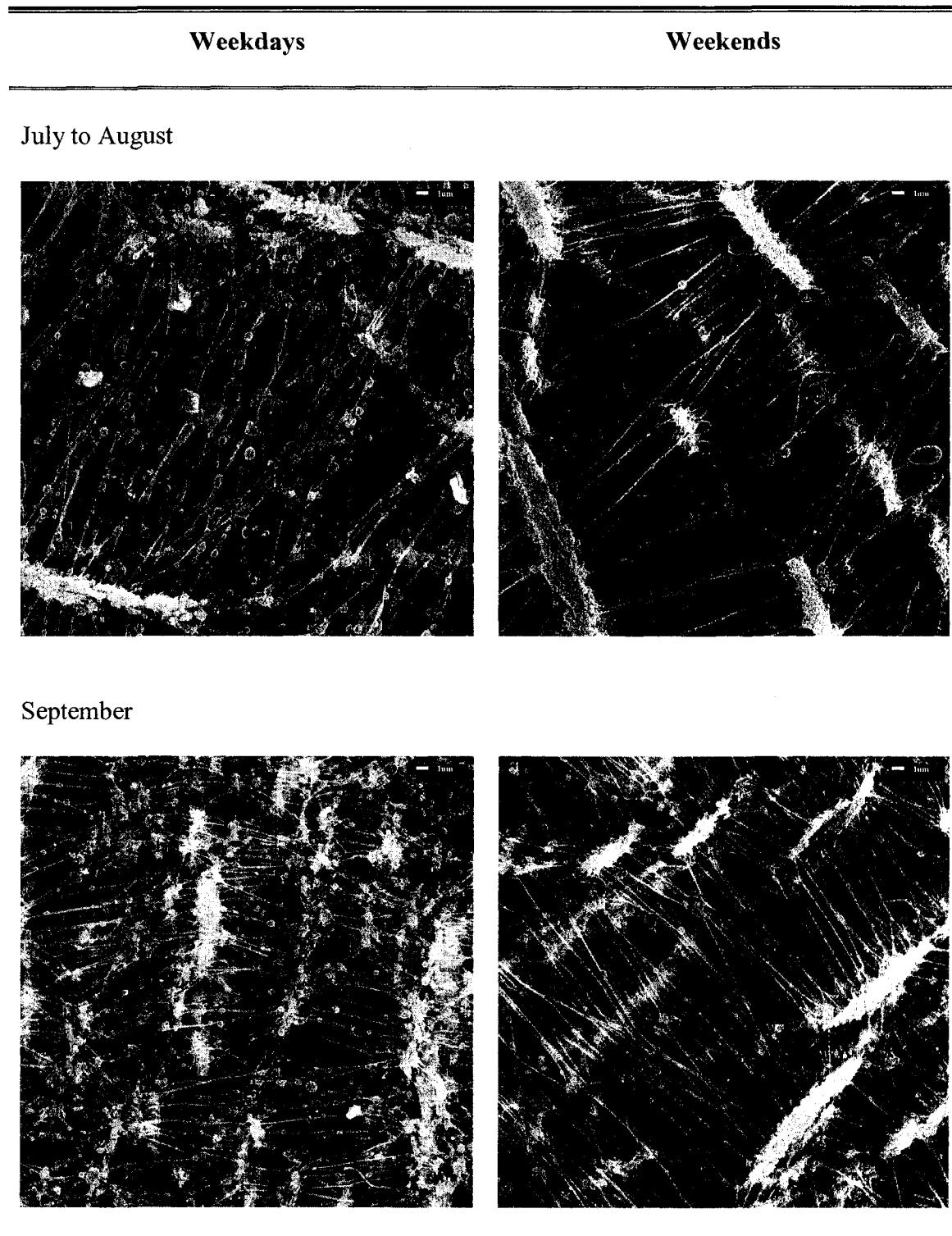
Figure 38   Comparison of SEM image of oil droplets at site B during weekdays and weekends (continued).
(Sampling periods from July 22 to November 30, 2004, scale bar=1 μm)

Weekdays	Weekend

October

November

111
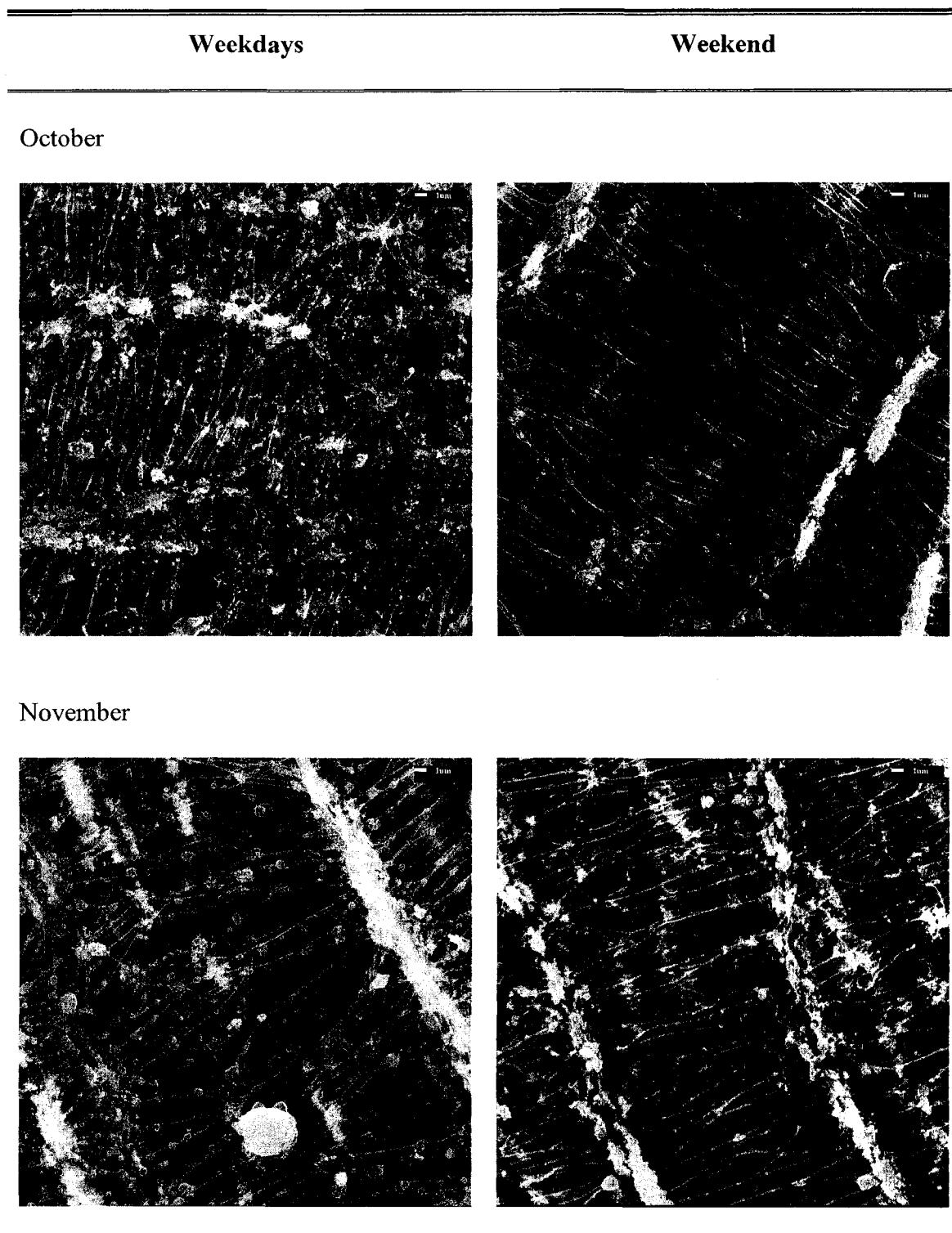
5.3   Particulate Matter Source Apportionment

5.3.1   Source Apportionment Results

A principle component analysis (PCA) was performed at sites B and C using elemental abundance (%) data provided by SEM-EDX analysis of $PM_{2.5}$ collected on filters. A total of sixty filters from each site were analyzed by SEM-EDX for a total of eighteen elements including: Si, Ca, Al, Mg, Fe, Na, K, Cl, S, Ti, Mn, Co, Pb, Cu, Cr, Cd, V, and Ba. These elements were chosen for analysis because of their abundances, strong tracer characteristics, and a qualitative knowledge of possible SEM-EDX elemental interference problems based on previous studies and personal communications (Braybrook, 2004; McCullum and Kindzierski, 2001; Schulz and Kindzierski, 2001) (Schulz and Kindzierski, 2001; McCullum and Kindzierski, 2004; Braybrook, 2004). PCA preparation adhered to techniques and protocols outlined in Section 4.6. Complete data descriptions, elemental abundance (%), and elemental concentrations (ng/m^3) over the entire sampling periods are presented in detail in Appendix 8.4.

Elemental concentration data for each of the eighteen elements were first standardized by calculating z-scores using Equation 6 (as discussed previously in Section 2.5). The z-scores were then used in conjunction with SYSTAT Version $10.0^®$ for PCA utilizing a Varimax rotation (SPSS, 2002). Subsequently elements were eliminated and the PCA repeated until all criteria outlined in Section 4.6.2 were satisfied. This elimination protocol resulted in a total of four factors with eigenvalues greater than one for both sites B and C. Eigenvalues which are less than one were presumably dominated by error variance and were ignored (Thurston and Spengler, 1985). A step-by-step account of how these results for both site B and C were achieved is provided below.

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- **Site B** (co-located at Alberta Environment Northwest Station)

PCA was initially conducted using data collected at site B (18 elements analyzed using SEM-EDX). This analysis resulted in identification of five factors with eigenvalues greater than one that combined to account for 88% of total variance of the original data set (Table 34). As no clear associations of elements with sources or source categories were apparent from examination of factor loadings, further analysis was required.

Table 34   Varimax rotated results of PCA at site B – step 1.

Factors	1	2	3	4	5
Si	0.92	0.20	-0.08	0.10	-0.05
Ca	0.67	0.38	-0.09	0.09	0.08
Fe	0.62	0.28	-0.04	0.71	0.03
Al	0.98	0.11	-0.01	-0.05	0.09
Mg	0.78	0.21	-0.03	0.08	-0.03
K	0.87	0.13	0.00	0.03	-0.05
Na	0.13	0.91	-0.02	0.13	0.33
Cl	0.08	0.99	-0.01	0.06	0.00
Ti	-0.02	-0.03	1.00	-0.03	-0.03
Mn	-0.04	0.19	-0.04	0.94	0.06
Cr	0.24	0.95	-0.03	0.18	-0.01
Cu	0.56	0.46	-0.19	0.19	0.02
Ni	0.97	0.07	0.14	-0.05	0.06
S	-0.02	-0.03	1.00	-0.03	-0.03
Pb	0.18	0.28	-0.04	-0.36	0.72
V	0.54	0.81	0.00	0.02	0.16
Co	0.99	0.05	0.01	-0.02	0.01
Ba	-0.12	0.05	-0.03	0.32	0.86
Eigenvalue	8.2	3.0	2.0	1.5	1.2
Variance Explained by Rotated Components	6.6	4.0	2.1	1.7	1.4
Percent of Total Variance Explained	36.8	22.4	11.4	9.7	7.9

The PCA was repeated after eliminating elements that had low abundance or that were thought to have been unreliably quantified by SEM-EDX (three elements):

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- Ba – which was only detected on three filters associated with sodium particles (<3% by count based upon a classification as an unknown type of particle).

- Ti – which was detected only on two filters associated with two sulphur particles out of a total of 500 exhaust-type particles based upon count).

- Na – which has been reported by Gordon et al. (1981) to be unreliably detected by SEM-EDX analysis due to spectral interferences.

This repeat analysis resulted in four factors with eigenvalues greater than one that combined to account for 84% of total variance of the original data set (Table 35).

Table 35   Varimax rotated results of PCA at site B – step 2.

Factors	1	2	3	4
Si	0.91	0.22	0.09	0.12
Ca	0.63	0.42	0.03	0.27
Fe	0.61	0.34	0.67	0.09
Al	0.97	0.16	-0.08	0.04
Mg	0.77	0.23	0.08	0.04
K	0.87	0.14	0.04	-0.03
Cl	0.05	0.97	0.07	-0.01
Mn	-0.04	0.25	0.89	0.08
Cr	0.21	0.94	0.19	0.02
Cu	0.52	0.49	0.14	0.38
Ni	0.97	0.11	-0.08	-0.11
S	0.02	0.00	-0.02	-0.93
Pb	0.14	0.44	-0.54	0.11
V	0.52	0.83	-0.02	0.00
Co	0.99	0.08	-0.03	0.00
Eigenvalue	7.8	2.3	1.5	1.1
Variance Explained by Rotated Components	6.4	3.4	1.6	1.1
Percent of Total Variance Explained	42.8	23.0	10.9	7.6

The PCA was repeated again after eliminating those elements that were clearly not distinctive to one source or factor. This elimination procedure was made based on a

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criterion that any element which had a factor loading greater than ±0.4 for three or more factors was not indicative of any one source (Harrison *et al.*, 1997; Statheropoulos *et al.*, 1998). The element did not satisfy this condition was Cu, as it was associated with three factors. This analysis resulted in four factors with eigenvalues greater than one that combined to account for 86% of total variance of the original data set (Table 36).

Table 36   Varimax rotated results of PCA at site B – step 3.

Factors	1	2	3	4
Si	0.91	0.20	0.09	-0.07
Ca	0.63	0.39	0.04	-0.09
Fe	0.62	0.32	0.67	-0.08
Al	0.97	0.15	-0.08	-0.03
Mg	0.77	0.22	0.09	-0.04
K	0.88	0.14	0.05	0.00
Cl	0.06	0.97	0.09	0.00
Mn	-0.03	0.24	0.90	-0.09
Cr	0.22	0.93	0.21	-0.02
Ni	0.97	0.11	-0.08	0.12
S	-0.01	-0.03	-0.03	0.99
Pb	0.15	0.45	-0.53	-0.15
V	0.53	0.83	0.00	-0.01
Co	0.99	0.07	-0.03	0.00
Eigenvalue	7.3	2.3	1.5	1.0
Variance Explained by Rotated Components	6.2	3.2	1.6	1.0
Percent of Total Variance Explained	44.5	22.6	11.7	7.5

The PCA was repeated a fourth time after eliminating elements that were not significantly contributing any further tracer information in identifying a source or source category. As the first factor was initially identified as crustal material, both Si and Co served no further use in the analysis primarily because they were only strongly associated with the first factor. Si had already supplied the necessary maker information to classify this source. As the element Co tends to be only be found in gasoline (<1% mass fraction)

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and biomass burning (Kitto, 1993; Someshwar, 1996) and it is not distinctive to the first factor, it was eliminated. This analysis again resulted in four factors with eigenvalues greater than one that combined to account for 85% of total variance of the original data (Table 37).

Table 37 ⌐ **Varimax rotated results of PCA at site B – step 4.**

Factors	1	2	3	4
Ca	0.66	0.37	0.04	-0.10
Fe	0.62	0.31	0.67	-0.08
Al	0.97	0.14	-0.08	-0.03
Mg	0.78	0.21	0.09	-0.05
K	0.89	0.12	0.05	0.00
Cl	0.07	0.98	0.08	0.00
Mn	-0.01	0.24	0.90	-0.10
Cr	0.23	0.94	0.20	-0.02
Ni	0.97	0.09	-0.08	0.12
S	0.00	-0.02	-0.04	0.99
Pb	0.19	0.56	-0.53	-0.17
V	0.54	0.82	0.00	-0.01
Eigenvalue	5.7	2.0	1.5	1.0
Variance Explained by Rotated Components	4.5	3.1	1.6	1.0
Percent of Total Variance Explained	37.5	25.5	13.5	8.7

Results of the PCA were then compared to previous studies, relevant literature, and particulate matter databases to identify the most likely source origins of $PM_{2.5}$ at site B. Further discussion of $PM_{2.5}$ source contributions and source descriptions for site B is presented in next the next section.

• **Site C (residential site with low local traffic volumes relative to site B)**

Similar to protocols used for site B, PCA was initially conducted using data collected (18 elements analyzed using SEM-EDX). This analysis resulted in six factors with eigenvalues greater than one that combined to account for 89% of total variance of

the original data (Table 38). As no clear associations of elements with sources or source

categories were apparent from examination of factor loadings, further analysis was

required.

Table 38   Varimax rotated results of PCA at site C – step 1.

Factors	1	2	3	4	5	6
Si	0.90	0.02	0.12	0.29	-0.07	-0.03
Ca	0.47	0.11	0.48	0.57	-0.08	-0.12
Fe	0.79	0.01	0.08	0.18	0.56	-0.03
Al	0.95	0.04	0.17	0.16	0.01	-0.04
Mg	0.70	0.08	0.12	-0.19	-0.05	-0.14
K	0.84	0.01	0.04	0.36	0.18	0.05
Na	-0.01	0.99	0.10	0.00	0.00	-0.03
Cl	0.23	0.02	0.84	-0.01	-0.11	0.16
Ti	-0.04	-0.05	-0.02	-0.03	-0.02	0.97
Mn	0.05	-0.01	0.04	0.05	0.99	-0.02
Cr	0.76	0.01	0.52	0.14	0.17	0.08
Cu	0.40	0.07	0.52	0.65	-0.10	0.01
Ni	0.87	0.01	0.02	0.45	0.06	0.06
S	0.14	-0.03	-0.15	0.85	0.14	-0.01
Pb	-0.02	0.09	0.83	-0.03	0.19	-0.19
V	0.55	0.81	0.15	0.07	-0.06	0.01
Co	0.99	0.04	0.06	0.04	-0.02	0.04
Ba	-0.11	0.99	-0.04	-0.01	0.02	-0.05
Eigenvalue	8.0	2.6	1.7	1.4	1.3	1.0
Variance Explained by Rotated Components	6.6	2.7	2.3	2.0	1.5	1.1
Percent of Total Variance Explained	36.6	14.8	12.7	11.2	8.1	5.9

PCA was repeated by following the same elimination protocol used for site B –

eliminating the elements Ba, Ti, and Na on the basis of low % abundance (Ba and Ti) or

unreliably detected by SEM-EDX analysis (Na). In addition, the element Ca was

eliminated as it was associated with three factors and met the "three-or-more factors"

elimination criterion used by Harrison et al. (1997) and Statheropoulos *et al.* (1998). This

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repeats analysis resulted in four factors with eigenvalues greater than one that combined

to account for 84% of total variance of the original data set (Table 39)

Table 39   Varimax rotated results of PCA at site C – step 2.

Factors	1	2	3	4
Si	0.88	0.13	0.35	-0.03
Fe	0.75	0.09	0.23	0.60
Al	0.94	0.17	0.21	0.06
Mg	0.73	0.09	-0.22	0.03
K	0.80	0.05	0.41	0.22
Cl	0.21	0.85	0.02	-0.13
Mn	0.00	0.04	0.06	0.99
Cr	0.72	0.54	0.22	0.19
Cu	0.40	0.52	0.57	-0.07
Ni	0.83	0.05	0.52	0.09
S	0.09	-0.09	0.89	0.11
Pb	-0.01	0.84	-0.08	0.19
V	0.66	0.22	0.01	-0.13
Co	0.98	0.05	0.08	0.04
Eigenvalue	7.4	1.7	1.4	1.2
Variance Explained by Rotated Components	6.2	2.1	1.9	1.5
Percent of Total Variance Explained	44.3	15.2	13.5	10.8

The PCA was repeated again after eliminating those elements that were not

significantly contributing any further tracer information in identifying a source. Again,

the first factor was initially identified as crustal material. Both V and Co served no

further use in the analysis primarily because they were only strongly associated with the

first factor. This repeat analysis resulted in four factors with eigenvalues greater than one

that combined to account for 86% of total variance of the original data set (Table 40).

Results of the PCA were then compared to the previous studies, the relevant

literature, and the particulate matter databases to identify the most likely source origins of

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$PM_{2.5}$ at site C. Further discussion of $PM_{2.5}$ source contributions and source descriptions for site C is given in next the next section.

Table 40 **Varimax rotated results of PCA at site C – step 3.**

Factors	1	2	3	4
Si	0.91	0.13	0.26	-0.08
Fe	0.79	0.08	0.15	0.56
Al	0.96	0.17	0.12	0.01
Mg	0.70	0.11	-0.27	-0.02
K	0.85	0.05	0.33	0.17
Cl	0.22	0.85	-0.01	-0.14
Mn	0.05	0.04	0.06	0.99
Cr	0.76	0.54	0.13	0.15
Cu	0.44	0.52	0.53	-0.09
Ni	0.88	0.05	0.44	0.05
S	0.16	-0.08	0.90	0.11
Pb	-0.02	0.85	-0.07	0.20
Eigenvalue	6.3	1.7	1.3	1.1
Variance Explained by Rotated Components	5.2	2.1	1.6	1.4
Percent of Total Variance Explained	43.4	17.3	13.3	12.0

5.3.2 Identification of Major Source in Study Area

Varimax rotated results of PCA from site B (Table 37) and the residential site C (Table 40) were compared to previous studies, relevant literature, and the U.S.EPA's Speciate 3.2 Database (2002) to identify and categorize the most likely source of $PM_{2.5}$ at each receptor site. Table 40 and Table 41 present the varimax-rotated results of PCA summarized by source contributions for site B and C, respectively. Source contribution summaries are shown in Figure 39 and Figure 40 for site B and C, respectively. More-detailed descriptions and discussions of each factor are also presented.

- **Site B (co-located at Alberta Environment Northwest Station)**

The first factor inferred at site B (Table 41) was crustal material due to its strong association with the geological maker elements Al, K, and Ni (Beceiro-Gonzalez *et al.*, 1997). Ca, Fe, and Mg – which are considered to make up an important part of the chemical profile of crustal material (Hammerle and Pierson, 1975; U.S.EPA, 1993; Chow, 1995) – had moderate associations to this factor.

Table 41   **Summary of PM$_{2.5}$ Source contributions at site B.**
(co-located with Northwest Stn.)

Factors	Crustal Material	Combustion	Transportation	Regional Sulphate
Ca	0.66			
Fe	0.62		0.67	
Al	0.97			
Mg	0.78			
K	0.89			
Cl		0.98		
Mn			0.90	
Cr		0.94		
Ni	0.97			
S				0.99
Pb		0.56		
V	0.54	0.82		
Eigenvalue	5.7	2.0	1.5	1.0
Variance Explained by Rotated Components	4.5	3.1	1.6	1.0
Percent of Total Variance Explained	37.5	25.5	13.5	8.7

The anthropogenic tracer V – which also had a moderate association with this factor – was considered due to near-field vehicular emissions (U.S.EPA, 1993; Chow, 1995; Chow and Watson, 1998). The anthropogenic tracer element V emitted near field (or locally) can be absorbed on the surface of geological fine particles and subsequently re-suspended as road dust particles due to vehicular movements. This factor contributed

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to 37% of the total variance of the original data set. In other word, crustal material was inferred to contribute to 37% of the makeup of $PM_{2.5}$ collected at site B. For comparison, U.S.EPA (1999b) reported that geological re-suspended dust typically consists of about 20% $PM_{2.5}$, however in summer months it can be as high as 40%.

The second factor was inferred as the total of contributions from numerous combustion sources because of its strong association to the marker elements Cl and Cr (Kleinman et al., 1980; Kitto, 1993; Gao et al., 1996). Its moderate association with V and Pb further supported labeling of this factor as combustion processes such as vehicular fuel, oil combustion, and biomass and vegetation burning (Kleinman et al., 1980; Lowenthal and Rahn, 1987; Morales et al., 1990; Sharma and Singh, 1992; Huang et al., 1994).

The presence of Cl could suggest a salt aerosol source. However, as this study was conducted in the summer and fall months, no road salts was used in the area. In addition, there was no marine aerosol source for thousands of kilometers. The most important source for Cl – after salt aerosols – is considered to be combustion activities (Marcazzan, 1998; U.S.EPA, 1993).

The third factor was inferred as a transportation source due to its strong association with the element Mn (manganese). Mn in the fine particulate matter fraction likely resulted from combustion of the manganese-based gasoline additive methylcyclopentadienyl manganese tricarbonyl (MMT), which has been used to enhance automobiles performance in Canadian gasoline for about 20 year (Pellizzari et al., 1999). It has also been suggested by others (Joselow et al., 1978; Davis et al., 1988) that an important primary anthropogenic source of human exposure to inorganic Mn in the urban

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atmosphere is from combustion of MMT in gasoline. A recent vehicle exhaust study by Zayed *et al.* (1999) reported that Mn is emitted from tailpipes primarily as a mixture of Mn-phosphate and Mn-sulphate with sizes ranging between 0.2 to 10 μm, where on average, more that 99% of exhaust particles were <5 μm and 86% were <1 μm in size.

Another study (Loranger and Zayed, 1997) suggested that variation of Mn concentrations in urban atmospheres were significantly correlated in time with traffic density. Also, several studies show that roadside soils and plant may be elevated in Mn due to traffic emissions (Brault *et al.*, 1994; and Loranger *et al.*, 1994, 1995, 1996). The element Fe, which had moderate association with this factor, is also indicative of transportation emissions. Kitto (1993) reported that the element Fe combined with other tracer elements (i.e., Na, K, Zn, As) attributed to greater than 1% mass fraction in vehicle emissions.

The final factor was identified as a regional sulphate source due to its strong association with sulphur element. Sulphate has long been recognized as a regional pollutant (Dzubay *et al.*, 1988). It is transformed slowly into secondary aerosols from SO_2 via atmospheric chemistry and in some cases travels distances of hundreds of kilometers, although ambient levels are not much affected by local sources (Tuncel *et al.*, 1985). In Alberta, background regional sulphate is inferred to be due to a high amount of oil and gas activity that often results in gas flaring and other industrial process emissions (e.g. coal-fired power plants and other non-specific industrial sources (Schulz and Kindzierski, 2001). Cheng *et al.* (1998) reported that the largest mass fraction of the fine particulate matter is sulphate for Edmonton and Calgary.

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Results of the source apportionment indicate that $PM_{2.5}$ sampled at site B was comprised of the contributions of at least four sources (not including biological material) (Figure 39):

- The largest contribution was from crustal material which accounted for 37% of $PM_{2.5}$ sampled.

- The next most significant source contributing 25% was of combustion origins.

- About 14% was being contributed from vehicle/transportation activities.

- About 9% of $PM_{2.5}$ sampled originated from regional sulphates.

- A total of 15% of $PM_{2.5}$ originated from unknown sources that could not be explained by PCA.

Unknown
15%

Crustal
Material
37%

Regional
sulphate
9%

Transportation
14%

Combustion
25%
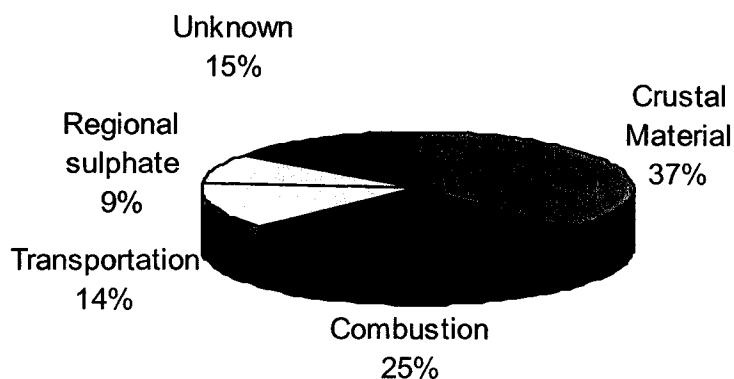
Figure 39   Diagram of $PM_{2.5}$ Source contributions at site B.
(Site B was co-located at the Northwest Station.)

- **Site C (residential site with low local traffic volumes relative to site B)**

The first factor inferred at site C (Table 42) was crustal material due to its strong association with the geological maker elements Si, Al, and K, and moderate association with Fe and Mg (Hammerle and Pierson, 1975; U.S.EPA, 1993; Chow, 1995; Beceiro-Gonzalez *et al.*, 1997). While element Cr and Ni also had moderate associations to this

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factor, they are considered to due to wood burning ash, which were probably from the sources including fireplaces, barbecue and forest fires, mixed with soil in vicinity of sampling site (Edward Aul & Associates Inc. and E.H. Pechan & Associates Inc., 1993; Someshwar, 1996). This factor contributed 43.4% of the total variance of the original data set. In other word, crustal material was inferred to contribute to 43.4% of the $PM_{2.5}$ collected at site C. Comparison to the same source component for the Site B (Table 41), suggests that the higher contribution of crustal material at site C may be explained by its proximity to a large open field.

Table 42   Summary of $PM_{2.5}$ Source contributions at site C.
(Epcor Reservoir Site)

Factors	Crustal Material	Combustion	Regional Sulphate	Transportation
Si	0.91			
Fe	0.79			0.56
Al	0.96			
Mg	0.70			
K	0.85			
Cl		0.85		
Mn				0.99
Cr	0.76	0.54		
Cu		0.52		
Ni	0.88			
S			0.90	
Pb		0.85		
Eigenvalue	6.3	1.7	1.3	1.1
Variance Explained by Rotated Components	5.2	2.1	1.6	1.4
Percent of Total Variance Explained	43.4	17.3	13.3	12.0

The second factor was inferred to originate from total contributions of numerous combustion sources because of its strong association to marker elements Cl and Pb (Kleinman et al., 1980; Kitto, 1993; Gao et al., 1996). Its moderate association with Cr

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and Cu further supported labeling of this factor as combustion type processes such as vehicular fuel, oil combustion, and biomass and vegetation burning (Kleinman *et al.*, 1980; Lowenthal and Rahn, 1987; Morales *et al.*, 1990; Sharma and Singh, 1992; Huang *et al.*, 1994).

The third factor was inferred as a regional sulphate source due to its strong association with the element S, as discussed above. The final factor was inferred as transportation, again as discussed above.

Results of the source apportionment at site C were quite similar in terms of the most-likely source components including crustal material, combustion, transportation, and regional sulphate (Figure 40).

Unknown
14%

Transportation
12%

Crustal
Material
44%

Regional
sulphate
13%

Combustion
17%
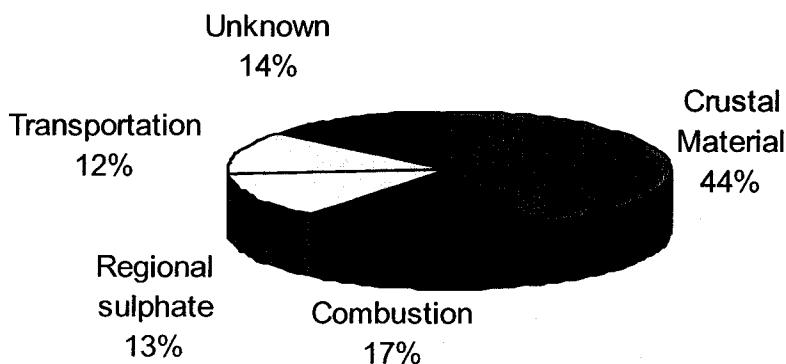
Figure 40 **Diagram of PM$_{2.5}$ Source contributions at site C.**
(Site C was adjacent in a typical residential area close to a large open field - Epcor Reservoir Site)

The results revealed that PM$_{2.5}$ sampled at site C − located within a typical residential area of Edmonton − was similar to that observed at site B:

- The largest contribution was from crustal material and accounted for 44% of PM$_{2.5}$ sampled.

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- The next most significant source accounting for 17% of $PM_{2.5}$ sampled was combustion-related particulates likely originating from surrounding sources.

- About 13% of $PM_{2.5}$ sampled originated from regional sulphates.

- About 12% was being contributed from vehicle/transportation activities.

- A total of 14% of the $PM_{2.5}$ at site B originated from unknown sources that could not be explained by PCA.

5.4   Comparison of Two Sites Source Profile

5.4.1   Comparison by Particle Counts Profile

Figure 41 presents an individual particle count comparison for the four dominant types of particle at sites B and C. As discussed in Section 5.2.2, a large amount of exhaust-type particles (combustion, fly ash, and oil droplets) were found at site B when compared to site C. Site C is located further from local traffic with little or no commercial activities, whereas site B is very close to a heavily-used roadway (<50m) with intensive traffic density during weekdays. It is also located in proximity to more commercial activities (e.g. garage, gas station, and shopping center within 150 m). These activities provide a reasonable explanation for higher exhaust-type particle counts observed at site B.

Counts for particle types observed at site C suggest slightly more-important contributions from open-field (crustal) sources and less-important contributions from combustion and traffic sources. This is sensible given that site C was located near a large open field and much further away from heavily used roadways. This comparison of particle counts shows the importance of the influence of near-field sources.

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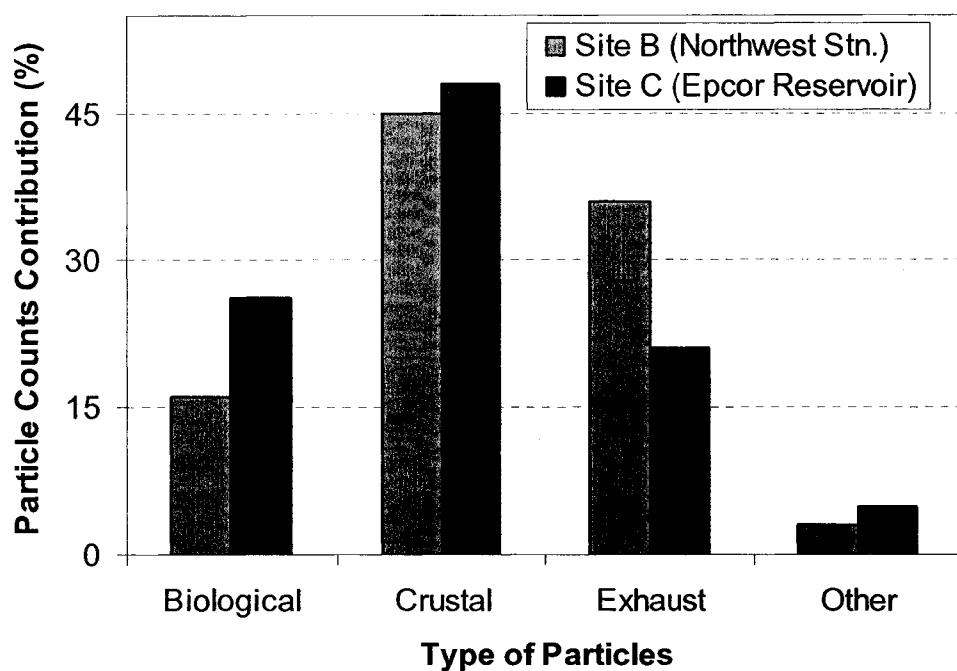
Figure 41 Comparison by source profiles for sites B and C based on particle counts classified by morphology and chemical speciation characteristics.

(Comparison is based on sixty 24-hr $PM_{2.5}$ samples over entire sampling period July 22 to November 30, 2004. Detailed classification of particle type is presented in Table 31 and Table 32 in the Section 5.2.2.)

5.4.2 Comparison by Elemental Profile

Figure 42 shows the comparison by elemental profiles at sites B and C as inferred from the PCA. Similar to the comparison by particle counts, higher contributions of exhaust-related sources (i.e. combustion, transportation) were found in site B compared to site C. In addition, lower contributions of crustal particles were inferred at B compared to site C.

Comparison of combustion sources inferred by elemental profiles at the two sampling sites showed higher correlations for elements Cl and Cr and moderate correlations for elements Pb and V at site B. These findings suggest the labeling as

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combustion sources more related to vehicular fuel, oil combustion. Whereas, higher correlations for elements Cl and Pb and moderate correlations for elements Cr and Cu at site C suggest the labeling as biomass burning source possibly more-related to wood burning sources (e.g. fireplaces, barbecue) at site C.
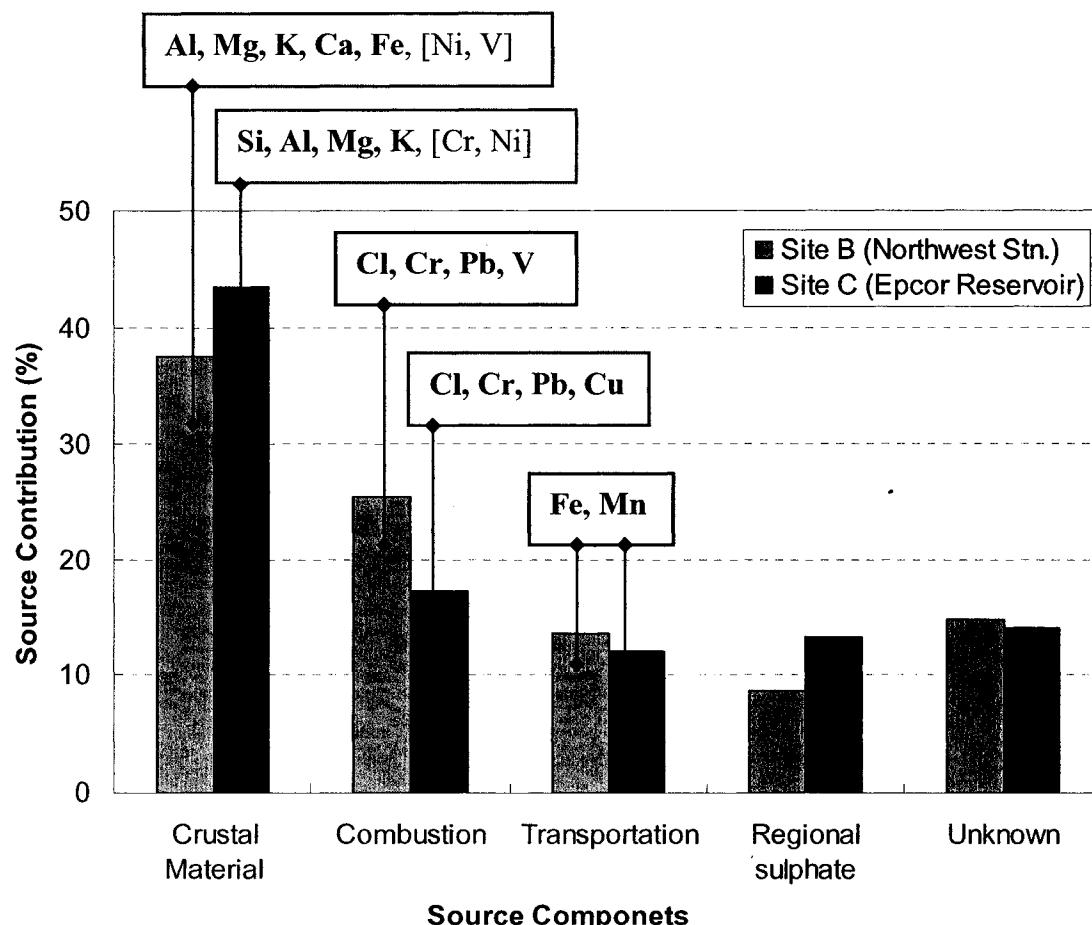
Figure 42   Comparison of PM$_{2.5}$ profiles for sites B and C based on PCA.

6. CONCLUSIONS AND RECOMMENDATION

Conclusions derived in this study relate only to the nearly five-month's of ambient $PM_{2.5}$ samples (July 22 to November 30, 2004) at the four sites. Nevertheless, on the basis of these samples and earlier related studies, statements presented below summarize the present understanding of $PM_{2.5}$ mass levels, temporal and spatial concentration variation, and elemental composition and probable source contributions at the four sites in Edmonton.

6.1 Conclusions

6.1.1 $PM_{2.5}$ Mass Trends

The 24-hr average $PM_{2.5}$ mass levels exhibited very similar trends across the four sites in Edmonton. Local (near-field) emission, however, was inferred to have influenced $PM_{2.5}$ concentrations close to some of the monitoring sites. An example was site B, which was situated close to a busy roadway and was observed to have slightly higher levels that at some of the other sampling sites. The 24-hr average $PM_{2.5}$ levels from the four sites ranged from about 0.6 to 28 $\mu g/m^3$ with the majority of the concentrations between 0.9 and 20 $\mu g/m^3$. The arithmetic mean concentration ranged from 6.3 at site D (residence at St. Albert) to 9.3 at site B (adjacent to 127th Street).

It was noted that 24-hr average $PM_{2.5}$ levels from all monitoring sites were lower than the Alberta Environment Surveillance Trigger Concentration (15 $\mu g/m^3$) for most of sampling period. Short-term fluctuations in peak $PM_{2.5}$ levels were inferred be attributed to near-field sources and/or regional sources further way under prevailing winds. The maximum 24-hr mean $PM_{2.5}$ concentration observed during the entire sampling period was 28 $\mu g/m^3$ at site B. None of the samples collected from the four sites exceeded the

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Canada-wide Standard (CWS) benchmark concentration of $30\mu g/m^3$ during the sampling period.

6.1.2 $PM_{2.5}$ Elemental Compositions and Particle Morphologies

Data from two sampling sites – one located at the Alberta Environment 127th Street Northwest Station and another one located adjacent in a typical residential area close to a large open field (Epcor Reservoir Site) – were chosen to evaluate and compare chemical composition profiles in $PM_{2.5}$. Elements analyzed in 24-hr average $PM_{2.5}$ filter samples from these two sites included: Si, Ca, Al, Mg, Fe, Na, K, Cl, S, Ti, Mn, Co, Pb, Cu, Cr, Cd, V, and Ba. Based upon abundance of elements in these samples and corresponding morphology as observed by SEM/EDX, the following was observed:

- Crustal particles were the most abundant type of particles. These particles accounted for 45% of particles identified at site B and 48% at site C.

- Exhaust-related particles (i.e. fly ash, combustion, and oil droplets) accounted for 36% of particles detected at site B and about 21% at site C.

- Biological particles accounted for 16% of particles identified at site B and 26% at site C.

6.1.3 $PM_{2.5}$ Source Contributions

Relevant literature was combined with results of PCA at the two sites to identify and categorize the most likely sources of $PM_{2.5}$. Four probable generic sources of particulate matter were identified. These included re-suspended crustal material, combustion, transportation, and regional sulphate. Generic sources inferred at sampling site B included the following:

- Re-suspended crustal material (37%).

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- Combustion sources (25%).

- Transportation (14%).

- Regional sulphates (9%).

- Unknown (15%).

Generic sources inferred at sampling site C included the following:

- Re-suspended crustal material (44%).

- Combustion sources (17%).

- Transportation (12%).

- Regional sulphates (13%).

- Unknown (14%).

Comparison of $PM_{2.5}$ profiles between the two sites (Figure 42) suggested similar source profiles.

6.2 Recommendation

Based on the findings and conclusions of the present study, a recommendation for future research was made:

- It is recommended that other chemical species should be analyzed to gain a better understanding of the profiles from vehicle and other, e.g. industrial, emissions. These chemicals could include organic carbon (OC), elemental carbon (EC), and gas-phase pollutants (NO_x, CO, SO_2). Supplementing these additional species may improve the ability to distinguish vehicular and industrial sources from natural and other anthropogenic sources based on source apportionment.

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8. APPENDICES

8.1 Particulate Matter Guidelines and Regulatory Limits.

(Provincial, National, and International Particulate Matter Guidelines and Regulatory Limits)

Location / Agency	Parameter	Guideline / Regulation
Canada (Environment Canada and Health Canada, 2000; AEP, 1999; CEPA and FPAC, 1999)	PM_{10} $PM_{2.5}$ $PM_{2.5}$ TSP	25 $\mu g/m^3$ averaged over 24 hours (*reference level*) 15 $\mu g/m^3$ averaged over 24 hours (*reference level*) 30 $\mu g/m^3$ averaged over 24 hours (Canada Wide Standard) [a] 120 $\mu g/m^3$ as a 24-hr average concentration (max acceptable) 120 $\mu g/m^3$ as a 24-hr average concentration (max tolerable) 60 $\mu g/m^3$ as an annual geometric mean (max desirable) 70 $\mu g/m^3$ as an annual geometric mean (max acceptable)
SK, MN, NB, PEI, NS, and NF	TSP	120 $\mu g/m^3$ as a 24-hr average concentration 70 $\mu g/m^3$ as an annual geometric mean
BC	TSP	150 $\mu g/m^3$ as a 24-hr average concentration (desirable) 200 $\mu g/m^3$ as a 24-hr average concentration (acceptable objective) 60 $\mu g/m^3$ as an annual geometric mean (desirable goals) 70 $\mu g/m^3$ as an annual geometric mean (acceptable objective)
ON	TSP	120 $\mu g/m^3$ as a 24-hr average concentration 60 $\mu g/m^3$ as an annual geometric mean
QB	TSP	150 $\mu g/m^3$ as a 24-hr average concentration 70 $\mu g/m^3$ as an annual geometric mean
United States Environmental Protection Agency (EPA, 1997)	PM_{10} $PM_{2.5}$	150 $\mu g/m^3$ as a 24-hr average concentration [b] 50 $\mu g/m^3$ as an annual mean concentration [c] 65 $\mu g/m^3$ as a 24-hr average concentration [d] 15 $\mu g/m^3$ as an annual mean concentration [c]
World Health Organization (Pryor and Barthelmine, 1996)	PM_{10}	70 $\mu g/m^3$ as a 24-hr average concentration

[a] based on the 98th percentile ambient measurement annually, averaged over 3 consecutive years.
[b] based on the 3 year average of the 99th percentile of 24-hr PM_{10} concentrations.
[c] based on the 3 year average of the annual arithmetic mean of the concentration.
[d] based on the 3 year average of the 98th percentile of 24-hr $PM_{2.5}$ concentrations.

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8.2   MiniVol Calibration Information.
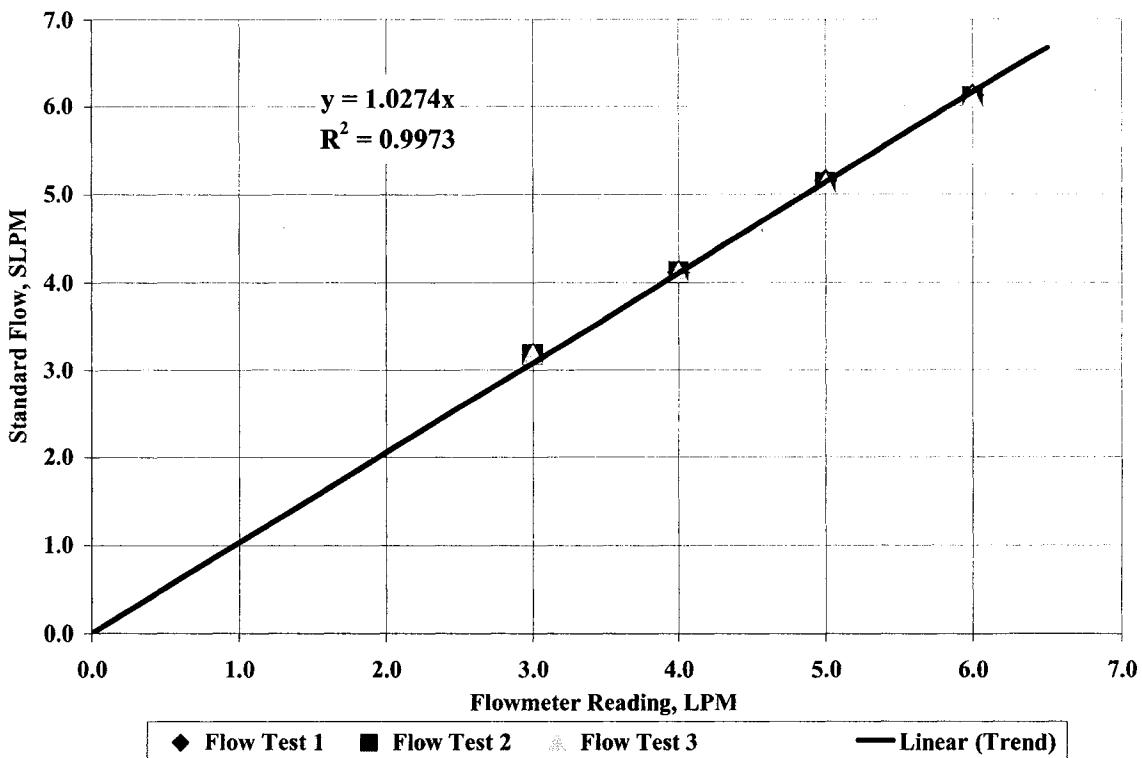
Figure A1. MiniVol #2325 Calibration Curve.

$$y = 1.0274x$$
$$R^2 = 0.9973$$
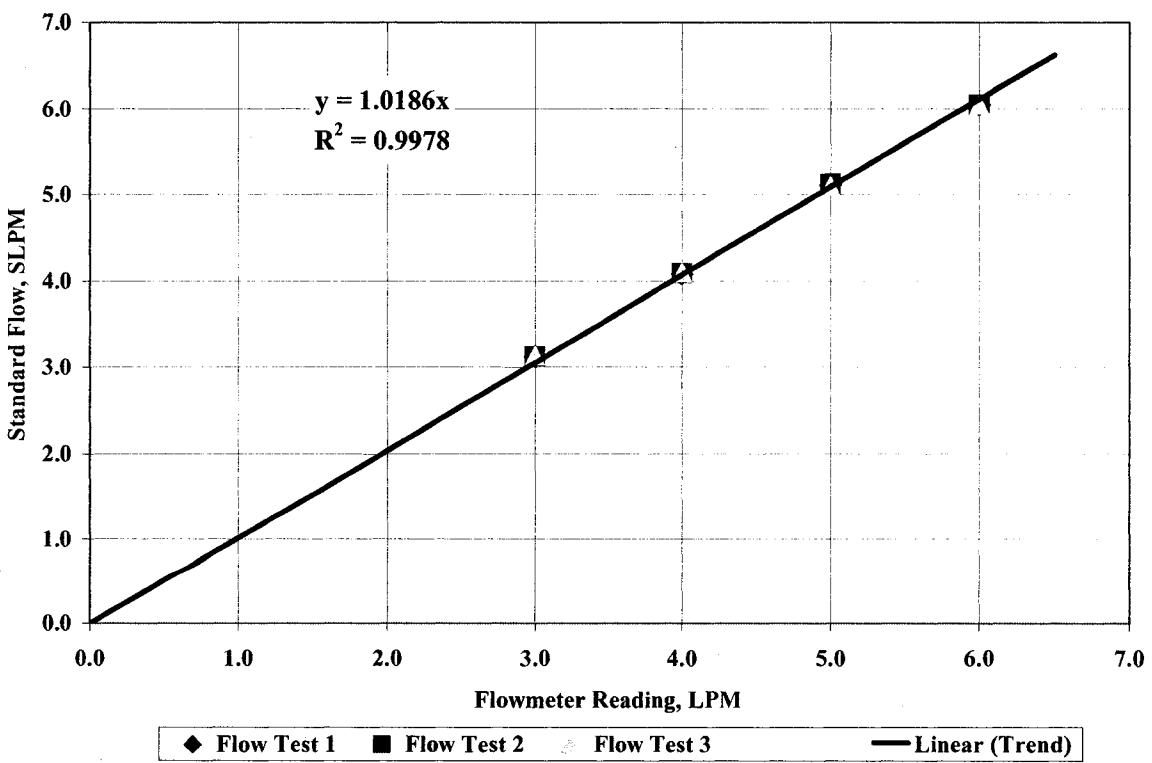
Figure A2. MiniVol #2324 Calibration Curve.

$$y = 1.0186x$$
$$R^2 = 0.9978$$

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$y = 0.9855x$
$R^2 = 0.9997$

Flow Test 1   Flow Test 2   Flow Test 3   ——Linear (Trend)
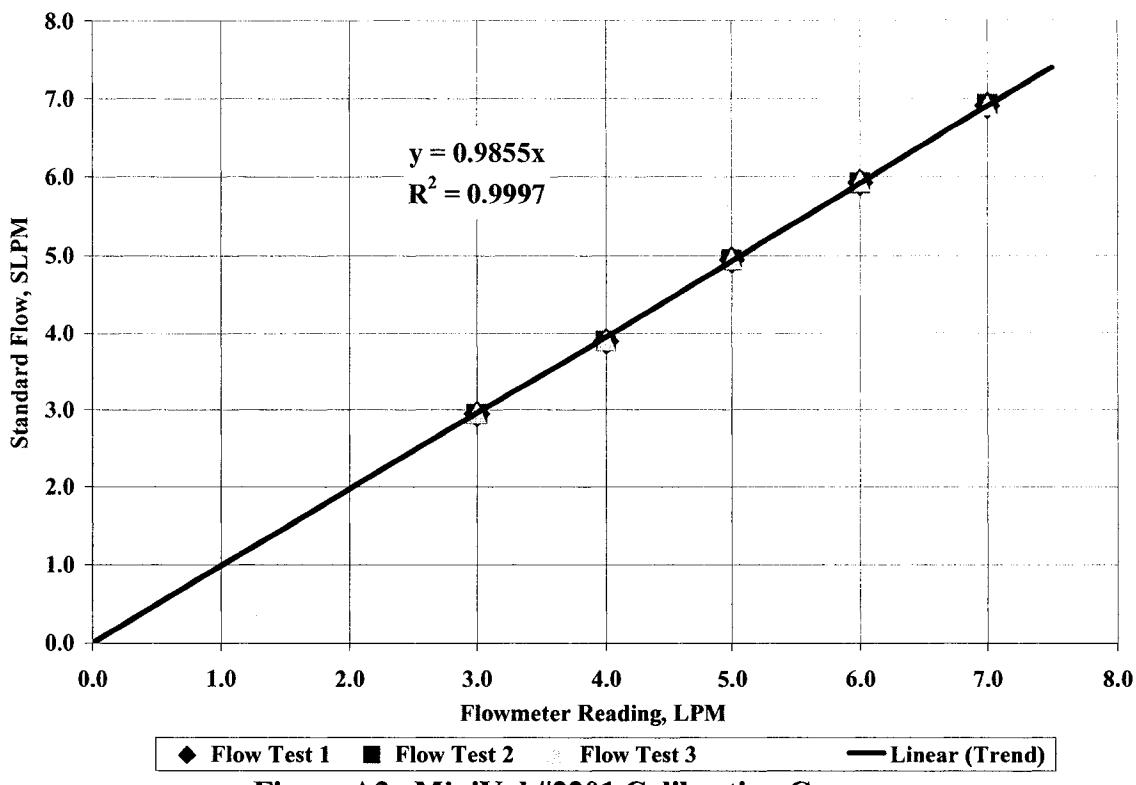
Figure A3. MiniVol #2201 Calibration Curve.

$y = 0.9889x$
$R^2 = 0.999$

Flow Test 1   Flow Test 2   Flow Test 3   ——Linear (Trend)
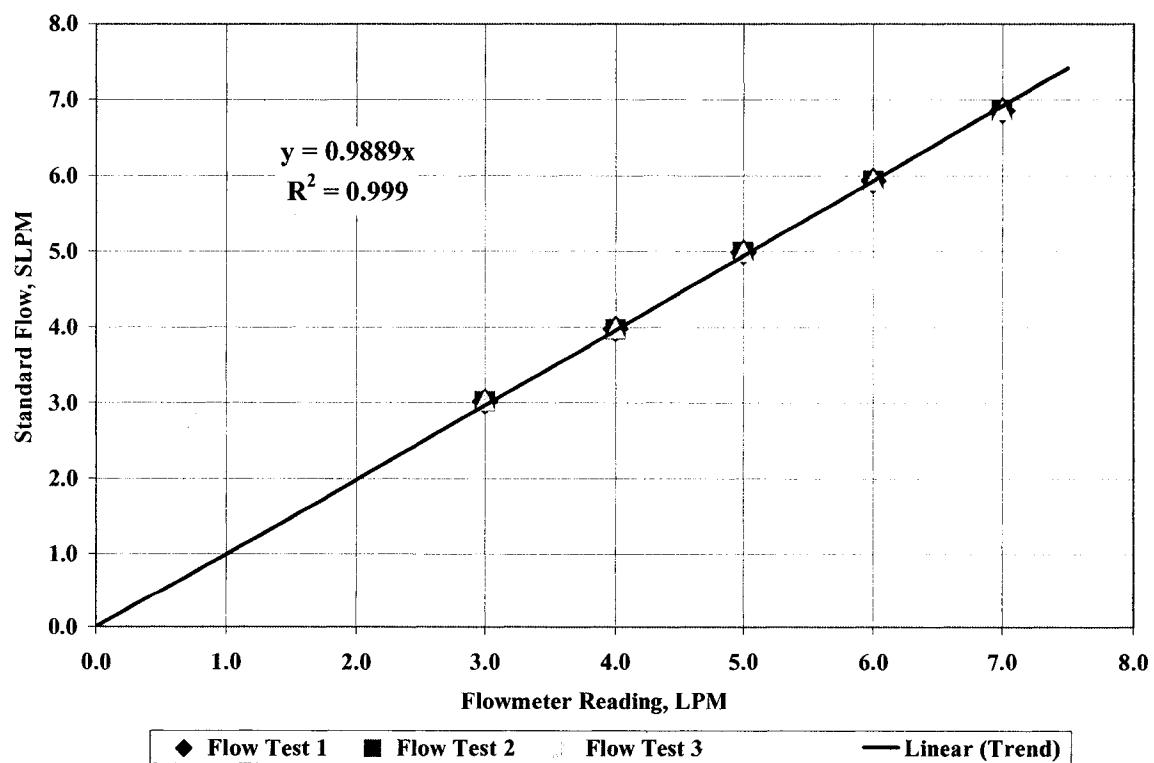
Figure A4. MiniVol #2127 Calibration Curve.

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8.3   MiniVol PM$_{2.5}$ Mass Raw Data (μg/m^3) and accordingly Meteorological Data.

n	Date mm/dd/yy	Site A UA Farm	Site B NW Stn.	Site C EPCOR	Site D St. AB	Site Ref.[1] NW Stn	Temp (°C)	PRECIP (mm)
1	7/22/2004	27.5	22.9	21.9	20.1	21.2	16.9	0.50
2	7/24/2004	16.0	18.7	19.5	17.8	14.2	22.1	0.00[2]
3	7/26/2004	7.8	8.3	8.6	8.9	5.0	16.6	1.00
4	7/28/2004	5.5	8.5	7.2	4.7	5.2	14.4	0.00
5	7/30/2004	7.0	8.7	6.1	5.9	5.1	19.9	3.00
6	8/1/2004	6.0	5.4	4.8	4.0	4.8	16.9	0.00
7	8/3/2004	6.2	6.1	9.3	7.4	6.1	20.3	0.50
8	8/5/2004	10.6	12.3	12.8	11.1	10.3	18.3	7.50
9	8/7/2004	1.6	0.7	1.6	1.9	1.3	13.8	0.00
10	8/9/2004	4.6	6.8	5.3	6.5	7.9	13.4	0.50
11	8/11/2004	15.7	19.8	18.7	12.3	22.8	17.9	0.00
12	8/13/2004	12.3	13.2	15.2	11.3	14.8	22.7	0.50
13	8/15/2004	19.7	24.1	21.1	18.1	24.1	18.8	0.00
14	8/17/2004	17.3	20.1	22.1	16.7	20.5	18.3	0.00
15	8/19/2004	19.7	18.1	20.3	17.0	18.0	15.7	0.00
16	8/21/2004	5.3	5.4	4.8	4.1	3.2	13.1	3.00
17	8/23/2004	4.2	2.8	3.4	2.4	2.0	8.5	0.50
18	8/31/2004	8.8	11.4	8.2	10.7	7.8	17.4	0.50
19	9/2/2004	2.1	3.7	3.5	2.1	2.6	13.2	15.50
20	9/4/2004	3.2	6.9	5.4	4.7	4.7	13.5	2.00
21	9/6/2004	6.5	7.0	5.5	5.9	6.4	10.6	0.00
22	9/8/2004	8.1	4.0	5.6	4.5	2.2	5.3	2.50
23	9/10/2004	0.8	1.5	0.6	0.9	1.7	3.2	0.50
24	9/12/2004	3.7	5.6	4.1	4.1	6.3	9.9	0.00
25	9/14/2004	3.0	6.8	4.7	5.6	6.6	10.4	0.00
26	9/16/2004	3.1	4.1	2.1	4.3	3.8	11.2	26.00
27	9/18/2004	5.9	4.6	1.8	1.9	3.6	9.3	1.00
28	9/20/2004	2.8	2.8	3.3	0.6	2.6	5.8	0.00
29	9/22/2004	3.5	1.8	2.5	0.6	5.1	12.6	0.00
30	9/24/2004	6.5	11.9	5.9	4.7	13.0	13.4	0.50
31	9/26/2004	1.3	5.5	5.2	3.1	6.5	10.4	0.00
32	9/28/2004	7.5	10.6	6.5	5.5	9.3	11.9	0.50
33	9/30/2004	2.4	4.5	2.7	3.0	3.6	1.9	0.00
34	10/2/2004	5.0	6.5	3.6	4.1	5.7	11.1	0.00
35	10/4/2004	12.0	17.0	14.0	10.6	16.8	11.8	0.50
36	10/6/2004	9.7	11.3	9.7	7.2	10.9	9.8	0.00
37	10/8/2004	8.1	10.5	10.3	10.2	8.4	10.3	0.00
38	10/10/2004	0.6	4.6	1.5	1.3	3.3	11.0	0.00
39	10/12/2004	0.6	1.3	2.2	0.6	3.1	8.2	1.50

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n	Date mm/dd/yy	Site A UA Farm	Site B NW Stn.	Site C EPCOR	Site D St. AB	Site Ref.[1] NW Stn	Temp (°C)	PRECIP (mm)
40	10/14/2004	0.7	0.6	0.6	0.6	1.9	10.7	0.00
41	10/16/2004	1.2	0.6	2.4	1.5	2.2	-0.3	5.50
42	10/24/2004	10.0	13.6	11.6	7.1	9.1	-2.5	0.00
43	10/26/2004	11.5	17.7	12.9	10.1	6.1	-2.0	0.00
44	10/28/2004	16.9	27.7	20.4	16.9	17.2	-1.3	0.00
45	10/30/2004	6.4	12.2	10.3	9.7	7.1	1.9	0.00
46	11/1/2004	1.4	6.5	5.0	4.7	1.9	-2.0	0.00
47	11/3/2004	0.6	8.2	3.6	2.0	5.9	0.5	0.00
48	11/5/2004	9.9	15.6	12.8	n/a	11.5	6.0	0.00
49	11/7/2004	4.6	8.5	4.7	0.6	6.1	-2.8	0.00
50	11/9/2004	n/a	8.9	6.3	n/a	6.9	0.5	1.00
51	11/11/2004	n/a	20.9	15.9	n/a	15.5	-0.3	0.50
52	11/13/2004	17.2	22.5	20.5	13.0	18.2	0.3	0.50
53	11/15/2004	1.2	6.5	3.2	0.6	4.4	8.5	0.00
54	11/17/2004	5.1	10.4	7.7	3.9	7.3	1.9	0.00
55	11/19/2004	0.6	4.3	2.7	4.6	4.3	-1.1	0.00
56	11/21/2004	1.5	3.6	3.1	1.5	1.5	4.5	0.50
57	11/23/2004	3.0	6.5	4.6	2.4	4.4	-2.5	0.00
58	11/25/2004	0.6	6.7	5.0	3.5	4.2	0.1	0.00
59	11/27/2004	0.6	0.6	2.3	1.5	4.1	-2.3	0.00
60	11/29/2004	0.6	10.5	6.9	7.1	7.3	1.3	0.00
n		58	60	60	57	60		

[1] the 24-hr average $PM_{2.5}$ concentrations were converted based on 1-hour continuous TEOM measurement collected at Edmonton Northwest Air Quality Station.

[2] refer to no precipitation observed.

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8.4 MiniVol PM$_{2.5}$ Raw Chemical Composition Data (ng/m^3) at Site B (Northwest Stn.).

Date	Si	Ca	Fe	Al	Mg	K	Na	Cl	Ti	Mn	Cr	Cu	Ni	S	Pb	V	Co	Ba
7/22/04	10193.8	4020.6	1506.4	3202.5	309.9	1190.9	1342.6	724.8	0.5	0.5	53.1	44.2	51.8	0.5	148.1	77.6	72.3	0.5
7/24/04	8223.0	2411.6	1430.4	2737.0	311.7	2969.2	345.6	43.4	0.5	20.4	19.3	12.2	49.4	0.5	0.5	52.4	74.8	0.5
7/26/04	4752.4	938.9	637.7	1145.4	116.8	483.9	134.5	16.9	0.5	0.5	10.2	14.8	19.2	0.5	0.5	20.4	29.1	0.5
7/28/04	2703.7	2590.2	578.5	1059.4	124.4	485.8	535.3	327.0	0.5	0.5	21.1	14.7	19.7	0.5	0.5	32.8	29.8	0.5
7/30/04	4967.6	981.4	666.5	1197.3	122.1	505.8	140.6	17.7	0.5	0.5	10.6	15.5	20.1	0.5	0.5	21.3	30.4	0.5
8/1/04	1691.0	1130.5	751.6	677.8	82.1	812.1	171.8	14.3	0.5	26.5	7.4	4.9	12.5	0.5	0.5	13.3	19.0	2.3
8/3/04	4556.6	295.3	360.1	518.1	58.4	216.4	42.3	5.3	0.5	0.5	8.4	24.6	6.0	0.5	0.5	6.4	9.2	0.5
8/5/04	5366.1	2576.2	878.1	1996.7	176.7	691.8	289.1	34.3	0.5	0.5	11.3	21.3	33.2	0.5	94.9	32.6	46.3	0.5
8/7/04	362.8	79.5	112.8	95.3	9.8	40.2	24.1	1.4	0.5	3.1	1.3	1.0	1.6	0.5	0.5	1.7	2.5	0.3
8/9/04	3604.3	1312.2	469.9	819.3	88.2	346.9	94.6	16.0	0.5	0.5	7.6	17.7	13.5	0.5	0.5	14.3	20.5	0.5
8/11/04	10448.7	2554.6	1605.8	2988.9	300.3	1264.6	366.1	46.0	0.5	0.5	23.4	24.2	52.3	0.5	0.5	55.5	79.2	0.5
8/13/04	5810.1	2128.6	1187.1	2341.2	229.8	993.0	305.0	38.3	0.5	0.5	14.5	1.3	43.6	0.5	0.5	46.2	66.0	0.5
8/15/04	13782.9	2722.9	1849.3	3322.0	338.8	1403.4	390.2	49.0	0.5	0.5	29.4	43.0	55.7	0.5	0.5	59.1	84.5	0.5
8/17/04	10575.2	2585.5	1625.2	3025.0	303.9	1279.9	370.5	46.5	0.5	0.5	23.7	24.5	52.9	0.5	0.5	56.1	80.2	0.5
8/19/04	10307.2	2036.2	1383.0	2484.3	253.4	1049.5	291.8	36.6	0.5	0.5	22.0	32.1	41.7	0.5	0.5	44.2	63.2	0.5
8/21/04	2410.3	703.4	822.2	801.3	80.3	339.0	185.1	12.6	0.5	20.7	8.9	3.5	14.4	0.5	0.5	15.2	21.8	2.3
8/23/04	1362.1	408.5	240.7	462.0	45.8	195.8	58.5	7.3	0.5	0.5	3.2	1.9	8.4	0.5	0.5	8.9	12.7	0.5
8/31/04	6016.2	1470.9	924.6	1720.9	172.9	728.2	210.8	26.5	0.5	0.5	13.5	13.9	30.1	0.5	0.5	31.9	45.6	0.5
9/2/04	1763.0	346.3	689.3	425.7	44.2	179.3	144.2	6.2	0.5	23.3	7.4	5.4	7.0	0.5	0.5	7.5	10.7	2.6
9/4/04	3355.3	579.2	928.2	710.7	658.8	310.3	186.7	52.1	0.5	26.3	13.2	12.1	11.4	0.5	0.5	12.1	32.5	2.9
9/6/04	3072.3	1125.6	627.7	1238.0	121.5	525.1	161.3	20.2	0.5	0.5	7.7	0.7	23.0	0.5	0.5	24.4	34.9	0.5
9/8/04	2129.1	520.5	327.2	609.0	61.2	257.7	74.6	9.4	0.5	0.5	4.8	4.9	10.7	0.5	0.5	11.3	16.1	0.5
9/10/04	555.7	156.6	203.1	177.1	19.4	84.3	107.1	50.8	0.8	5.2	4.4	0.9	6.1	121.8	0.5	5.3	4.8	0.6
9/12/04	2484.1	741.7	816.7	841.7	84.2	356.1	185.3	13.3	0.5	19.4	8.9	3.4	15.1	0.5	0.5	16.1	23.0	2.1
9/14/04	2683.8	992.5	574.4	1081.4	106.1	478.4	140.9	17.7	4.1	0.5	6.7	0.6	34.9	603.8	0.5	21.3	30.5	0.5
9/16/04	1667.0	1080.5	525.4	437.0	49.4	185.6	110.3	11.1	0.5	14.3	5.9	10.7	7.4	0.5	0.5	7.9	11.3	1.6
9/18/04	2601.2	674.0	565.9	397.4	45.9	167.2	104.2	7.4	0.5	16.0	7.5	15.6	5.5	0.5	0.5	5.9	8.4	1.8
9/20/04	1593.3	250.1	378.5	323.1	33.9	136.0	75.8	4.5	0.5	9.8	4.8	6.0	5.1	0.5	0.5	5.4	7.7	1.1
9/22/04	931.9	227.8	143.2	266.6	26.8	112.8	32.7	4.1	0.5	0.5	2.1	2.2	4.7	0.5	0.5	4.9	7.1	0.5

Date	Si	Ca	Fe	Al	Mg	K	Na	Cl	Ti	Mn	Cr	Cu	Ni	S	Pb	V	Co	Ba
9/24/04	7144.5	1223.5	880.5	1541.7	159.0	650.6	175.3	22.0	0.5	0.5	14.9	25.5	25.0	0.5	0.5	26.6	37.9	0.5
9/26/04	2252.8	646.6	768.5	736.6	79.6	331.5	403.4	187.3	0.5	19.1	16.7	3.3	13.2	0.5	0.5	21.0	20.0	2.1
9/28/04	5525.0	1402.7	870.6	1630.1	163.4	689.9	201.0	25.2	0.5	0.5	12.5	11.9	28.7	0.5	0.5	30.5	43.5	0.5
9/30/04	2169.0	786.8	574.8	522.8	56.1	221.1	119.5	10.0	0.5	14.4	6.9	9.8	8.7	0.5	0.5	9.2	13.2	1.6
10/2/04	2885.2	1220.1	851.4	824.3	86.9	349.1	184.6	15.9	0.5	20.7	9.7	11.1	14.3	0.5	0.5	15.2	21.7	2.3
10/4/04	8859.9	1745.3	2332.9	2137.4	219.9	901.6	489.1	31.3	0.5	58.8	28.1	27.5	35.6	0.5	0.5	37.8	54.0	6.5
10/6/04	4494.4	3436.1	790.3	1456.5	159.0	620.2	182.8	36.7	0.5	0.5	10.4	26.0	26.1	0.5	0.5	27.7	39.6	0.5
10/8/04	4625.2	3016.6	686.3	1211.9	135.6	515.5	145.3	31.0	0.5	0.5	10.1	30.0	20.8	0.5	0.5	22.0	31.4	0.5
10/10/04	2059.9	867.6	1075.7	180.3	28.2	75.0	203.9	6.3	0.5	47.6	11.1	18.8	1.4	0.5	0.5	1.5	2.1	5.3
10/12/04	434.6	466.2	166.1	136.2	16.0	58.1	35.7	4.3	0.5	4.6	1.7	3.8	2.4	0.5	0.5	2.6	3.6	0.5
10/14/04	286.3	85.9	50.6	97.1	9.6	41.1	12.3	1.5	0.5	0.5	0.7	0.4	1.8	0.5	0.5	1.9	2.7	0.5
10/16/04	242.6	122.9	83.2	80.5	8.4	34.2	18.6	1.6	0.5	2.1	0.9	0.8	1.4	0.5	0.5	1.5	2.2	0.2
10/24/04	6223.8	1740.9	1592.5	741.4	124.1	419.3	1541.7	970.8	0.5	51.8	65.8	42.5	9.0	0.5	0.5	47.6	13.6	5.7
10/26/04	6966.9	6906.7	958.0	1578.8	198.5	675.3	181.8	58.8	0.5	0.5	14.6	72.2	26.0	0.5	0.5	27.5	39.3	0.5
10/28/04	10390.9	4437.8	1496.2	2220.3	341.4	1272.7	4136.6	2971.0	0.5	0.5	162.8	55.7	36.6	0.5	0.5	155.3	55.5	0.5
10/30/04	3860.8	251.4	1574.3	423.3	119.9	419.3	3125.8	2152.6	0.5	58.3	120.0	17.6	5.0	0.5	0.5	91.0	7.6	6.4
11/1/04	2983.7	422.8	844.2	557.1	74.1	286.1	770.2	465.8	0.5	24.9	32.0	11.4	8.6	0.5	0.5	27.4	13.0	2.7
11/3/04	4268.6	731.1	542.3	1142.7	107.1	418.1	503.3	274.3	0.5	0.5	20.9	15.1	17.6	0.5	57.4	27.5	24.3	0.5
11/5/04	6282.1	3181.7	2155.5	2085.6	217.8	884.4	481.5	41.5	0.5	53.9	23.1	20.9	37.4	0.5	0.5	39.6	56.6	5.9
11/7/04	3065.2	1646.3	1783.3	962.9	103.5	407.5	383.5	20.1	0.5	65.0	17.2	12.5	16.9	0.5	0.5	17.9	25.6	7.2
11/9/04	2611.7	2081.1	407.7	947.8	86.0	309.1	2227.9	21.0	0.5	0.5	5.2	18.9	15.2	0.5	57.5	51.1	20.6	48.8
11/11/04	5111.6	4773.1	1056.0	2147.9	272.1	971.7	3585.2	2499.7	0.5	0.5	128.9	34.5	35.8	0.5	135.2	131.9	48.5	0.5
11/13/04	7025.0	4803.8	3784.6	1537.2	229.1	800.6	2505.0	1361.6	0.5	142.9	100.5	53.3	24.8	0.5	0.5	78.8	37.5	15.8
11/15/04	2353.2	838.8	967.3	926.2	99.3	418.1	523.3	242.9	0.5	24.7	20.7	0.5	17.1	0.5	0.5	27.2	26.0	2.7
11/17/04	4128.5	2021.1	1426.7	1518.9	134.1	511.8	382.6	26.1	0.5	39.6	14.6	18.0	24.7	0.5	80.5	24.0	34.1	4.4
11/19/04	2389.5	619.1	519.9	365.0	42.1	153.6	95.7	6.8	0.5	14.7	6.9	14.4	5.1	0.5	0.5	5.4	7.7	1.6
11/21/04	1319.4	1194.5	196.0	318.7	42.3	149.1	189.3	124.9	0.5	0.5	8.3	12.0	5.4	0.5	0.5	10.2	8.1	0.5
11/23/04	2348.2	443.4	308.5	1057.0	69.6	245.0	1574.2	217.9	0.5	0.5	13.6	8.4	14.9	0.5	137.8	39.8	16.8	26.0
11/25/04	2790.8	1178.6	425.3	708.2	89.7	349.1	656.8	445.0	0.5	0.5	26.9	12.4	12.1	0.5	0.5	30.0	18.4	0.5
11/27/04	314.9	79.9	49.6	92.9	9.3	39.3	11.5	1.4	0.5	0.5	0.7	0.7	1.6	0.5	0.5	1.7	2.5	0.5

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Date	Si	Ca	Fe	Al	Mg	K	Na	Cl	Ti	Mn	Cr	Cu	Ni	S	Pb	V	Co	Ba
11/29/04	3817.7	4427.0	563.4	938.4	119.2	402.2	110.5	37.2	0.5	0.5	8.1	43.1	15.8	0.5	0.5	16.7	23.9	0.5

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8.5 MiniVol PM$_{2.5}$ Raw Chemical Composition Data (ng/m^3) at Site C (Epcor Reservoir Site)

Date	Si	Ca	Fe	Al	Mg	K	Na	Cl	Ti	Mn	Cr	Cu	Ni	S	Pb	V	Co	Ba
7/22/04	8811.5	5642.0	1162.0	2507.5	254.6	874.8	1387.0	825.1	0.5	0.5	53.7	68.1	37.7	0.5	169.8	65.9	50.0	0.5
7/24/04	6218.4	5375.3	2026.4	1628.2	222.3	2085.2	410.4	49.8	8.4	68.4	21.8	51.5	58.1	1243.8	0.5	29.3	41.9	5.9
7/26/04	4919.2	971.8	660.0	1185.6	120.9	500.9	139.3	17.5	0.5	0.5	10.5	15.3	19.9	0.5	0.5	21.1	30.1	0.5
7/28/04	3223.2	1778.3	416.4	670.3	85.0	310.8	380.9	247.4	0.5	0.5	17.7	22.4	10.8	0.5	0.5	20.6	16.4	0.5
7/30/04	3212.3	1552.7	344.1	541.9	65.0	229.8	56.1	14.5	0.5	0.5	6.3	24.2	8.0	0.5	0.5	8.5	12.2	0.5
8/1/04	2369.0	698.3	945.4	353.6	42.4	148.4	183.6	7.2	0.5	36.8	10.3	15.2	4.8	0.5	0.5	5.1	7.2	4.1
8/3/04	4908.6	1200.1	754.4	1404.1	141.1	594.1	172.0	21.6	0.5	0.5	11.0	11.4	24.6	0.5	0.5	26.1	37.2	0.5
8/5/04	2869.0	6751.7	479.8	744.0	114.9	324.0	1286.1	50.1	0.5	0.5	6.1	60.7	12.7	0.5	0.5	34.4	19.2	28.0
8/7/04	654.1	546.7	193.9	110.8	15.0	47.2	36.6	4.4	0.5	6.2	2.3	7.4	1.6	0.5	0.5	1.7	2.4	0.7
8/9/04	2780.3	788.1	646.1	603.6	54.8	193.0	156.4	9.4	0.5	18.5	8.0	17.9	8.4	0.5	37.6	7.8	11.1	2.0
8/11/04	8232.1	2151.5	2711.9	3061.8	262.0	1057.6	731.5	40.9	0.5	71.2	28.4	20.3	50.6	0.5	144.8	49.7	70.6	7.8
8/13/04	6723.2	4385.0	997.7	1761.6	197.2	749.3	211.2	45.1	0.5	0.5	14.6	43.6	30.2	0.5	0.5	32.0	45.7	0.5
8/15/04	11107.8	2715.8	1707.0	3177.4	319.3	1344.4	389.2	48.9	0.5	0.5	24.8	25.7	55.6	0.5	0.5	59.0	84.2	0.5
8/17/04	13588.5	2137.3	1595.9	2750.3	285.5	1159.7	306.3	38.5	0.5	0.5	27.8	51.7	43.8	0.5	0.5	46.4	66.3	0.5
8/19/04	10678.8	2610.9	1641.1	3054.7	306.9	1292.5	374.1	47.0	0.5	0.5	23.9	24.7	53.4	0.5	0.5	56.7	81.0	0.5
8/21/04	2149.6	1065.4	538.3	318.7	40.4	134.7	511.5	9.2	0.5	16.8	6.7	19.6	4.4	0.5	0.5	11.8	6.6	11.5
8/23/04	1506.3	647.0	228.3	412.9	44.8	175.2	50.1	8.2	289.1	0.5	3.3	10.8	9.7	0.5	0.5	8.4	14.6	0.5
8/31/04	3978.4	1445.8	493.4	837.8	94.9	354.9	94.6	16.9	764.1	0.5	8.2	33.0	20.1	0.5	0.5	16.5	30.3	0.5
9/2/04	1557.4	454.5	531.2	517.7	51.9	219.0	119.6	8.2	0.5	13.4	5.7	2.7	9.3	0.5	0.5	9.8	14.1	1.5
9/4/04	2865.1	1043.1	373.5	651.3	70.1	275.8	75.2	12.7	0.5	0.5	6.0	14.1	10.7	0.5	0.5	11.4	16.3	0.5
9/6/04	1738.4	626.1	1168.4	692.2	71.6	292.8	259.7	11.2	512.9	41.9	10.8	9.6	17.2	0.5	0.5	14.9	25.8	4.6
9/8/04	1759.2	628.2	365.3	688.4	88.0	851.0	348.4	206.0	517.5	6.0	13.8	8.4	17.3	0.5	0.5	22.8	26.1	0.5
9/10/04	141.1	52.1	119.2	54.4	57.2	26.3	110.1	25.7	0.5	4.6	2.3	0.2	1.0	0.5	0.5	2.9	2.8	1.8
9/12/04	1837.9	267.9	1119.7	357.0	38.8	149.4	228.7	4.7	0.5	46.8	11.0	12.1	5.4	0.5	0.5	5.7	8.2	5.2
9/14/04	2670.1	685.8	268.1	401.3	50.8	186.2	239.5	158.1	0.5	0.5	12.4	15.9	5.7	0.5	0.5	12.0	8.6	0.5
9/16/04	995.1	242.4	291.9	284.6	28.8	120.3	63.8	4.4	0.5	7.1	3.3	3.0	5.0	0.5	0.5	5.3	7.5	0.8
9/18/04	1094.9	114.8	236.4	167.3	18.2	70.1	43.9	2.1	0.5	6.8	3.2	5.3	2.3	0.5	0.5	2.5	3.5	0.7
9/20/04	1583.8	296.2	424.6	360.7	37.4	152.0	367.4	5.2	0.5	11.4	5.1	6.1	5.9	0.5	0.5	11.2	9.0	7.8
9/22/04	1108.8	323.6	378.2	368.6	36.9	155.9	85.1	5.8	0.5	9.5	4.1	2.1	6.6	0.5	0.5	7.0	10.0	1.1

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Date	Si	Ca	Fe	Al	Mg	K	Na	Cl	Ti	Mn	Cr	Cu	Ni	S	Pb	V	Co	Ba
9/24/04	3381.9	476.6	811.9	634.0	67.1	266.6	159.6	8.5	0.5	22.4	10.3	14.6	9.7	0.5	0.5	10.3	14.7	2.5
9/26/04	1425.6	922.0	1036.5	644.1	61.5	227.9	498.8	192.6	0.5	39.3	17.8	6.2	10.6	0.5	40.0	17.3	14.3	4.3
9/28/04	2853.0	1243.4	417.3	745.5	82.0	316.3	89.4	15.2	602.2	0.5	6.2	22.4	18.0	0.5	0.5	15.2	27.1	0.5
9/30/04	1433.4	521.9	186.9	325.8	35.1	138.0	37.6	6.4	0.5	0.5	3.0	7.1	5.4	0.5	0.5	5.7	8.1	0.5
10/2/04	1574.7	674.0	477.6	433.3	46.1	183.5	102.4	8.5	0.5	12.3	5.4	7.1	7.5	0.5	0.5	7.9	11.3	1.4
10/4/04	6140.1	3829.5	832.4	1849.8	170.7	608.3	265.6	39.6	0.5	0.5	11.9	43.7	28.7	0.5	108.5	27.4	38.9	0.5
10/6/04	3889.3	2029.8	1393.9	1260.9	132.8	534.6	308.4	25.7	0.5	37.1	14.8	16.1	22.5	0.5	0.5	23.8	34.0	4.1
10/8/04	4554.2	1536.5	1183.9	1184.2	125.2	1224.6	297.3	19.1	0.5	42.2	13.8	25.3	17.7	0.5	66.7	16.9	23.9	3.6
10/10/04	702.8	178.7	110.9	289.0	22.2	88.2	44.8	3.5	0.5	0.5	1.4	1.6	4.6	0.5	20.8	4.3	6.1	0.5
10/12/04	522.1	822.1	281.2	201.0	26.8	95.0	164.9	85.9	0.5	8.5	6.4	6.0	3.7	0.5	0.5	7.0	5.6	0.9
10/14/04	288.0	86.8	33.3	47.9	6.0	24.0	30.1	19.8	0.3	0.5	1.5	1.7	1.9	47.9	0.5	1.5	1.1	0.5
10/16/04	1154.2	545.1	281.0	216.1	25.4	91.5	54.3	5.4	0.5	7.6	3.5	8.5	3.3	0.5	0.5	3.5	5.0	0.8
10/24/04	2146.9	3957.1	968.4	889.1	886.9	150.9	2123.9	88.4	0.5	36.8	11.4	44.8	10.9	0.5	149.6	39.1	31.6	46.3
10/26/04	2532.9	651.1	322.3	571.4	58.6	241.2	8100.6	8.3	0.5	0.5	5.3	8.4	9.4	0.5	0.5	150.6	14.3	187.8
10/28/04	9850.0	3611.9	1296.3	2081.7	227.7	940.5	235.0	41.9	12.2	0.5	20.3	52.7	77.9	1812.7	0.5	35.6	50.9	0.5
10/30/04	3191.6	3151.4	672.5	1279.6	138.3	545.8	1131.0	33.5	0.5	0.5	7.9	17.8	23.8	0.5	0.5	42.1	36.0	22.5
11/1/04	1327.2	2176.5	196.9	462.6	46.9	135.0	541.0	17.4	0.5	0.5	2.4	21.0	7.0	0.5	38.8	14.5	8.9	11.0
11/3/04	1596.1	813.2	281.4	530.5	55.0	225.3	66.9	10.6	0.5	0.5	3.7	5.4	9.6	0.5	0.5	10.1	14.5	0.5
11/5/04	6725.4	1644.3	1033.6	1923.8	193.3	814.0	235.6	29.6	0.5	0.5	15.0	15.6	33.7	0.5	0.5	35.7	51.0	0.5
11/7/04	1705.7	1043.0	352.7	685.8	70.0	291.5	491.7	13.8	0.5	0.5	4.3	4.0	12.8	0.5	0.5	20.6	19.3	9.4
11/9/04	2226.9	1055.8	775.8	919.8	66.1	228.5	845.7	13.3	0.5	24.2	7.5	15.0	13.4	0.5	98.3	21.9	16.2	16.6
11/11/04	8410.4	3061.9	1096.5	1911.8	205.9	809.5	220.7	37.4	0.5	0.5	17.7	41.4	31.5	0.5	0.5	33.4	47.8	0.5
11/13/04	9039.2	2767.1	1622.1	3063.6	162.1	1327.8	388.2	162.8	0.5	0.5	27.3	12.3	55.5	0.5	0.5	58.8	125.3	22.5
11/15/04	1298.4	1275.4	142.9	299.2	31.3	90.4	42.3	10.2	0.5	0.5	2.3	15.7	4.1	0.5	22.9	3.7	5.2	0.5
11/17/04	3382.1	916.2	1075.8	1267.5	110.0	447.5	289.4	17.3	0.5	26.6	11.4	9.3	21.2	0.5	54.1	21.0	29.9	2.9
11/19/04	1324.3	741.8	166.7	279.6	32.3	118.8	31.5	7.3	0.5	0.5	2.7	9.3	4.5	0.5	0.5	4.8	6.8	0.5
11/21/04	770.9	1278.5	341.4	218.4	29.4	93.9	337.2	10.2	0.5	10.8	3.4	11.5	3.8	0.5	0.5	8.7	5.7	7.4
11/23/04	1157.7	912.2	910.4	631.8	44.3	144.0	565.9	10.2	0.5	37.1	7.6	9.0	9.3	0.5	75.5	13.1	10.9	11.2
11/25/04	1863.4	534.5	634.8	606.9	67.3	273.3	332.4	154.3	384.5	15.7	13.8	9.6	14.2	0.5	0.5	18.4	21.4	1.7
11/27/04	903.5	622.6	128.4	222.5	25.5	94.7	239.2	6.1	0.5	0.5	1.9	6.5	3.8	0.5	0.5	7.7	5.7	5.0

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Date	Si	Ca	Fe	Al	Mg	K	Na	Cl	Ti	Mn	Cr	Cu	Ni	S	Pb	V	Co	Ba
11/29/04	3510.5	698.1	868.3	1013.9	90.4	360.6	220.5	13.2	0.5	20.3	10.3	11.3	16.2	0.5	41.2	16.0	22.8	2.2

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