University of Alberta

Low Volume Sampling and Individual Particle Analysis of Airborne Particulate Matter

By

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DEDICATION

This work is dedicated to my parents and my family who have a great influence on my life. My mother, Sandra McCullum and father Vern McCullum who have taught me the importance of life and dealing with hardships and to never give up trying to reach goals.

My wife Catherine, son William, and daughter Darlene McCullum who have always been there for me when I needed help, and have given me their love an support to continue in my pursuit of knowledge.

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LIST OF ABBREVIATIONS AND NOMENCLAURE

ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
AD	Aerodynamic Diameter
ARC	Alberta Research Council
CEB	Chemical Elemental Balance
CEPA	Canadian Environmental Protection Act
CMB	Chemical Mass Balance
CO	Carbon Monoxide
EPMA	Electron Microprobe Analysis
FPAC	Federal-Provincial Advisory Committee
FRM	Federal Reference Method
HCHO	Formaldehyde
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectroscopy
INAA	Instrumental Neutron Activation Analysis
Lpm	Litres per minute
NAAQS	National Ambient Air Quality Surveillance
NAPS	Canadian National Air Pollution Surveillance
NIST	National Institute of Standards and Technology
NO_X	Oxides of Nitrogen
PAH	Polycyclic Aromatic Hydrocarbon
PCA	Principle Component Analysis
PGT	Princeton Gamma-Tech
PIXE	Proton Induced X-ray Analysis
PM_{10}	Particulate matter with aerodynamic diameter of 10 μm
$PM_{2.5}$	Particulate matter with aerodynamic diameter of 2.5 μm
SEM-EDX	Scanning Electron Microscopy – Energy Dispersive X-ray
SRM	Standard Reference Material
STP	Standard Temperature and Pressure
TEOM	Tapered Elemental Oscillating Microbalance
TSP	Total Suspended Particulate
USEPA	United States Environmental Protection Agency
VAPS	Versatile Air Pollutant Sampler
VOC	Volatile Organic Compounds
WTP	Water Treatment Plant
XRF	X-Ray Fluorescence

1. INTRODUCTION

1.1 Emerging Challenges of Particulate Matter Monitoring

Small particles are present within the atmosphere in varying quantities and size ranges. Human exposure to these ambient particles on a daily basis is unavoidable. The ability to identify source contributions has become an important objective of monitoring for regulatory agencies, industries and other stakeholder groups for establishing airshed management practices (Alberta Environment, 1999). Properly collecting and analyzing airborne particles to allow the identification of the relationship between source and receptor is necessary in order to establish this type of airshed management. A "fingerprinting" method referred to as source apportionment is a promising tool that may help with this management objective.

Current methods for source apportionment use fixed Federal Reference Method (FRM) air samplers with flow rates of 10 to 20 L/min (Chow, 1995; U.S. Environmental Protection Agency, 1994a). Speciation of particulate matter collected on filters can be made using elemental analysis techniques such as X-Ray Fluorescence (XRF) or Inductively Coupled Plasma Mass Spectrometry (ICP-MS). However, Koutrakis (1998) indicated that although XRF analysis is sensitive enough for detection of crustal elements, it is not sensitive enough for trace elements. In addition, he stated that ICP-MS is a promising analytical technique that is more sensitive than XRF; however, it needs further validation because its performance on crustal elements is not as good as XRF. Further, these limitations are expected to become more problematic if the airborne particle mass collected decreases.

These limitations have created a need to examine alternative methods of sampling and analysis of airborne particulate matter for source apportionment applications. A unique combination of procedures was examined whereby low volume air sampling was used along with an individual particle analysis technique to assess whether these procedures provided representative data for ambient particulate matter source apportionment. These procedures require only a small amount of particulate matter to be collected on filters during air sampling so that the analysis technique could be used on individual particles, not the bulk filter sample. This is something that low volume sampling (≤5 L/min) may be able to achieve.

1.2 Low Volume Samplers as an Alternative Approach

Low volume samplers typically have air flow rates ≤5 L/min. They have been used in conjunction with personal exposure monitors for several years, monitoring primarily for mass concentrations of particulate matter (Chow, 1995). These samplers offer portability, low cost and ease of use (Tropp and Berg, 1998). One such low volume sampler is called the MiniVol (Airmetrics, Portland, OR). The MiniVol is capable of sampling at 5 L/min, for 24 hours on a single battery charge. Particulate matter is collected on 47-mm diameter, 2-µm pore size filters.

These low volume samplers have been used in co-location studies with real-time particle counters as well as FRM samplers, demonstrating comparable gravimetric results (Heal et al., 2000; Baldauf et al., 2001). EPA (1994a) reported that the amount of material collected on filters from low volume samplers is generally insufficient for conventional analysis such as XRF. However, it is unknown whether this limitation applies to individual particle analysis techniques. Therefore, examination of an alternative analysis technique for particulate matter became a research goal.

1.3 The Analytical Challenge

In the past, ambient air sampling was performed to give an indication of the mass concentration of particulate matter of different size fractions (PM_{10} or $PM_{2.5}$) collected. Using portable low volume samplers to report this mass concentration has been shown to be promising (Tropp and Berg, 1998). However, when source to receptor relationship (source apportionment) information was needed, bulk analytical techniques such as XRF were employed for the particle analysis. These bulk analytical techniques require mass loading generally >100 $\mu g/cm^2$ for the filter area (Gordon et al., 1984). Low volume samplers typically collect a much lower mass concentration on the filter, well below the detection limit of analytical procedures used for bulk analytical techniques. Therefore an alternative analytical technique was sought, one that could identify elements present in a smaller mass of particles collected on filters used in low volume samplers.

A promising technique for elemental analysis of low particle concentrations uses Scanning Electron Microscopy with Energy Dispersive X-ray (SEM-EDX) for analysis (Newbury et al., 1986). This type of analysis has a broader identification capability than bulk analysis, with the ability to sample extremely small masses and the capability of identifying particle size, morphology and elemental composition. This method of individual particle analysis is not typically used for fixed FRM samplers because the filters are too heavily loaded (Pinto et al., 1998). Others (ARC, 1998; Jambers et al., 1995) have indicated that individual particle analysis for ambient air is quite rare, primarily based on concerns about the number of particles required for identification, cost, and time consumption. Thus a research opportunity existed for examining whether low volume air sampling coupled with individual particle analysis (SEM-EDX) could provide representative data for ambient particulate matter source apportionment.

1.4 Thesis Objective and Overview

The focus of this thesis was to examine the potential of using individual particle analysis techniques collected by low volume samplers for source apportionment applications. The ability of this technology to identify particulate sources will address the growing need to classify particulate matter exposure on the receptor population. Based on a review of literature regarding particulate matter properties and source to receptor relationships, it was postulated that low volume samplers in conjunction with individual particle analysis techniques could represent particulate matter exposure to receptors as reliably as conventional techniques. The principle hypothesis was that low volume samplers can be used as an alternative air sampling approach in source to receptor studies based on individual particle analysis. A second hypothesis was that assessment of morphology and elemental composition of individual particles could be used to estimate probable sources of the particulate matter.

Initial research involved laboratory testing of the low volume sampler collection ability to accurately sample airborne standard reference material followed by an evaluation of analytical techniques for identification of elements in the reference material. Research then involved field evaluation of low volume sampling and analytical techniques for identification of elements in ambient particulate matter. Additional research involved field-testing of the low volume samplers in a small receptor study conducted in a rural community. The ability of the low volume sampler to fingerprint generic particulate sources from the community throughout four seasons was investigated.

2. BACKGROUND AND LITERATURE REVIEW

2.1 Particulate Matter Fundamentals

Particulate matter (PM) refers to all airborne particles, in both solid and liquid phase with the exception of pure water. Particles found in outdoor air range in size from approximately 0.005 μm to 100 μm aerodynamic diameter (AD) (Myrick, 1996a). When referring to ambient PM, the aerodynamic diameter or equivalent diameter is the most common expression used for defining particle size.

From this vast size range, there are two primary size ranges of particulate matter that are of interest to regulatory and health agencies. PM_{10} refers to particulate matter less than 10 μm in aerodynamic diameter. $PM_{2.5}$ refers to particulate matter less than 2.5 μm in aerodynamic diameter. The size range of PM_{10} is generally subdivided into a fine fraction (<2.5 μm AD) referred to as $PM_{2.5}$, and a coarse fraction (2.5 μm to 10 μm AD) (Pryor and Barthelmine, 1996; Health Canada and Ontario Ministry of Health, 1997). Particles less than 10 μm AD (PM_{10}) are also referred to as "thoracic particles" or "inhalable particles". This represents the association of particle inhalation into tracheobronchial and alveolar regions of the respiratory system (Myrick, 1996a; Myrick, 1996b).

The fine fraction of particulate matter ($PM_{2.5}$) is also referred to as "respirable particles" (CEPA and FPAC, 1999). Size ranges for both PM_{10} and $PM_{2.5}$ are important based on their association with human health effects rather than their chemical composition (Alberta Environment, 1999; CEPA and FPAC, 1999). Of greatest concern are fine (respirable) particles, as they are small enough to travel deep into the lungs, potentially delivering attached chemicals (e.g. polycyclic aromatic hydrocarbons (PAHs), metals and acid aerosols such as sulphates) (Health Canada, 1996).

Given the ability of particulate matter to have adverse effects on health from exposure, it becomes important to identify sources of particulate emissions. The ability to identify these sources is based on interpretation of PM data collected with FRM sampling coupled with elemental analysis techniques such as X-Ray Fluorescence (XRF). FRM samplers are limited to their collection site because of their size and the need for an available power supply. Portable air samplers capable of collecting minute mass concentrations of PM_{10} and $PM_{2.5}$ may offer an alternative to FRM samples.

2.1.1 Particulate Matter Characteristics

To identify particulate matter sources, it is important to develop an understanding of particulate characteristics. The chemical composition of particulate matter encompasses a broad range including elemental carbon, organic carbon, silicon, aluminum, iron, trace metals, sulphates, nitrates, and ammonia (CEPA and FPAC, 1999). With wide variation in chemical properties, particulate matter is an atmospheric pollutant that is a function of aerodynamic diameter rather than chemical composition (Spektor, 1998).

The size of particulate matter is important and is typically related to mechanisms of production that include (Beckett et al., 1998):

- aerosol formation from condensation of vapour,
- smoke formation from combustion,
- particulate formation from chemical reactions in the atmosphere,
- dust and salt crystals from mechanical disruption (erosion) of the earth's surface,

- particulate formation from coagulation of small particles, and
- particulate emission from direct anthropogenic sources.

Therefore it is important to be able to characterize morphology and elemental composition of particulate matter in order to relate it to emission sources.

Particle number density in the atmosphere can often exceed 10^7 or 10^8 per cm^3 of urban or non-urban airsheds (EPA, 1998a). The size range of these particles can span over three orders of magnitude (0.01 μm to >10 μm), thus it is best to characterize particulate matter in terms of particle size distribution. The total number of particles (N) is typically defined by a size distribution function (CEPA and FPAC, 1999):

$$N = \int_0^\infty n(D_p)dD_p \quad \text{.......} \quad \textbf{(1)}$$

where; $n(D_p)$ represents the size distribution function for particle size. A normalized size distribution function can then be expressed as $\bar{n}(D_P) = n(D_p)/N$, where $\bar{n}(D_P)dD_p$ is the fraction of particles per cubic metre of air having diameters in the range of D_P to $D_P + dD_P$ (CEPA and FPAC, 1999). From this base the size distribution was expressed by Whitby et al. (1972) in terms of the logarithm of the diameter as:

$$\frac{dN}{d\log D_P} = n(\log D_p) \quad \text{for number distributions.......} \quad \textbf{(2a)}$$

$$\frac{dS}{d\log D_P} = n_S(\log D_p) \quad \text{for surface area distributions.......} \quad \textbf{(2b)}$$

$$\frac{dV}{d\log D_P} = n_V(\log D_p) \quad \text{for volume distributions.......} \quad \textbf{(2c)}$$

where; S represents surface area and $n_s(\log D_p)$ represents surface area distribution function, and V represents volume and $n_V(\log D_p)$ represents volume distribution function. An advantage of representing data in this form is that the area under a "relative particle concentration versus aerodynamic diameter" curve is proportional to the quantity in the given size interval (refer to Figure 1).

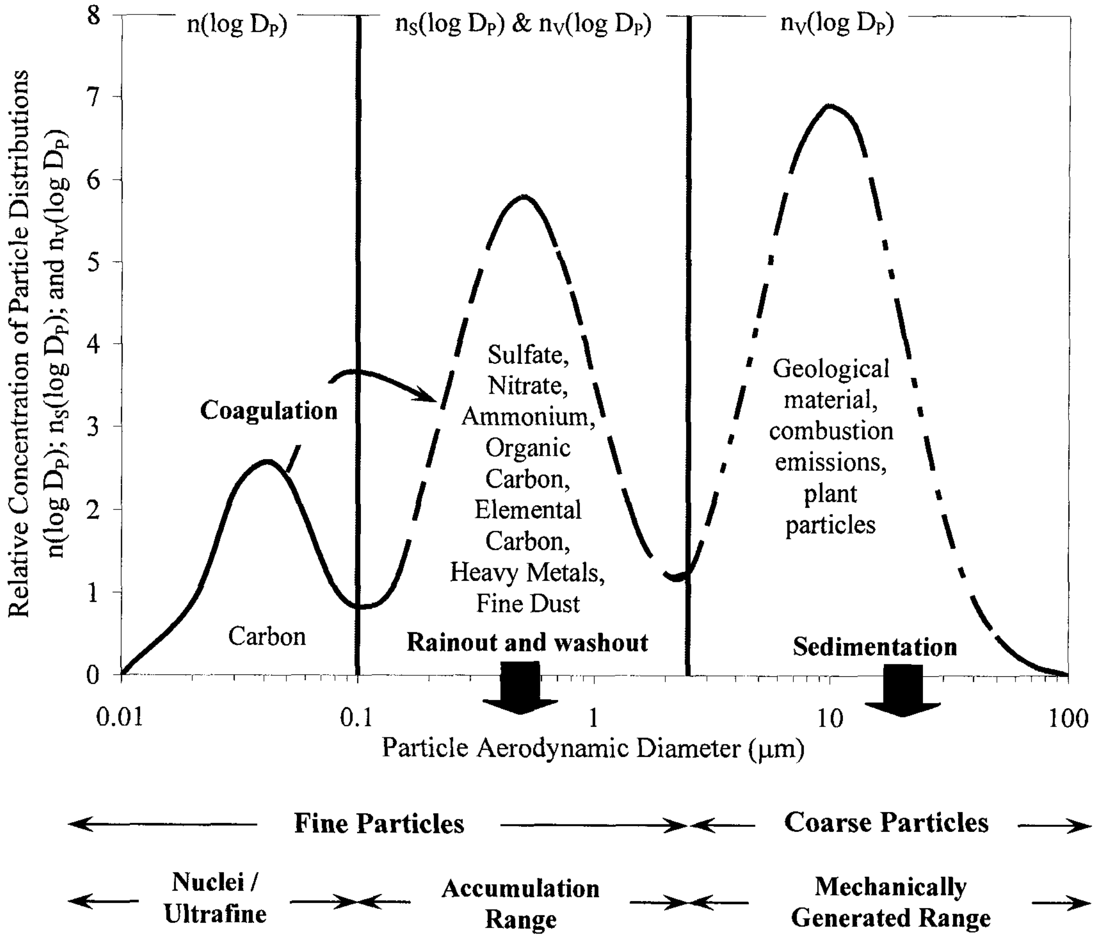


Figure 1. Idealized Tri-modal Distribution of Particulate Matter
(after Tiittanen et al., 1999; EPA, 1998a; CEPA and FPAC, 1999; National Academy of Sciences, 1979)

Based on particle count, volume and surface area distributions, Figure 1 demonstrates the idealized tri-modal nature of airborne particulates (UK Department of the Environment, 1995). The fine size fraction (<2.5 μm AD) is broken into nuclei mode (ultrafine) and accumulation mode. The largest fraction of particles by count is in nucleation mode (ultrafine), with diameters less than 0.1 μm and a peak at 0.04 μm (Spektor, 1998). A breakdown of particle types and size ranges is presented in Table 1.

Condensable species can nucleate to form a new particle or can condense onto the surface of an existing particle (EPA, 1999c). Particles in this size range possess a very short lifetime (≤ 1 hour) due to rapid condensation and are generally found close to an emission source. These particles are associated with combustion processes, such as vehicular, industrial processes or vegetative material burning (ARC, 1998; EPA, 1999c). Due to rapid condensing and coagulation of ultrafine particles, these particles form larger particles in accumulation mode size range of 0.1 to 2.5 μm (EPA, 1998a). For capturing these ambient particles, filters tend to have 2 μm pore sizes that are woven in an overlapping fashion which enable entrainment of ultrafine particles (Whatman Inc., Clifton, NJ).

Unlike ultrafine particles, accumulation particles have a longer lifetime, lasting from several days to weeks in the atmosphere and traveling vast distances (ARC, 1998). These particles are associated with combustion sources formed from gas to particle conversion and finely ground dust (EPA, 1999c).

Formation of coarse particles, 2.5 μm to 10 μm AD, tends to be associated with mechanical processes such as wind erosion and grinding operations. Due to the size of these particles their residence time in the atmosphere is short, of the order of hours to days (EPA, 1999c). Coarse particles found in ambient air are dominated by biological material from pollen, spores and decaying leaves, geological material from crustal erosion, anthropogenic material from direct emissions, mechanically ground up trash, vehicular emissions and agricultural emissions (EPA, 1999c; UK Department of the Environment, 1995; Chow, 1995). Understanding particle size ranges as a function of their potential sources, together with particulate fingerprinting, helps to identify source origins.

Table 1. Particle Size Ranges and Types

(after Klemm and Gray, 1982; Israël and Israël, 1974; National Academy of Sciences, 1979; Beckett et al., 1998; Wolff, 1985; National Tuberculosis and Respiratory Disease Association, 1971)

Particle size	Name	Potential sources / origins	Properties
<0.1 µm	Nuclei mode (Ultrafine particle)	Condensation[1], combustion[2], chemical reactions[3]	Roughly obey same laws of light scattering as molecules but have little effect on visibility
0.1–2.5 µm	Accumulation mode (Fine particle)	Industrial dusts[4,5], fly ash from combustion[6], sea salt[7]	Particles are of same order as visible wavelength, thus they are most effective in light scattering and visibility reduction
>2.5 µm	Coarse mode (Coarse particle)	Mechanical process[8], erosion[9], spraying[10]	Particles obey scattering laws of large bodies, visibility reduction is minor compared to smaller particles

[1] aerosols (aerocolloids) – particles that are dispersed in gases; can act as nuclei for vapors

[2] smoke – gas borne particles from incomplete combustion, present in sufficient quantity to be observable

[3] small and large ions – important component for atmospheric electricity and also condensation

[4] fume – solid particles generated by condensation, often chemical reactions are involved (oxidation)

[5] haze – an aerosol comprised of water droplets, dust and pollutants that impedes vision

[6] soot – an agglomeration of individual spheroid particles (generally carbon with "tar") that is formed by incomplete combustion of carbonaceous species.

[7] large nuclei – important for cloud physics, air chemistry, and optical phenomena in atmosphere

[8] dusts – solid particles generally associated with mechanical disintegration

[9] giant nuclei (large aerosols) – important for cloud physics, air chemistry

[10] mists – liquid with particles suspended near the surface of the earth, distinguished as being more transparent than fog

2.1.2 Health Issues Related to Particulate Matter

Key health problems associated with particulate matter relate to chronic and acute exposure, as well as aesthetic environmental issues. 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 is the basis of 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" (May 2000). From this report, Environment Canada and Health Canada specified that (Environment Canada and Health Canada, 2000):

> "*PM_{10} and particularly $PM_{2.5}$ be considered "toxic" as defined in Section 64 of the Canadian Environmental Protection Act (CEPA)*".

Coarse particles tend to accumulate in the nose, throat and airways of the lung and can potentially aggravate asthma (EPA, 1997e; Chow and Watson, 1998). Fine particles, <2.5 μm AD, have the greatest chance of reaching the furthest regions of the lung. Delicate tissues involved in exchange of oxygen and carbon dioxide are present in this alveoli region (UK Department of the Environment, 1995; Farber and Wilson, 1961).

Previous studies have found that for inhalation by the mouth, particles 3 μm AD had a maximum alveolar deposition, while for nostril inhalation particles 2.5 μm AD had a maximum alveolar deposition (National Academy of Sciences, 1979). Depending upon properties of the fine particles inhaled, they could potentially cause alveolar inflammation and lead to more severe health problems (Beckett et al., 1998; ALA, 1998).

Inhaled particles can affect pulmonary functions either temporarily or permanently, which can potentially lead to 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 (National Tuberculosis and Respiratory Disease Association, 1971; Health Canada, 1996; Health Canada and Ontario Ministry of Health, 1997; EPA, 1997b; Brook et al., 1997; Tiittanen et al., 1999). Particles may also affect defensive mechanisms of the body and create scarring of lung tissue, 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 to exposure of particulate matter are children, elderly and those with chronic respiratory problems (EPA, 1997f; Health Canada and Ontario Ministry of Health, 1997). Children tend to be the highest level of concern, as they breathe 50% more air per pound of body weight than adults and their respiratory systems are still developing (EPA, 1997a). Thus 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 (EPA, 1994a).

To identify receptor exposure there is a need to identify contact between a substance (particulate mass) and a specific concentration introduced to the respiratory tract of the body (CEPA and FPAC, 1999). Exposure to particulate matter (mass) that people come in contact with may be related to ambient air concentrations recorded at a fixed Federal Reference Method (FRM) sampler as (CEPA and FPAC, 1999):

$$E_i = \sum_{j=1}^{n} C_j F_i t_{ij} \quad \text{.......} \quad \textbf{(3)}$$

where; E_i is the total integrated exposure for person "i" over the exposure period (μg), C_j is the pollutant concentration at location "j" (μg/m^3), F_i is air flux through the sampler for person "i" (m^3/hr) and t_{ij} is time spent at location "j" for person "i" (hr). The most difficult variable to evaluate is the time a person spends at a given location.

Studies have demonstrated that the general population only spends about one hour per day outdoors, 1.5 hours in a vehicle and 21.5 hours indoors (CEPA and FPAC, 1999). There is difficulty associated with epidemiological studies identifying causality, based on exposure evidence collected from fixed FRM samplers (CEPA and FPAC, 1999). These studies require the assumption that all people experience the same pollutant concentration as that recorded by a FRM sampler. These samplers are typically located centrally in a study area and collected over 24-hours, tending to ignore micro-scale fluctuations in particulate concentrations experienced by a receptor. Using these FRM samplers to relate exposure to a receptor population is ineffective when much of the time is spent away from outdoor sources and influenced by indoor air quality (Alberta Environment, 1999).

2.1.3 Emission Issues related to Particulate Matter

Aesthetic effects of fine particulate matter ($PM_{2.5}$) are a potential visual impairment (Pacific Environmental Services Inc., 1999). This fraction, primarily in the accumulation mode, causes scattering and absorption of light in the atmosphere, resulting in regional haze (Environment Canada, 1998). The degree to which particles scatter visible light depends upon particle size, shape and index of refraction, which is dependant upon chemical composition (EPA, 1998a). This can become very serious when dealing with a low ceiling haze obscuring visibility for traffic on highways. In addition, haze can cause problems around airports for planes landing and taking off (Rhebergen et al., 1999). Impaired visibility is not aesthetically pleasing in cities, national parks and other scenic areas (EPA, 1997f).

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, laundry (outside), homes, buildings and statues, resulting in a nuisance impact on the environment (Rhebergen et al., 1999, EPA, 1997a). This includes damage or discolouration of the surface on which the particles settle (EPA, 1997a).

2.1.3.1 Guidelines and Regulations for Particulate Matter

Given the current state of knowledge of health and aesthetic issues relating to particulate matter, government agencies have the responsibility of limiting emissions for protection of public health. Current guidelines and regulations for limits of particulate matter have used evidence gathered from health studies conducted with conventional air sampling techniques (D'Innocenzio et al., 1998). 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 total suspended particulate (TSP – particulate matter of all size fractions) are based on nuisance effects and visual reduction of particulate matter (Myrick, 1996a).

A summary of the Alberta Guidelines is presented in Table 2. Other Provincial, National and International guidelines and regulations are summarized in Appendix A.

Table 2. 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-hour 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)

2.2 Field Collection Methods for Particulate Matter

Measurement of airborne particle concentrations can be performed by a variety of methods. The simplest is to draw high volumes of air through a filter and to weigh the mass accumulated on a filter over a given time period (UK Department of the Environment, 1995). This method is used to collect particulate matter in the airborne suspended phase, commonly referred to as total suspended particulate (TSP) (CEPA and FPAC, 1999). Growing health concerns about specific size ranges of particles have resulted in improved methods that employ the use of size selective inlets to collect $PM_{2.5}$ or PM_{10} on a membrane filter.

The primary method used for particle size separation is impaction. This simple separation technique employs an impaction plate, which uses inertial forces to separate particles by size. However, if size, hardness, and velocity are great enough, the particle may bounce upon contact with the surface. Coating the impaction surface with oil or grease can minimize particle bounce. Re-suspension of the particle from the surface can potentially occur when external forces acting upon the particle overcome adhesive forces, releasing the particle, thus increasing mass collected on the filter.

2.2.1 Types of Samplers

There are two types of particulate samplers; an integrated gravimetric sampler and a continuous sampler. An integrated gravimetric sampler requires a changeable filter for each test, with particle mass determined by pre- and post-weighing of the filter. A continuous sampler however, employs in-situ methods to determine particle mass on a real-time or average time basis. Many of the commercially available samplers are designed to collect 24 m^3 of air per day and are designated a United States Environmental Protection Agency (USEPA) Federal Reference Method (FRM) sampler or equivalency designation sampler. These samplers have been tested to meet strict guidelines to comply with the National Ambient Air Quality Standards (NAAQS) for particulate matter (40 CFR Part 50).

If elemental analysis of particles is required from collected samples, an integrated gravimetric sampler is generally employed. There are two types of integrated gravimetric samplers that can be used: a high volume FRM samplers or low volume personal or portable samplers. The FRM samplers are the most common type used for outdoor field collection studies of TSP, PM_{10} or $PM_{2.5}$. Both types of samplers use appropriate size selective inlets for particle separation, with sample flow rate being the primary difference. A FRM sampler typically draws approximately 17 litres per minute or greater to draw 24 m^3 of ambient air (Chow, 1995). Newer developments with smaller, portable low volume samplers have reduced sampling rates as low as one to five litres per minute

(Chow, 1995). These low volume samplers are smaller in size and much more cost effective than FRM samplers, however their use in outdoor studies has been limited.

One such low volume monitor is the MiniVol (Airmetrics, OR, USA), a small inexpensive battery operated sampler that does not require complicated siting or power sources. The MiniVol sampler was co-developed by the Lane Regional Air Pollution Authority and US Environmental Protection Agency (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). In one study, a MiniVol was compared indoors to four samplers (Heal et al., 2001). The authors found good agreement between the samplers with 24-hour average PM_{10} mass measurements. In a separate outdoor co-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).

There are currently no elemental characterization studies of particles collected with low volume samplers using best available elemental and chemical analysis methods. This is important as MiniVol samplers are believed to provide better spatial representation and improved assessment of human exposure due to sampler size and mobility (Heal et al., 2000). The ability to characterize elements in particles collected from low volume samplers would encourage their use for particulate matter source to receptor modeling.

2.2.2 Types of Filters

Before elemental analysis of particulate matter can be done, the type of filter with the least background contamination must be identified. This is important when dealing with small amounts of particles on filters. The slightest background contamination can skew potential elemental fingerprints of ambient particles. There are several types of filters that can be used based upon study requirements and filter composition. Filter types include cellulose-fiber, glass-fiber, Teflon coated glass fiber, Teflon membrane, etched polycarbonate membrane, quartz fiber and nylon membrane (EPA, 1994a).

In order to identify an appropriate filter material for analytical testing in receptor modeling studies, the filter must meet certain basic requirements. For example, the filter should be mechanically, thermally and chemically stable, and have a high sampling efficiency based on sample type. Also, filters should not have significant concentrations of the material being determined by the analytical technique used (EPA, 1994a; ARC, 1998).

Most commercially available filters encounter difficulty with gravimetric stability (i.e. absorption of moisture) and elemental interference (i.e. quartz filters would interfere with silica evaluations). Teflon filters have been noted for their durability, their ability to not adsorb gases and ability to remain non-catalytic to particles collected (EPA, 1999c; Lioy and Daisey, 1987). Proper filter identification is crucial to field collection and detailed chemical analysis. This may be a significant issue requiring further investigation for low volume sampler filters.

2.3 Particulate Matter Elemental Identification Methods

Once gravimetric analysis of collected particulate matter is complete, further analyses can be performed to characterize particle size and shape characteristics (morphology) and to identify chemical/elemental properties (EPA, 1994a). For current elemental analytical methods, the net mass of particles on a filter needs to be greater than the analytical method detectable limit (EPA, 1994a). With current studies relying on filters collected with FRM samplers, the net mass collected should be on the order of 10^3 to 10^4 μg over 24-hours. Net mass collected by low volume samplers is considerably less, typically less than 100 μg over a 24-hour collection period. This may represent insufficient material for analysis or proper particle identification using conventional analytical techniques.

2.3.1 Analytical Methods

Identification of physical or elemental properties of collected particulate matter is very important for source to receptor modeling. These properties can be used to apportion PM to various sources, which can in turn be used to prioritize emission reduction strategies (EPA, 1994a).

Prior to analysis of a filter used for ambient air collection, the net mass of a filter must first be determined by gravimetric analysis. Pre and post weighing should be performed after initial stabilization for 24-hours at 20°C and 30% relative humidity. The balance used for weighing should be capable of reading to one microgram (μg) (EPA, 1997c).

Next is identification of physical or elemental properties of PM by a bulk or individual analysis method. Bulk elemental analysis methods are most commonly performed on filters from ambient air studies (EPA, 1994a). There are current drawbacks to conventional bulk analysis methods. One drawback is that the filter is required to have a substantial loading, a loading generally associated with FRM sampling tests (Pinto et al., 1998). This requirement causes difficulty for low volume samplers. If a low volume sampler is used for collection of particles the filter generally has too few particles present, thus the filter itself will interfere with analysis (Pinto et al., 1998).

Another issue with bulk analysis is that testing is performed without physical knowledge of the types of particles present. For example, if the size selective inlet was malfunctioning, particles tested would be outside the size range desired. As the vast majority of current air studies are performed using FRM samplers, bulk analysis is still the method of choice.

There are two prominent bulk analysis methods: X-Ray Fluorescence (XRF) and Proton Induced X-Ray Emission (PIXE) (EPA, 1994a; EPA, 1999b). These methods are favored due to their non-destructive nature and elemental analysis can be performed allowing additional testing of the same filter. Other elemental analysis methods include; Instrumental Neutron Activation Analysis (INAA), Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Ion Chromatography (IC) (EPA, 1999b). These methods are known as destructive methods and further analysis of the filter is not possible. In receptor modeling studies utilizing filters collected with FRM samplers for TSP, PM_{10} and $PM_{2.5}$, all of these elemental analysis methods have been utilized (Ontario Research Foundation et al., 1982; Dzubay et al., 1988; Swietlicki et al., 1996; Alves et al., 1998; Maenhaut and Cafmeyer, 1998; Van Der Zee et al., 1998; Chan et al., 1999; Motallebi, 1999).

A promising new technique of individual particle analysis has evolved due to limitations described above for bulk analysis. For individual particle analysis, either Electron Microprobe analysis (EPMA) or Scanning Electron Microscopy with Energy

Dispersive X-ray analysis (SEM-EDX) is required (Jambers et al., 1995). These techniques can be used to study morphology of individual particles collected from ambient air. Unlike bulk analysis, these methods have a drawback if filters are too heavily loaded, as described by Pinto et al. (1998). Thus for individual particle analysis it is better if the filter is spatially covered with a limited number of particles. Only those samples taken in remote areas (with low ambient concentrations) using FRM samplers have been used for individual particle analysis (Zwozdziak et al., 1986).

Individual particle analysis (in particular SEM-EDX) is a promising technique for use with low volume samplers, which collect a lower mass than comparable FRM samplers. The most significant advantage is an ability to identify morphological properties. This can aid identification of sources based on particle surface and shape characteristics. However, particle identification requires a categorical morphology list for comparison; a list that could be infinite to match infinite varieties of unique particles.

For practical purposes, categories developed for morphological analysis only need to be sophisticated enough to enable distinction among particles by discriminating detail with additional ties to elemental properties. An example of categorical properties needed for identification would include homogeneity, shape, surface texture, and elemental composition (CEPA and FPAC, 1999; Pinto et al., 1998).

Using previous morphological studies conducted on similar particles and visual shape comparators from a particle atlas, Table 3 was compiled to enable the study of particle morphology using SEM-EDX in order to aid identification of their probable sources. However, micro-analytical and surface analysis techniques used to study individual environmental particles in ambient air are quite rare (Jambers et al., 1995).

This is primarily based on concerns regarding the minimum number of particles required for proper identification, cost and analytical time required (ARC, 1998; Jambers et al., 1995). Thus there is a research need to address the development of standard protocols relating to individual particle analysis techniques.

2.4 Methods for Attributing Particulate Matter to Sources

The function of particulate matter characterization is to determine sources of ambient particles. The relationship between collected particulate matter and source identification is referred to as “source-to-site”, “source receptor”, or “source apportionment”. The two approaches in identifying source to receptor relationships are a receptor-orientated approach and a source-oriented approach. In a receptor approach, chemical or elemental composition of ambient particulate matter collected is apportioned to contributions of different source types (Cooper and Watson, 1980). Thus, receptor models use physical and elemental characteristics of PM measured at receptor sites to estimate source contributions. Receptor models have a limitation in that they cannot distinguish between sources with similar composition profiles (Watson and Chow, 1981). In addition, receptor models cannot predict consequences of emission reductions thus making it necessary to use a source-oriented approach, such as emission modeling, for this determination.

Table 3. Morphological and Descriptive Characteristics of Particles

(Zou and Hooper, 1997; CEPA and FPAC, 1999; Pinto et al., 1998; Zwozdziak et al., 1986; Kozinski and Saade, 1998; Beckett et al., 1998; Mikhailov et al., 1996; Hueglin et al., 1997; Dzubay and Mamane, 1989)

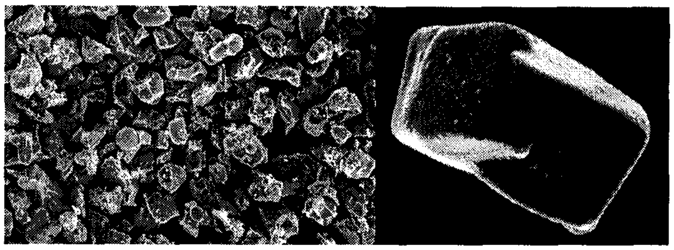
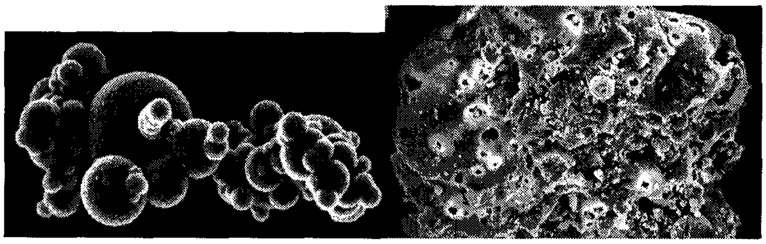
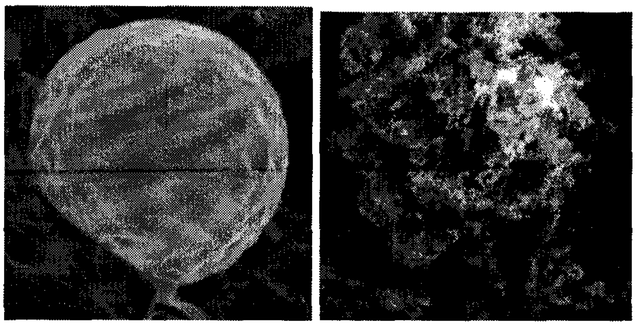
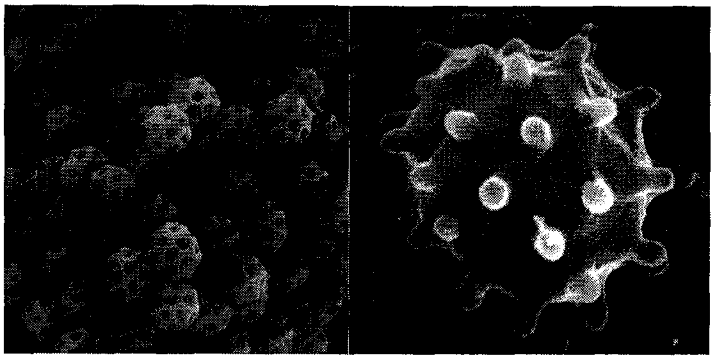
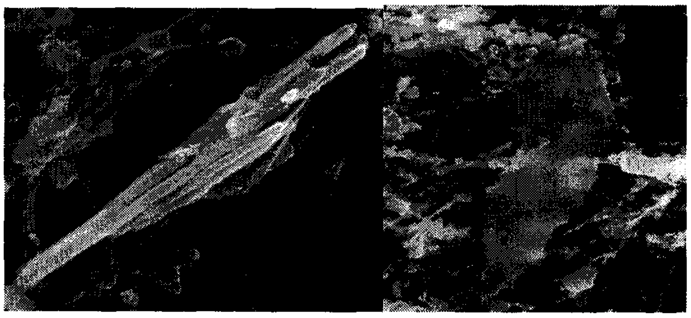
Particle	Descriptive Properties	Physical Properties
Crustal	Minerals; Silica Clay Salt	Irregular / cubical flakes; nonspherical, highly mineral; crystalline / angular fractured grains; elemental composition of silica and clay consists mainly of Si and Ca; for salts mainly Na and Cl 
Industrial exhaust	Process particles; Flyash Sintered Combustion	Combustion produces spherules which have porous structures; the porous particles are produced from expansion and escape of gases during combustion. Flyash can also be produced in coal burning power plants which results in nearly spherical particles. Sintered particles are produced under extreme heat, resulting in agglomerated (melted) particles 
Vehicular Exhaust	Soot Oil	Consist of nearly spherical particles having relatively uniform diameters; particles tend to be in two forms, (1) individual particles joined in simple short chains, and (2) branched clusters of these chains; typical size range of 0.01 to 0.1 μm; soot particles are formed due to incomplete hydrocarbon pyrolysis, relating to combustion temperature 

Table 3. Morphological and Descriptive Characteristics of Particles (Continued)

Particle	Descriptive Properties	Physical Properties
Biological	Pollen fragments, Spores Epidermis lint, Plant fibres, Insect fragments	Pollen particles tend to be very smooth in appearance with an egg like shape; Spores tend to be more spherical however with "spikes", identified generally as a "Spiked" fungal uredospore  Other biological particles can be fibrous or fragmented in appearance 
Other	Variable	Category for particles that do not fit into the specific classifications

In source-oriented approaches, a numerical model can be used to simulate dispersion and reactions of pollutants emitted from specific sources. Dispersion models use estimates of pollutant emission rates, meteorological transport and chemical transformation mechanisms to estimate the contribution of each source at receptor sites (Young, 1982). Dispersion models have commonly been used as a tool for development of particulate matter control strategies. However these models also have limitations, which have resulted in inaccurate modeling and over- or under-estimating concentration exposures (Young, 1982).

These two approaches are complementary, each having strengths that can compensate for weaknesses of the other. Source modeling is still widely used for a general estimate of airborne pollutant levels from emission sources, whereas receptor models are used to estimate source contributions of airborne pollutants collected at a receptor site (Lioy and Daisey, 1987).

2.4.1 Receptor Modeling

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 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 concepts:

- source identities and their respective contributions to ambient pollutant can be inferred from chemical composition of particulate matter collected at 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, and

- source types may be identified (inferred) from characteristic elements or tracers.

There are two main types of receptor model approaches: chemical elemental balance / chemical mass balance (CEB / 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; ARC, 1998; Chan et al., 1999). A drawback 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 can be used.

A multivariate approach extracts source contribution information based on variability of tracers, such as elements or chemical indicators of a source present on a set of filters. This approach 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., 1980a; Alpert and Hopke, 1981; Morandi et al., 1987; Chang et al., 1988; Pratsinis et al., 1988; Fung and Wong, 1995; Song and Hopke, 1996a; Song and Hopke, 1996b; Baldasano et al., 1998; Chan et al., 1999; Paatero and Hopke, 2003).

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-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).

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

$$m = \sum_{j=1}^{p} M_j \qquad \textbf{(4)}$$

where; p sources (each labeled j) are emitting M_j mass of particles. This represents total mass on a filter, however if mass of a specific chemical or elemental species (m_i) is required then equation (4) can be re-written as:

$$m_i = \sum_{j=1}^{p} M_{ij} F_{ij} \qquad \textbf{(5)}$$

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 (5) is then divided by the total mass of deposited particulate matter, yielding:

$$C_i = \sum_{j=1}^{p} S_j F_{ij} \qquad \textbf{(6)}$$

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 contribution, that is the ratio of the mass contributed from source j to 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 equalization of both large and small magnitude variables, otherwise the results will be influenced more by the variable that has the greatest magnitude (Henry and Hidy, 1979; Gordon, 1988):

$$Z_{ik} = \frac{\left(C_{ik} - \overline{C}_i\right)}{\sigma_i} \quad \text{.......}(7)$$

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 i^{th} element over all observations k; and σ_i is the standard deviation of the i^{th} element over all observations k. This leads to the principle component model (Henry and Hidy, 1979; Gordon, 1988):

$$Z_{ik} = \sum_{q=1}^{r} A_{iq} P_{qk} \quad \text{.......}\mathbf{(8)}$$

where; A_{iq} is the loading matrix of the components, also known as eigenvectors or scoring coefficients, and P_{qk} is the q^{th} (q=1,..r; number of underlying components influencing the data) component value for observation k. In interpretation of scoring data, Table 4 is used as a guide.

Table 4. Interpretation of the PCA Eigenvectors (A_{iq})

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 instances where elemental profiles overlap, secondary information such as particle morphology can be used to help distinguish sources. This would not be possible if a destructive bulk analysis method were used. Hence, individual particle analysis may aid in determining the final factors calculated in the PCA and can be given a physical interpretation.

In order to identify and delineate independent sources with PCA there should be a large data set of samples such that there are 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 each other (Statheropoulos et al., 1998).

There is currently no data pertaining to low volume samplers used in association with receptor modeling studies. This is related to a limitation of bulk analysis techniques to determine elemental quantities from particles collected by low volume ambient samplers. While use of low volume samplers shows promise in field studies due to their gravimetric performance and portability, data pertaining to receptor modeling with these samplers is lacking.

2.4.2 Tracer Analysis

2.4.2.1 Elemental Tracer Analysis

Tracer studies are useful for quantifying dispersion characteristics of plumes, qualitatively characterizing transport directions and providing empirical data for evaluating trajectory and dispersion models (Blanchard, 1999). Tracer analysis involves characterization of elemental concentrations found at each receptor and use of the results to identify source types by assessing concentration of specific tracer species (Chow, 1995). Based upon summarized elemental tracer data collected at receptor locations, a multivariate approach (PCA) can be used to associate tracer species with a probable source by assessing relative abundance of different tracer species.

For example, vanadium, sulfur, nickel, sodium and chloride are indicative of oil or oil source origins (Chow, 1995; EPA, 1999c). However, apportionment of ambient particulates collected at receptor locations can be difficult if no source emission profile exists and if source profiles overlap (Song et al., 1999). Currently there is no Alberta specific source emission profile database; therefore previous studies (Chow, 1995; ARC, 1998; Lowenthal et al., 1997) were reviewed to identify current elemental source profiles relevant to Alberta. From these previous studies it was apparent that sources of particulate matter can be classified as anthropogenic or natural.

Anthropogenic Sources

Anthropogenic sources are those directly related to human activity and therefore, are theoretically controllable. Sources of anthropogenic emissions of both $PM_{2.5}$ and PM_{10} size fractions include vehicles, agricultural activities, wood burning (fireplace or fire pit), and industrial activities (oil, gas, coal, cement, mining, smelting, construction, biomass burning, and refuse burning) (Cooper and Watson, 1980; Cheng et al., 1998).

Primary emissions associated with anthropogenic PM_{10} in Alberta are road dust, while contributions from industrial sources tend to be minimal (Cheng et al., 1998). Road dust has been found to include a complex mixture of particles including garden soil, tire dust, brake and clutch wearing, plant fragments, deposited atmospheric particulates (i.e. industrial fallout), ground plant and pollen fragments (both of which are potential allergens) (Glovsky et al., 1997). In addition, road dust typically includes elements such as aluminum, iron, silica, and potassium, with trace levels of elements such as chromium, strontium, lead and cadmium (Chow, 1995; Chow and Watson, 1998). From Alberta $PM_{2.5}$ studies, the major anthropogenic sources of fine particles include vehicle and wood burning (including fireplaces, open pit, and barbecues) (Cheng et al., 1998). Vehicle emissions include elements such as sulfur, bromine, calcium and iron. Biomass (wood) burning includes elements such as potassium, chloride and rubidium (Chow, 1995; Baisden et al., 1995).

Natural Sources

Natural sources are extremely important to identify as they represent the minimum airborne particle concentration and may be used to develop regulatory standards. Based on natural emissions of $PM_{2.5}$ and PM_{10} size fractions, sources include wind blown dust, wildfires, sea salts, vegetation, meteor dust and volcanic dust (CEPA and FPAC, 1999; Cooper and Watson, 1980). Of these potential sources, the primary emission source associated with PM_{10} is fugitive dust. Fugitive dust sources were estimated to contribute as much as 89% of the United States total coarse fraction, however geological material varies greatly from site to site with levels of fugitive dust ranging from 20% to 80% (Chow and Watson, 1998). In contrast, Alberta coarse particle fugitive dust levels range from approximately 55% to 65% (Cheng et al., 1998). Fugitive dusts typically have geological origins with primary elements including silica, aluminum, magnesium and calcium with trace levels of elements such as manganese, zinc, phosphorus and titanium (Chow, 1995; EPA, 1999c). Alberta $PM_{2.5}$ studies have found that major natural sources of fine particles include wild fires (forest fires) and wind erosion, accounting for approximately 7% to 8% of Alberta's fine particle levels (West Central Airshed Society, 1997; Cheng et al., 1998).

2.4.2.2 Other Substance Tracer Analysis

Other tracer substances, aside from elemental markers were reviewed, which include gaseous compounds and organic species. These substances can be similarly used like elements to aid in identification of source types by analyzing substance concentrations found at receptor locations. Species that are of interest based upon their health-related effects are (Rhebergen et al., 1999; Johnson, 1999):

- carbon monoxide (CO)
- formaldehyde (HCHO)
- nitrogen oxides (NOx)
- individual volatile organic compounds (VOCs)
- polynuclear aromatic hydrocarbons (PAHs)

PAHs represent a potential tracer for primary emission sources. PAHs can occur naturally through forest fires, geothermal activities (volcanic), and biosynthesis, or through anthropogenic sources such as smelters, transportation, residential wood heating, incineration and power generation (Government of Canada et al., 1994; Lioy and Daisey, 1987; Baek et al., 1991; UK Department of the Environment, 1999). In Canada and the United States, the most common source of natural PAHs are from forest fires. (Government of Canada et al., 1994; Benner et al., 1989; Harrison et al., 1996). Since forest fire occurrences are generally separated by vast spaces (and time), releases of PAHs to the atmosphere are not considered a continuous source. Thus a person would not experience chronic exposure to PAH through natural sources such as forest fires (Government of Canada et al., 1994). However, anthropogenic sources of PAH tend to be related to urban settings including residential heating with wood, agricultural burning, transportation and burning of wood wastes (Harrison et al., 1996; Government of Canada et al., 1994; Baek et al., 1991).

PAH measurements have gained interest in their use as a vehicle tracer. Common tracers used in the past were lead and bromine, however with phasing out these elements from gasoline, PAHs have been recommended as new tracers for vehicle emissions (Benner et al., 1989; Harrison et al., 1996). Vehicular exhaust can act as nuclei for

PAHs, due to their size (0.2 to 2 μm). Depending upon atmospheric conditions, PAH-bound particles can remain airborne for days (Harrison et al., 1996; Lioy and Daisey, 1987; Harrison et al., 1996). Prior to 1980, it was believed that a majority of PAH emissions (80-90%) resulted from stationary sources and were transported long distances. However, mobile sources of PAH have been examined more recently as major contributors to ambient PAH levels. Vehicles are believed to account for the majority of PAH emissions in urban areas (Baek et al., 1991).

2.4.3 Trajectory Analysis

Trajectory analysis involves analyzing the mass and/or elemental composition of PM along with meteorological conditions (e.g. wind speed, wind direction) and using the results to infer general source types based upon locations of where an airmass affecting a monitor originated (Blanchard, 1999). Trajectory analyses are routinely used to estimate atmospheric transport directions.

There are two primary trajectory approaches: forward and backward (Stohl, 1996). By using ambient air measurements collected at receptor locations and making back trajectory calculations on air masses arriving at a receptor location, one can attempt to establish potential correlation between sources and receptor sites (Stohl, 1996). Back trajectories have been used in combination with air quality measurements to identify potential source areas of air pollutants (Stohl, 1996). However if there are many emitters of similar pollutants where air masses originate from, it is more difficult to relate the air pollution to an origin (Stohl, 1996). This has been used successfully to determine source areas of air pollutants, using sulfur emissions, however it was recognized that there is a potential to use other species such as metals (Stohl, 1999). This method may be helpful to aid interpretation of receptor modeling studies using low volume samplers in a setting with only a few source types.

2.5 Summary

With rising public awareness to exposure of particulate matter, there is an increased need for better source to receptor identification. Mass concentration data have been obtained with conventional particulate matter sampling techniques. Further information has been obtained from bulk analysis conducted with these samples.

Source to receptor studies using these techniques are limited in their ability to characterize population exposure because they do not necessarily represent locations where exposure occurs. For the purpose of public health assessment, using techniques that are more portable and representative of receptor locations would be a better method of determining source exposures. Therefore, it is proposed that using portable low volume samplers with source identification would lead to more representative information on the importance of sources contributing to receptor population exposure. In particular, portable low volume sampling coupled with individual particle analysis may show promise for source to receptor relationships but has remained largely unexplored.

3. PROBLEM STATEMENT AND RESEARCH OBJECTIVES

3.1 Problem Statement

Exposure to particulate matter on a daily basis is unavoidable, thus the ability to identify source contributions will aid public health and regulatory issues related to PM exposure. As outlined in Chapter 2, conventional studies for particulate matter source apportionment typically use FRM samplers followed by bulk analytical techniques. Because of limitations posed by common bulk analytical techniques identified by Koutrakis (1998), a need exists to examine alternative sampling and analytical techniques. A low volume sampler that has grown in popularity due to the low cost and high portability is the MiniVol (AirMetrics, Portland, OR). Testing of this sampler has demonstrated comparable gravimetric findings with fixed FRM samplers (Tropp, el al., 1998). However given the low particle masses collected by this sampler, a more suitable analytical technique is required for source apportionment applications. One such technique proposed is SEM-EDX analysis, which is capable of simultaneous examination of particle size, morphology and elemental composition.

3.2 Research Objectives

The primary objective of this research was to develop and demonstrate the feasibility of low volume air sampling coupled with individual particle analysis to provide quantitative data for ambient PM source apportionment. Specific activities that were undertaken in fulfillment of this research involved:

1. Development of an analytical protocol for SEM-EDX to analyze individual particles collected on the filter:

   a. Review, identification and selection of a bulk analysis method capable of comparison to individual particle (SEM-EDX) analysis from low volume sampler filters.
   b. Development of a procedure to determine how many individual particles to analyze on a filter using SEM-EDX to provide an accurate representation of elemental masses on the filter.
2. Identification of an elemental profile database based on a detailed literature review to assist in source apportionment analysis.
3. Pre-testing filter types using SEM-EDX to determine which type of filter is best suited for SEM-EDX analysis.
4. Design and construction of a sampling chamber and testing of the low volume samplers:
   a. Co-location of low volume samplers with a real-time particle counter inside the chamber to determine if the low volume samplers were capable of measuring a similar mass concentration as that reported by the real-time particle counter.
   b. Injection of a National Institute of Standards and Technology (NIST) standard reference particulate matter inside the chamber to determine if low volume sampling and individual particle analysis can measure the appropriate mass of elements as reported by the NIST standard reference.
   c. Comparison of analytical procedures for bulk analysis and individual particle (SEM-EDX) analysis using the standard reference particulate matter.

5. Low volume sampling in a field monitoring program followed by SEM-EDX and ICP-MS analysis:
    a. Comparison of analytical procedures for bulk analysis and individual particle (SEM-EDX) analysis for ambient particulate matter.
6. Low volume sampling in a field receptor monitoring program followed by SEM-EDX analysis:
    a. Analysis of results using PCA for identification of particulate matter source contributions (source apportionment).
    b. Comparison of results with a trajectory analysis to assist in the interpretation of potential sources identified from PCA.

Two stages were used to illustrate the sampling and analytical approach examined here. In the first stage, ambient air is drawn into the low volume sampler using a size selective inlet with particulate matter collected on a filter. The second stage involved individual particle identification through simultaneous assessment of morphology (size and shape) and elemental composition using SEM-EDX. With adequate sample sizes, elemental data from the second stage could be analyzed using principle component analysis to identify probable origin (Henry and Hidy, 1979; Buhr et al., 1992). An important assumption that was investigated in the second stage was that particulate matter was uniformly distributed over the filter surface during collection. This would determine whether SEM-EDX analysis of partial amounts of individual particles collected on the filter surface would be representative of the composition of all particles deposited on the entire filter.

4. EXPERIMENTAL METHODS

4.1 Elemental Profiles

In order to define source fingerprints from emitters, elemental analysis should be performed on all significant sources when the resources are available. When this is not possible, source composition data from previous studies should be compiled from literature (Lowenthal et al., 1997). This data can then be used to aid in interpretation of results of receptor modeling. Source elemental profiles were compiled from a detailed review of literature and summarized into primary sources based on the two main size fractions of particulate matter ($PM_{2.5}$ and PM_{10}). Results are discussed in detail in Chapter 5.

4.2 Particle Analysis of Filters

An appropriate filter material to be used with low volume samplers needed to be identified for gravimetric and elemental analysis using SEM-EDX. To identify an acceptable filter material, four filter types were analyzed for impurities with Scanning Electron Microscopy Energy Dispersive X-Ray (SEM-EDX, JEOL-6301F, University of Alberta, Edmonton, AB). These impurities consisted of elements that can skew potential fingerprinting of ambient particles.

Filters chosen for analysis included:

- Cellulose (Whatman, Clifton, New Jersey, USA)
- Pure quartz-fiber (Pallflex, Pall Corporation, Ann Arbor, Michigan, USA)
- Ringed Teflon-membrane (Gelman Scientific, Pall Corporation, Ann Arbor, Michigan, USA)

- Ringed Teflon-membrane (Whatman, Clifton, New Jersey, USA).

The results are discussed in Chapter 6.

4.3 Particle Sampling Methods

Calibration and flow checks were initially required for equipment used in this research. This included: four MiniVol samplers (Airmetrics, Eugene, OR), a Grimm dust monitor (Series 1.104 Occupational Health Dust Monitor, GRIMM Technologies Inc., Douglasville, GA), a Tapered Elemental Oscillating Microbalance (TEOM Series 1400a, Rupprecht & Patashnick Co., Inc., Albany, NY) and a PAS-2000 PAH monitor (EcoChem Analytics, Wet Hills, CA). Flow checks were performed on all equipment with a wet test meter (GCA/Precision Scientific, Chicago, IL).

Accurate airflow is critical for instrument operation as concentration is determined by the ratio of mass collected to volume of air passed through the sample filter (Cohen and Hering, 1995):

$$C_m = \frac{m}{Q_s \cdot t} \qquad \text{(9)}$$

Where, C_m ($\mu g/m^3$) is mass concentration, m (μg) is net mass increase on the filter, Q_s (m^3/hr) is the sampling flow rate, and t (hr) is the sampling period.

If flow rates fluctuate, air volume will be inaccurate due to this flow rate variation; in turn the mass concentration collected per unit volume will be incorrect (Cohen and Hering, 1995). Normal airflow fluctuations can be expected due to factors such as filter overload and mechanical instabilities. By performing flow checks and calibrations on the equipment prior to use the mechanical instabilities can be accounted for and corrected. The following sections briefly describe the air sampling equipment used and the calibrations performed on each.

4.3.1 MiniVol Filter Sampling

The MiniVol samplers are capable of collecting a multitude of time-integrated samples. The MiniVol is a small battery-operated portable sampler, which can be operated by either AC or DC supplies. The MiniVols twin cylinder vacuum pump is designed to pull air at 5 litre per minute (Lpm) through an impactor (with 10 μm or 2.5 μm aerodynamic diameter cutoff). The air is drawn through a 47 mm Teflon filter, leaving the entrained particles on the surface of the filter (Airmetrics, 1998). Mass of the deposited material can be weighed and then analyzed for elementals. To ensure adequate operation of the MiniVols, they were re-calibrated prior to sampling with post flow checks performed for optimal performance. Refer to Appendix B for calibration graphs. In addition the impactor heads were greased according to the manual specifications (Airmetrics, 1998) to reduce the frequency of particle bounce and entrainment of larger particles.

MiniVols are not referenced samplers; however research has demonstrated results that closely match USEPA reference methods. For example the PM_{10} samplers have demonstrated comparable results with PM_{10} equivalent method dichotomous samplers (Jones et al., 1998). In addition, Environment Canada uses the MiniVol as a saturation sampler, such that many are deployed to “saturate” the environment with samplers. Environment Canada has used them extensively in several parts of Alberta under a variety of climatic conditions (Alberta Health, 1997). The USEPA also has encouraged state and local agencies to conduct short-term, multi-site monitoring studies using the saturation monitoring technique (EPA, 1999c). These small portable samples have been a useful tool for finding "hotspots" in a community, and helping local agencies gather preliminary information for the development of monitoring networks (EPA, 1999c).

4.3.1.1 Gravimetric Analysis

For the gravimetric analysis 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 USEPA guidelines in which the filter was pre-conditioned and post-conditioned for 24-hours at 20°C and 30% relative humidity (EPA, 1997c). Protocols for weighting and handling of individual filters are presented in Appendix C.

4.3.2 TEOM Real Time Sampling

A Tapered Element Oscillating Microbalance (TEOM) Series 1400a Ambient Particulate Monitor was used to collect real time PM_{10} (Rupprecht & Patashnick Co., Inc., 1996). The TEOM is able to collect TSP, PM_{10}, $PM_{2.5}$, or PM_1 depending on the inlet size used during the monitoring period. For the purpose of the field survey, only the PM_{10} inlet head (collection of particles ≤10 μm aerodynamic diameter) was used for the entire period.

The TEOM Series 1400a has been designated by the USEPA as an equivalent method for the determination of 24-hour average PM_{10} concentrations in ambient air. The instrument works by drawing ambient air through an inlet head at a rate of 16.7 Lpm. From the inlet, flow is isokinetically split into a 3 Lpm stream which is sent to the mass transducer and 13.7 Lpm stream is exhausted. Within the mass transducer, air passes through a filter made of Teflon coated borosilicate glass at a constant rate (3 Lpm). The filter is weighed continuously (every two seconds) and the readings of total mass are smoothed exponentially to reduce noise. The mass concentration is then computed by dividing the mass by the flow rate (Rupprecht & Patashnick Co., Inc., 1996). Internal storage allows large quantities of data to be stored for later viewing either on the instrument display or downloading through an RS-232 port. The equipment was set to collect the following data every 30 minutes: instantaneous mass concentration, 30-minute average mass concentration, 1-hour average mass concentration, 24-hour average mass concentration, total mass, ambient temperature and ambient pressure. The TEOM was calibrated prior to field work (calibration notes in Appendix B), and flow checks were done periodically to ensure operational conditions.

4.3.3 Grimm Real Time Sampling

A Grimm real-time dust monitor (Series 1.104) was used to collect samples during the laboratory study. The Grimm samples air directly at a rate of 1.2 Lpm. The air sample passes through the light of a laser diode scattering the light relative to the level of particles in the air stream. The signals are collected and classified by a multi-channel pulse height analyzer for particle size classification. Data are recorded every six seconds via a computer interface for both simultaneous readings of PM_{10} and $PM_{2.5}$ mass concentrations ($\mu g/m^3$). The unit is lightweight and portable, with a battery capacity of approximately seven hours of continuous operation.

This sampler was used in the laboratory study based on its relatively small size and real-time particle collection ability. The TEOM was not feasible for the laboratory study due to its inlet size and inability to monitor multiple particle sizes simultaneously.

A flow check was routinely performed on the inlet side of the Grimm to ensure air flow rate was 1.2 litres per minute.

4.3.4 PAS Monitor Real Time Sampling

This monitor was used to collect real time total PAHs during the field receptor sampling program. The PAS 2000 utilizes a photoelectric aerosol sensor (PAS) for identifying total particle-bound polycyclic aromatic hydrocarbons. Air is drawn into the equipment at a set flow rate of 2 Lpm (no inlet head for particle size separation). The air sample with the PAHs bound to ultrafine particles is irradiated, which causes the particles to emit a photoelectron, making the particle positively charged. A typical particle is not capable of photoemission, however particles that have a layer of PAHs (which condense or adsorb onto the particle surface) are easily photoionized. The charge rate is measured and this rate has a direct relationship to the concentration of total particle bound PAHs. This monitor has a lower operation threshold of 3 ng/m^3 of total particle bound PAHs (EcoChem Analytics, 1998). A flow check was performed prior to every sampling period to ensure air flow was 2 litres per minute.

4.4 Individual Particle analysis of Filters (SEM-EDX)

Analysis of individual particles was conducted with a SEM - JEOL 6301F (Field Emission SEM) equipped with a Princeton Gamma-Tech (PGT) Light Element Energy Dispersive X-ray (EDX) Analyzer for elemental analysis (SEM-EDX, JEOL-6301F, University of Alberta, Edmonton, AB). The EDX is capable of scanning for all periodic elements, with a detection limit of approximately 0.1 wt% for particles occupying a volume of less than 1 μm^3 (Friel, 2003). The quantitative detection is reported by weight percent of the mass detected per volume (wt%). The presence of an element is considered a major fraction when there is >10 wt%, minor for 1 to 10 wt%, and trace for <1 wt% (Newbury et al., 1986; Woldseth, 1973).

For quantitative analysis of individual particles the general principles are briefly described as follows. When a particle is chosen for quantification analysis, the particle would be bombarded with an electron beam. If the electron beam had sufficient energy (commonly a few kilovolts) it would strike an atom (comprising the particle) and eject a bound K-shell electron leaving a vacancy (and higher energy state). An electron from the L shell may drop into the K-shell vacancy, lowering the energy of the atom and emitting Kα X-ray in the process (Friel, 2003). If an electron from the M-shell fills the vacancy, then a Kβ X-ray would be emitted in the process. If the energy of a given K, L or M line is measured, the energy would be unique with each atomic number, thus the atomic number (element) can be determined (Friel, 2003).

Detailed information gathered on an individual particle analysis is key to identifying its origin, formation, transport potential, reactivity, transformation potential, and its environmental impact (Jambers et al., 1995; Owari and Nihei, 1994). As monitoring equipment has become smaller and more portable, there is still a need for analysis of the collected sample (Zeisler, 1998), where individual particle analysis enables elemental quantification of these small samples. In addition, analysis using SEM-EDX requires the least amount of sample of those analytical methods considered in this research. Detailed preparation and analysis methods used in this research are described in Appendix C.

4.5 Bulk Particle Analysis of Filters

For bulk analysis, two techniques were initially investigated as potential methods for elemental detection of particulate matter collected with low volume samplers. These techniques included X-ray fluorescence (XRF) and inductively coupled plasma mass spectroscopy (ICP-MS).

4.5.1 XRF

XRF is a conventional technique used for elemental analysis from samples collected with FRM samplers. A Philips XRF unit (PW1606 X-Ray Fluorescence Spectrometer, Philips Electronics Ltd., St Laurent, PQ), was used by permission at a laboratory of Lehigh Inland Cement Limited (Edmonton, AB). This unit was equipped to detect Al, Ca, Fe, K, Mg, Mn, Na, P, S, Si, and Ti (PW1606 X-Ray Fluorescence Spectrometer). Procedures for filter preparation were followed according to the X-ray Fluorescence Methods Manual for Chemical Analysis of Atmospheric Pollutants (Method Number 23536 – Alberta Environmental Centre, 1993).

A test filter was collected for 24 hours with the MiniVol, yielding a PM_{10} mass concentration of 8 $\mu g/m^3$ (58 μg of material). The loaded filter and a blank filter were prepared for analysis. Results from the loaded filter indicated that all eleven elements were non-detectable from this instrument and indistinguishable from the blank (Appendix D). With concern of the required mass loading, it was decided that filters from MiniVol samplers could not be analyzed using this XRF technique.

4.5.2 ICP-MS

A second method investigated was ICP-MS at the University of Alberta (Perkin-Elmer Elan 5000, PerkinElmer, CT) and at the Alberta Research Council (ARC, Vegerville, AB) (Perkin-Elmer Elan 5000, PerkinElmer, CT).

The ICP-MS unit used at the University of Alberta was located in the Department of Chemistry and the ICP-MS unit used by the ARC was located at the ARC facility in Vegerville, AB. At the University the Department of Chemistry technicians identified that this instrument only required 0.1 to 10 mg of sample for analysis. It was believed that this method would provide a sensitive enough test to determine major and minor trace elements. With the ability to load filters in chamber experiments, this level of mass was possible and this method was pursued.

The University of Alberta ICP-MS unit was used for analysis of thirteen filter samples. Samples included 10 chamber tests, one spiked sample and two blank samples. Sample methodology and preparation followed SW-846 3050B – Acid Digestion of Sediments, Sludges, and Solids (EPA, 1996b). This method is not a total digestion technique. Elements bound in silicate structures are not totally dissolved (SW-846 3050B, EPA, 1996b). Therefore silica can be used as an elemental "check" between the analytical procedures. The ICP-MS unit was able to scan for: Na, Mg, Al, Si, S, K, Ca, Ti, Fe, Zn, and Pb (refer to Appendix E for methods and detection limits). Results from the laboratory study using this ICP-MS are discussed in Chapter 7.

With the sensitivity from the University of Alberta ICP-MS, MiniVol samples collected in field studies were expected to not have enough mass for analysis. Therefore, the ARC was contacted regarding their ICP-MS method. The methodology used was expected to be sensitive enough for analysis of field samples collected with MiniVols (refer to Appendix F for methods and detection limits).

A total of 10 field samples from duplicate sampling events and one blank were sent to ARC for analysis. The digestion and analysis was performed by Dr. Feng at ARC and a total of sixty-five elements were scanned for including; Ag, Al, As, Au, B, Ba, Be, Bi, Br, Ca, Ce, Cd, Cl, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hg, Ho, I, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, S, Sc, Sb, Se, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, U, V, W, Y, Yb, Zn, and Zr. Results from the field study are discussed in Chapter 8.

4.6 Meteorological Data Measurements

Meteorological instruments used in the final component of the field study included a Campbell Scientific CR-10X datalogger, in conjunction with a Met-One Wind direction sensor (model 023A), and a Met-One Wind Speed Sensor (model 013A). The Met-One Wind Speed sensor is a three-cup anemometer, which uses a sealed magnetic reed switch whose closure frequency is proportional to wind speed (Campbell Scientific, Inc., 1990). This equipment has an operating range of 0.5 to 65 m/s (±0.1 m/s). The Met-One Wind Direction sensor is a lightweight airfoil vane with a wound potentiometer that produces a resistance proportional to the degrees of wind direction (Campbell Scientific, Inc., 1986). The wind vane has a range of 0 to 360^{o} ($\pm10^{o}$) with a starting threshold of 0.65 m/s.

The anemometer and wind vane were mounted to a cross arm assembly on a 3 m tall CM10 tripod (Campbell Scientific, Inc., 1998). This allowed for MiniVols to be mounted on the main shaft of the tripod. Having the meteorological data collected at the same location as the PM_{10} samples helps in determining the potential trajectory of the particulate matter collected.

4.7 Chamber Experiments

A small-scale sampling chamber was designed and constructed. A conceptual design of the sampling chamber is displayed as a simplified schematic in Figure 2. The purpose of the sampling chamber was to load a known material onto filters collected by low volume samplers.

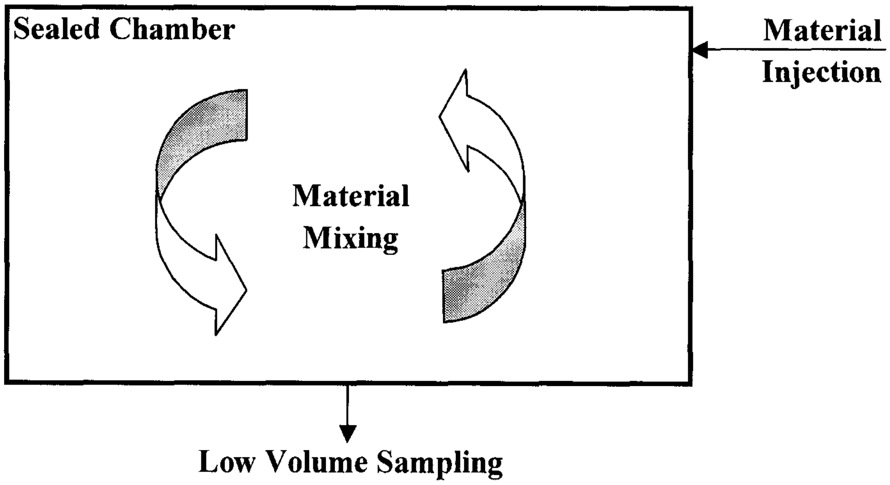


Figure 2. Simplified Schematic of the Sampling Chamber

4.7.1 Experimental Variables

This chamber allowed for a sample injection and simultaneous particulate matter sampling by two MiniVols and the Grimm monitor. Filters from injection tests were then analyzed by individual particle analysis and bulk elemental analysis. Results would allow for a comparison with the known injection material, individual particle analysis (SEM-EDX) and bulk analysis (ICP-MS).

Key experimental variables included dust injection mass and duration of sampling. In order to ensure a maximum loading of the low volume sample filters, injection masses ranged from 100 mg to 300 mg. This was to determine if the low volume samplers could handle excessive dust loads and to ensure enough material was loaded for ICP-MS analysis. The duration of sampling was 24-hours.

The experimental control variable was the sampling flow rate. The low volume sampler was required to be set and maintained at a standard temperature and pressure (STP) flow rate of 5 Lpm. Adjustments were made during sampling according to prepared calibration curves (Appendix B). The experimental response variable in the experiments was mass collected on the filters related to the amount of material injected into the sampling chamber.

4.7.2 Injection Material

National Institute of Standards and Technology-1648 Urban Particulate Matter (NIST, Gaithersburg, MD, USA) was used as the injection material for all experimental chamber injections (refer to Appendix G for the Certificate of Analysis).

4.7.3 Chamber Materials and Test Methods

The airtight sampling chamber was constructed with 19 mm Plexiglas and dimensions of 1.2 m (L) x 0.8 m (W) x 1.1 m (H). It had an internal volume of approximately 1.0 m^3 (chamber schematic is shown in Figure 3 and photograph in Figure 4). The top of the tank was removable, with a rubber seal around the lip, which required weights on four corners to seal it. Inside the chamber were three sampling ports and one injection port. Sampling ports were connected to the MiniVols, 0.2 m from chamber edge and 0.6 m from chamber end, standing 0.25 m off the chamber bottom.

A Grimm monitor was situated between the MiniVol heads at the chamber's center, 0.4 m from the edge and 0.6 m from the end, standing 0.3 m off the bottom. Sampling equipment inlets were placed perpendicular in the airflow (supplied by two 12 volt fans). This allowed for air movement in the chamber and to maintain particle re-suspension. The air samplers were situated under the chamber with short extensions for the sampling heads connected through the bottom. The Grimm was situated as close as possible, with a short sampling extension made of Teflon tubing, attached to a radial symmetric sampling pipe inside the chamber.

The chamber was monitored for steady conditions of particulate matter by the Grimm for both $PM_{2.5}$ and PM_{10} (in $\mu g/m^3$). Background levels in the chamber were determined through a full blank check consisting of duplicate settling blanks (no air flow through the MiniVols), and two blank injections with MiniVol samples collected once with PM_{10} and once with $PM_{2.5}$ inlets. To ensure the chamber was ready for injection, $PM_{2.5}$ mass concentration was monitored for steady readings $<1\ \mu g/m^3$ prior to the next injection (refer to Appendix C for protocols).

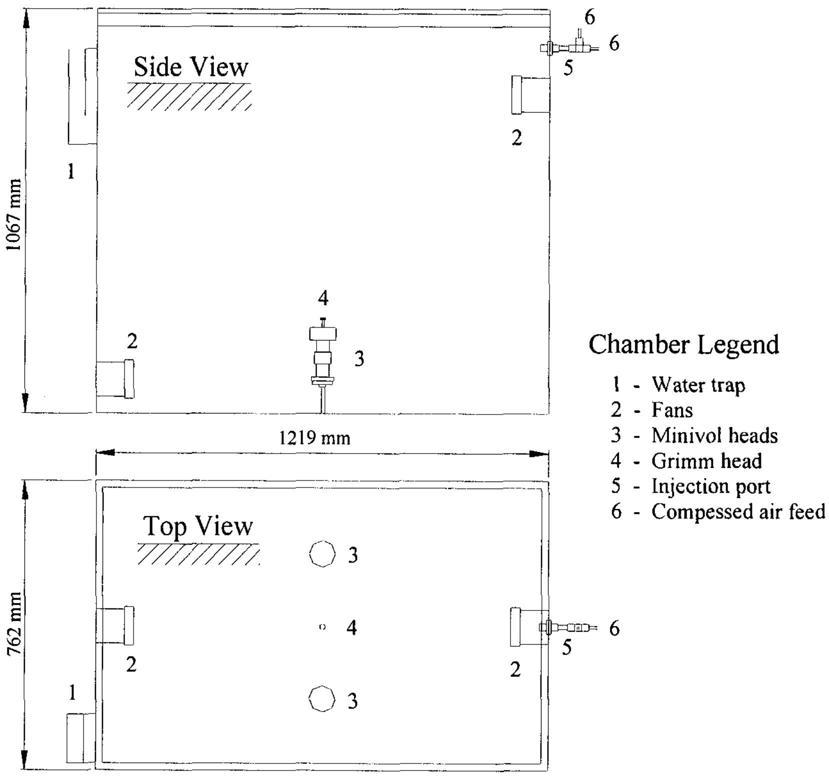


Figure 3. Chamber Design Schematic

Figure 4. Finished Air Sampling Chamber

Injection masses of NIST-SRM 1648 were varied and conducted in duplicate. Varying the injection masses of NIST-SRM 1648 allowed for a comparison of mass concentrations measured by the Grimm particle analyzer, as well as to determine if there was a maximum loading condition in which individual particle analysis was no longer practical. Injection masses included duplicates of 100 mg, 200 mg, and 300 mg injections using the PM_{10} sampling heads for both MiniVols. In addition, a duplicate test injection of 200 mg was performed while sampling with $PM_{2.5}$ heads for both MiniVols.

Mass loading on the MiniVol samplers was determined from pre and post weighing of 10 sets of filters collected in the experiments (eight sets from the injections of NIST-SRM 1648 and two sets from blank tests). Mass concentration was then calculated according to equation 9. With filter samples collected in duplicate, 10 were taken for individual particle analysis (SEM-EDX) and 10 were for bulk analysis (ICP-MS) at the University of Alberta.

Mass concentrations collected by the Grimm were compared to the overall mass concentration collected by the MiniVols using paired t-tests to determine if the particulate matter sampling methods were equivalent over a 24-hour period. A test statistic can be determined with two sets of measured values (Grimm (X_i) and MiniVol (Y_i)) assuming that the paired differences are independent and normally distributed (Goulden, 1952):

$$t = \left(\bar{X} - \bar{Y}\right)\sqrt{\frac{n(n-1)}{\sum_{i=1}^{n}\left(\hat{X}_i - \hat{Y}_i\right)^2}} \quad \textbf{(10)}$$

$$\hat{X}_i = \left(X_i - \bar{X}\right) \quad \textbf{(11)}$$

$$\hat{Y}_i = \left(Y_i - \bar{Y}\right) \quad \textbf{(12)}$$

Where, $\overline{X}$ and $\overline{Y}$ are means from each distribution, n is the sample number, and degrees of freedom is determined by n-1. The t-statistic was compared to a two-tail t-distribution to determine the significance level at which the distributions were different.

Least Squares were used to compare all results from the Grimm analyzer to the MiniVols. This was done to examine similarities between the collection ability of the samplers. The comparison was performed on the Grimm (X_i) and MiniVol (Y_i). The method of Least Squares can be determined by (Acton, 1959):

$$Y = mX + b \quad \text{....................} \mathbf{(13)}$$

$$m = \frac{\left(\sum_{i=1}^{n} X_i Y_i\right) - n\overline{XY}}{\sum_{i=1}^{n} X_i^2 - n\overline{X}^2} \quad \text{....................} \mathbf{(14)}$$

$$b = \frac{\overline{Y}\left(\sum_{i=1}^{n} X_i^2\right) - \overline{X}\sum_{i=1}^{n} X_i Y_i}{\sum_{i=1}^{n} X_i^2 - n\overline{X}^2} \quad \text{....................} \mathbf{(15)}$$

Where, m is the regression coefficient, b is the intercept, $\overline{X}$ and $\overline{Y}$ is means from each distribution, and n is the sample number. The overall quality of fit can then be parameterized by the coefficient of determination and standard errors (Acton, 1959):

$$r^2 = \frac{\left(\sum_{i=1}^{n} X_i Y_i - n\overline{XY}\right)}{\left(\sum_{i=1}^{n} X_i^2 - n\overline{X}^2\right)\left(\sum_{i=1}^{n} Y_i^2 - n\overline{Y}^2\right)} \quad \text{....................} \mathbf{(16)}$$

$$SE(m) = \frac{\sqrt{\dfrac{\left(\sum_{i=1}^{n} Y_i^2 - n\overline{Y}^2\right) - b\left(\sum_{i=1}^{n} X_i Y_i - n\overline{XY}\right)}{n-2}}}{\sqrt{\sum_{i=1}^{n} X_i^2 - n\overline{X}^2}} \quad \text{....................} \mathbf{(17)}$$

$$SE(b) = \sqrt{\frac{\left(\sum_{i=1}^{n} Y_i^2 - n\overline{Y}^2\right) - b\left(\sum_{i=1}^{n} X_i Y_i - n\overline{XY}\right)}{n-2}} \sqrt{\frac{1}{n} + \frac{\overline{X}^2}{\sum_{i=1}^{n} X_i^2 - n\overline{X}^2}} \quad \text{..........} \mathbf{(18)}$$

Where r^2 is the coefficient of determination, SE(m) is the standard error of the regression coefficient, and SE(b) is the standard error of the intercept.

Results from the injection tests were used to examine the mass loading of individual particles for SEM-EDX, specifically:

1. If there was a maximum or minimum mass loading required for individual particle analysis to enable quantitation of elements in the NIST-SRM 1648 in relation to the certified amounts.
2. If increasing mass loading had any effect on quantitation of elements as determined by bulk elemental analysis.

Results are discussed in Chapter 7.

4.8 Field Elemental Sampling Tests

In addition to the laboratory study comparing bulk and individual particle analysis, a field sampling study was conducted. The purpose was to compare individual particle analysis (SEM-EDX) and bulk analysis (ICP-MS) of ambient particulate matter under varying ambient conditions over a period of six months. Sampling was conducted at an industry site using MiniVols and a TEOM Series 1400a ambient particulate monitor.

Duplicate filters were collected with the MiniVols. One filter was analyzed by SEM-EDX and the other duplicate filter was used for bulk analysis (ICP-MS). Similar to the laboratory experiments, the results were compared using a paired t-test.

4.8.1 Field Site Characteristics

Edmonton is the capital of Alberta and is a major urban center located in the central Alberta, approximately 55°33' latitude by 113°28' longitude, with an elevation of 668 m (refer to Figure 5). Edmonton has a population of 666,000, however with the urban and rural influence this population number is increased to approximately 938,000 (2001 Canada Census). Edmonton has a large diverse industrial base, with potential of distinct elemental tracers found specifically from industrial influences. The most prevalent sources of PM_{10} are still related to open sources such as roadways, which have been found to account for nearly 60% of this size fraction (Alberta Environment, 1999).

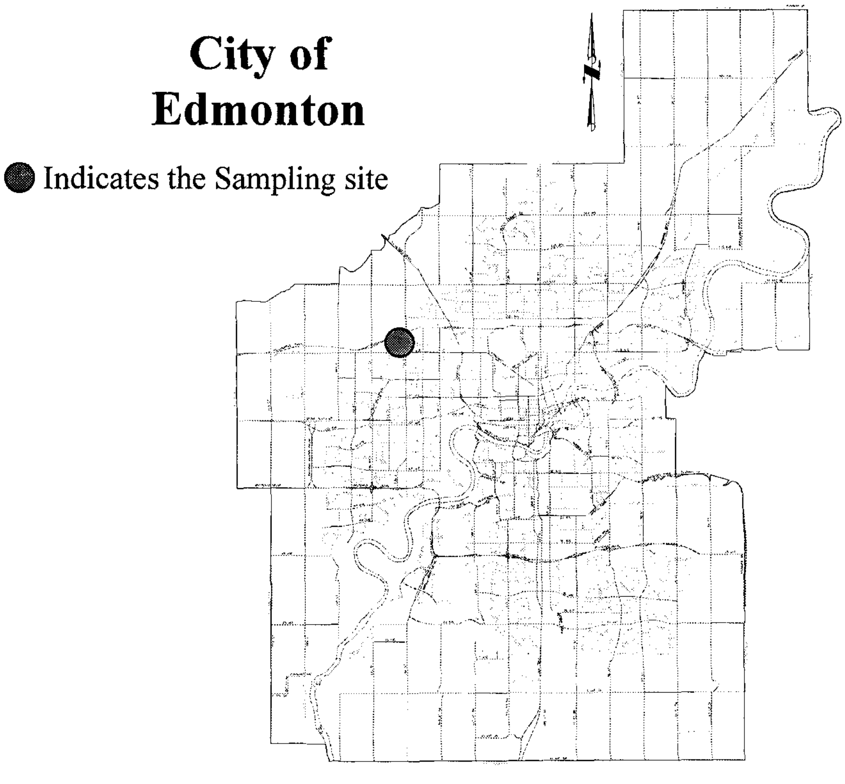


Figure 5. City of Edmonton, Alberta Field Sampling Location
(With acceptance by the City of Edmonton)

4.8.2 Field Sampling Location

The sample site was located in a medium to heavy industrial section of Northwest Edmonton (Figure 6). The sampling equipment was located on ground level, with MiniVols mounted on a CM10 tripod assembly. This site was deemed adequate for security for the TEOM collection of continuous data.

4.8.3 Field Sampling Frequency and Duration

Sampling was conducted following the Canadian National Air Pollution Surveillance (NAPS) schedule for a 24-hour period. The NAPS sampling program consists of one 24-hour sample, every six days. A sampling schedule was developed to collect a series of duplicates under a variety of climatic conditions from July to December 2002. The sampling schedule (Table 5) was used to collect a series of 10 duplicate filters with the MiniVols over this six month period. Results are discussed in Chapter 8.

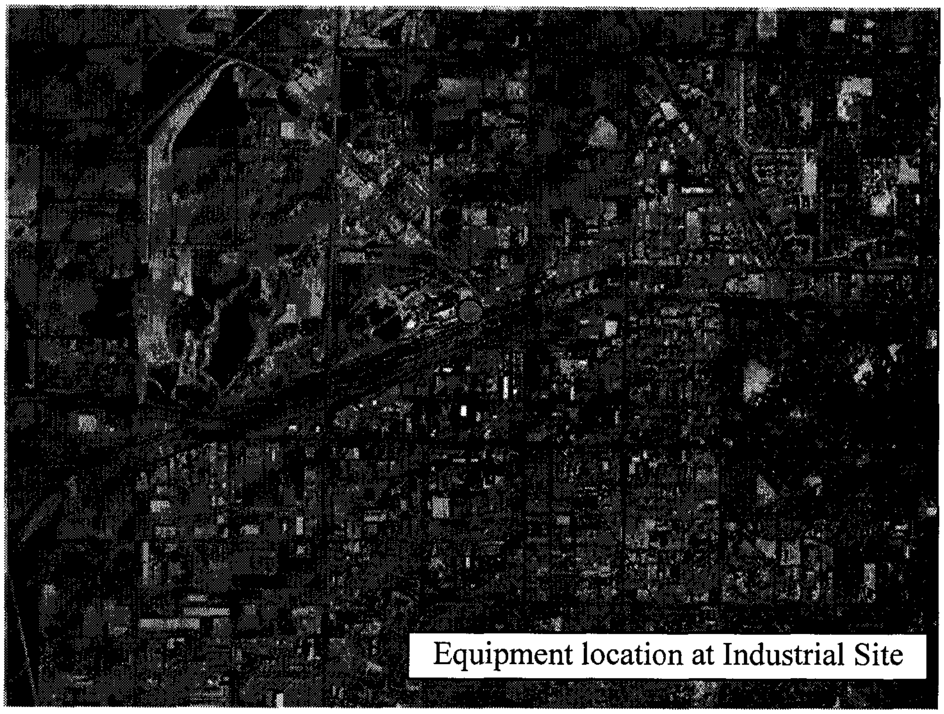


Figure 6. City of Edmonton, Alberta Industrial Sampling Location

Table 5. Sampling Schedule for Field Study in Edmonton, AB

Month	Date and Time			
	Start		End	
July	July 19, 2002	Fri	July 20, 2002	Sat
July	July 31, 2002	Wed	August 1, 2002	Thus
August	Aug 12, 2002	Mon	Aug 13, 2002	Tue
August	Aug 24, 2002	Sat	Aug 25, 2002	Sun
September	Sept 5, 2002	Thus	Sept 6, 2002	Fri
October	Oct 12, 2002	Sat	Oct 13, 2002	Sun
November	Nov 10, 2002	Sun	Nov 10, 2002	Mon
November	Nov 16, 2002	Sat	Nov 16, 2002	Sun
November	Nov 28, 2002	Thus	Nov 28, 2002	Fri
December	Dec 22, 2002	Sun	Dec 22, 2002	Mon

4.9 Field Receptor Sampling Tests

A limited field receptor-sampling program was designed and conducted to employ data from low volume sampling/individual particle analysis in a source apportionment. This field study was conducted in the northern rural community of High Level, Alberta. Analysis of data collected during the sampling program is displayed as a simplified plan in Figure 7. Sampling was conducted with two MiniVols, a TEOM Series 1400a, a PAS-2000 PAH monitor, a Wind Speed and Wind Direction vane. The TEOM continuous PM_{10} monitor was used to compare mass concentrations collected with the low volume samplers (MiniVols). The PAS-2000 monitor was used to collect particle bound PAHs as a potential tracer for anthropogenic sources.

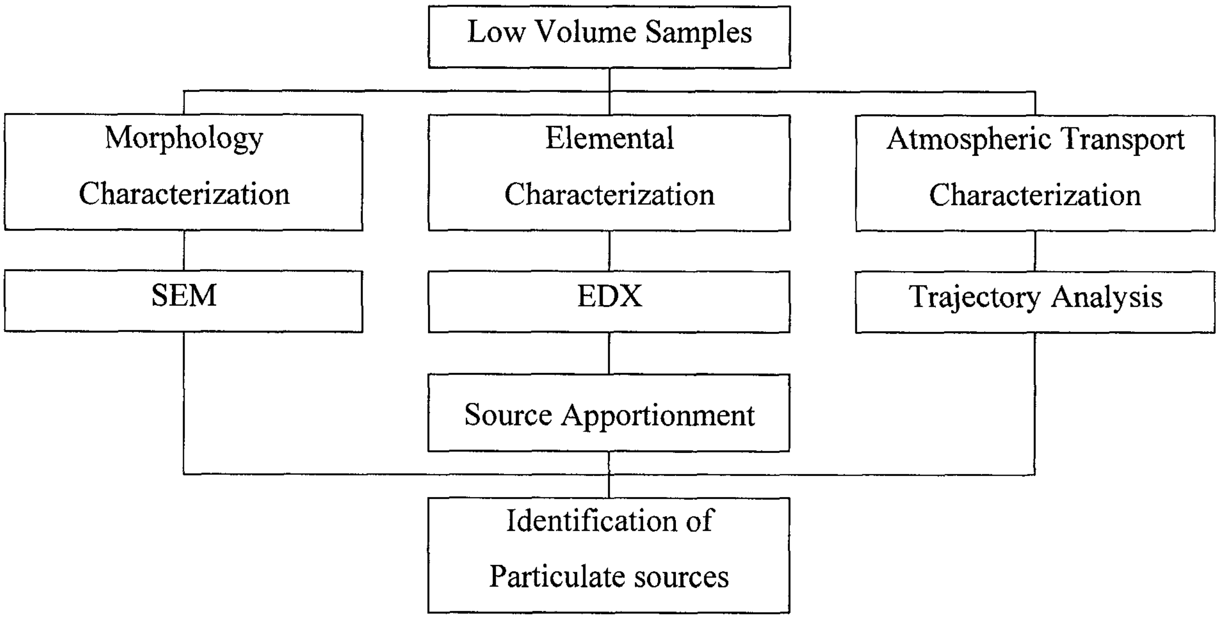


Figure 7. Conceptual Analysis of Plan for Field Data

Morphological and elemental analysis was performed on individual particles collected on filters from MiniVols. Wind measurements were used for an analysis of trajectories. Wind trajectories were evaluated during high particulate matter concentration periods as found by the TEOM in order to examine unique source receptor relationships and check whether they were consistent with findings of the PCA.

Results of the elemental analysis and total particle-bound PAHs concentration were used in a multivariate analysis to identify likely sources of particle matter. This source apportionment utilized the Principle Component Analysis by forming a matrix ($n \times m$) from the number of samples (n) and the number of variables (elements and PAH concentration) measured on each sample (m) and performing the following steps (Buhr et al., 1992):

1. Form a $m \times m$ covariance matrix from the $n \times m$ data matrix.
2. Extract eigenvectors and eigenvalues from the $m \times m$ covariance matrix. Eigenvectors are the principle components and eigenvalues are the magnitudes.

A Least Squares test was conducted for comparison between the MiniVol and TEOM mass concentration results.

4.9.1 Site Characteristics

High Level is a community located in the northwestern corner of Alberta, approximately 58°30' latitude by 117°08' longitude, with an elevation of 325 m (refer to Figure 8). For the source apportionment it is important to identify the surrounding sampling area and soils profile based on potential for re-suspended material as this source tends to dominate the makeup of ambient particulate matter in rural Alberta.

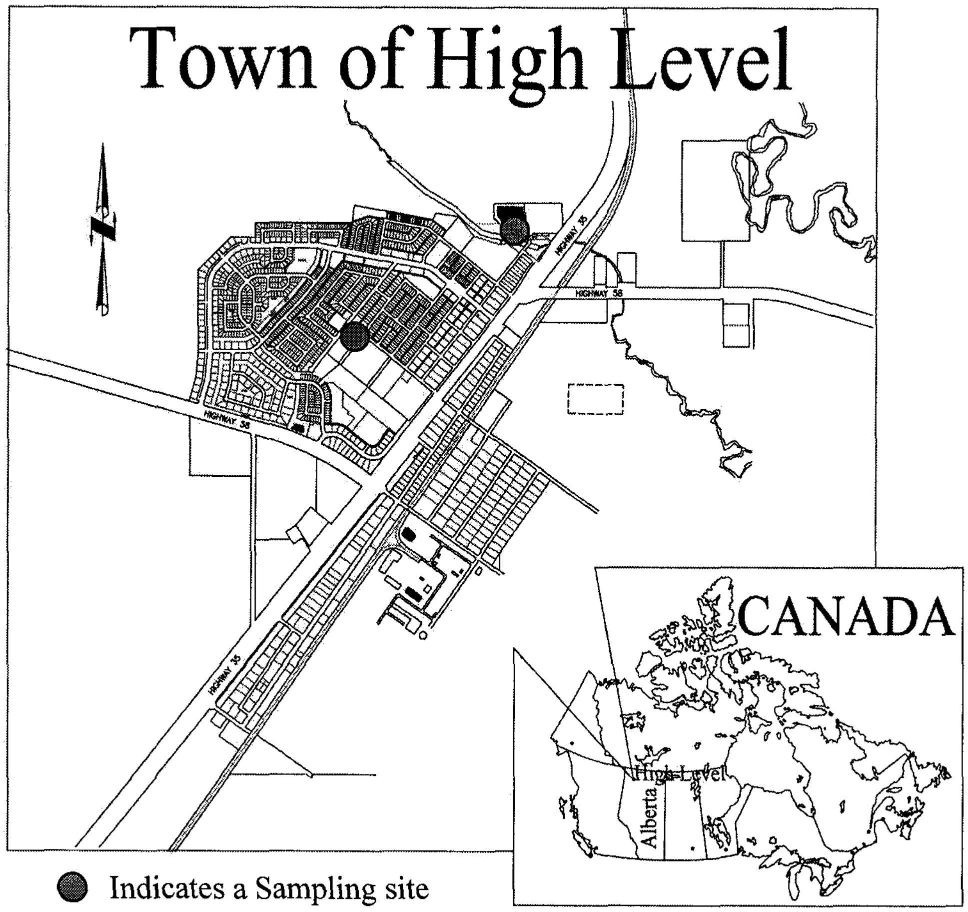


Figure 8. High Level, Alberta Field Sampling Program
(With acceptance by the Town of High Level)

High Level is located within the Boreal Forest Region and surrounded by marsh north, south, southwest, west and northwest of town and agricultural land to the northeast, east and southeast of town. Soil in the surrounding area includes; lacustrine sediments with fine and medium texture, moderately calcareous and gray clay deposits (Department of the Environment, 1972; Scheelar and Macyk, 1972).

High Level is classified as a rural industrial community. Particulate matter sources include a complex mix of small and large sources. Possible sources include: industrial exploration (oil and gas), agricultural including grain storage and handling, diesel and gasoline vehicle exhaust, road dust from vehicle re-suspension and street cleaning, gravel road dust, wood burning from residential fireplaces and fire pits, and a wood waste (teepee) burner. The wood waste burner (located south-southeast of the residential area in the community) is the largest non-controlled anthropogenic emission source in the community.

4.9.2 Identification of Field Sampling Locations

Ambient air quality in a community tends to exhibit seasonal and spatial variability. The seasonal variability is primarily a function of metrological conditions, for example snow cover in the winter tends to inhibit crustal re-suspension. In turn during a dry summer the re-suspension from fields and roadways would likely dominate particulate matter in the ambient air. Spatial variability will also be a factor in sampling in a community, sampling near buildings, or near roadways may skew overall results due to influences from near field sources. Where near field source are defined as source in very close proximity to which air is sampled. In order to characterize this variability it would be necessary to sample continuously in a community at many receptor locations. Alternatively, it is possible to sample during specific time periods to represent seasonal variation and at specific locations to represent similar spatial variations such as sampling from an open elevated site.

Sampling over four different time periods, representing the four seasons, was undertaken in the community. Seasonal sampling would include early March constituting a snow covered winter sample, May to represent spring sampling, July to represent summer sampling and late September for fall sampling. Two sample sites were chosen that would have accessibility and security for all monitoring equipment identified (Figure 8).

In locating these sites for sampling, prevailing wind directions played an important role, as did the need for electricity for the continuous sampling equipment. With predominant winds from the north (Bovar Environmental, 1997a; 1997b); one site was selected at the north end of the community. A site chosen was at the local water treatment plant (WTP) (Figure 9) located at the north end of High Level. Equipment was situated on top of a water reservoir approximately 4.5 m from the ground (Figure 10). This site was deemed adequate for security and electricity was available by extension cord.

A second site was chosen at the local hospital. The hospital is located near the center of town with open fields located primarily to the south (Figure 11). Equipment was situated on the roof of the hospital, approximately 3.5 m from the ground (Figure 12). Access to the roof was from inside the hospital which was secure and electricity was available.

4.9.3 Field Sampling Frequency and Duration

Key experimental variables for this field study component included duration of sampling, period of sampling and location of sampling. A sample schedule was drawn up to account for monitoring during each season in 1999 (Table 6). The period of sampling for both PM_{10} and $PM_{2.5}$ samples were conducted over 24-hours. The sampling results are discussed in Chapter 9.

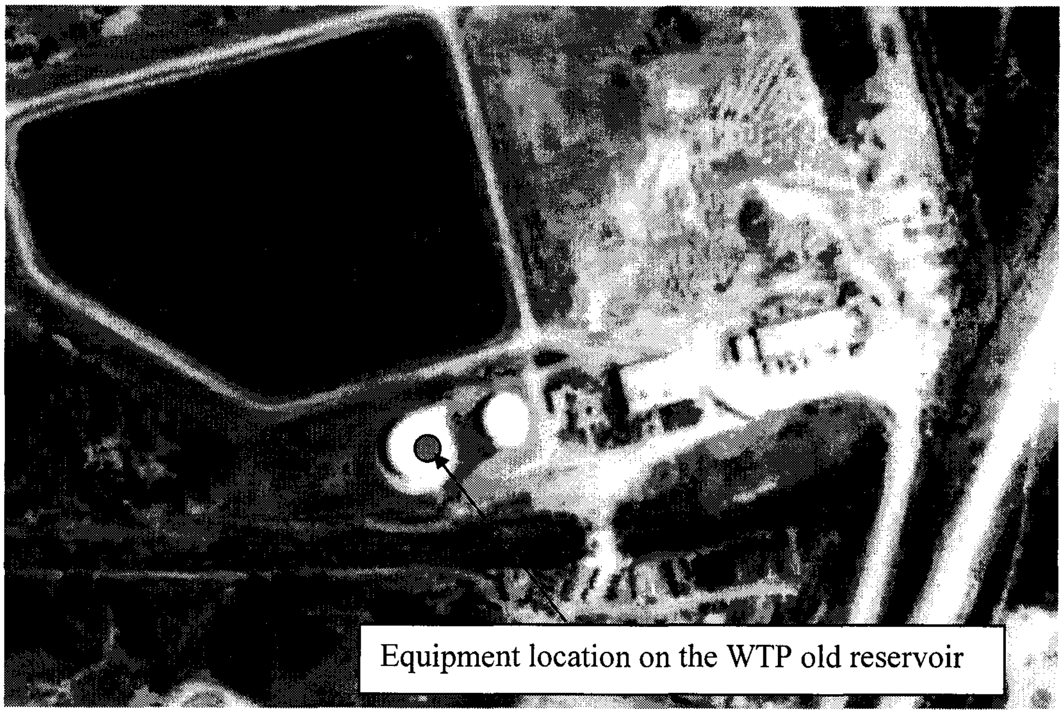


Figure 9. Water Treatment Plant Sampling Site

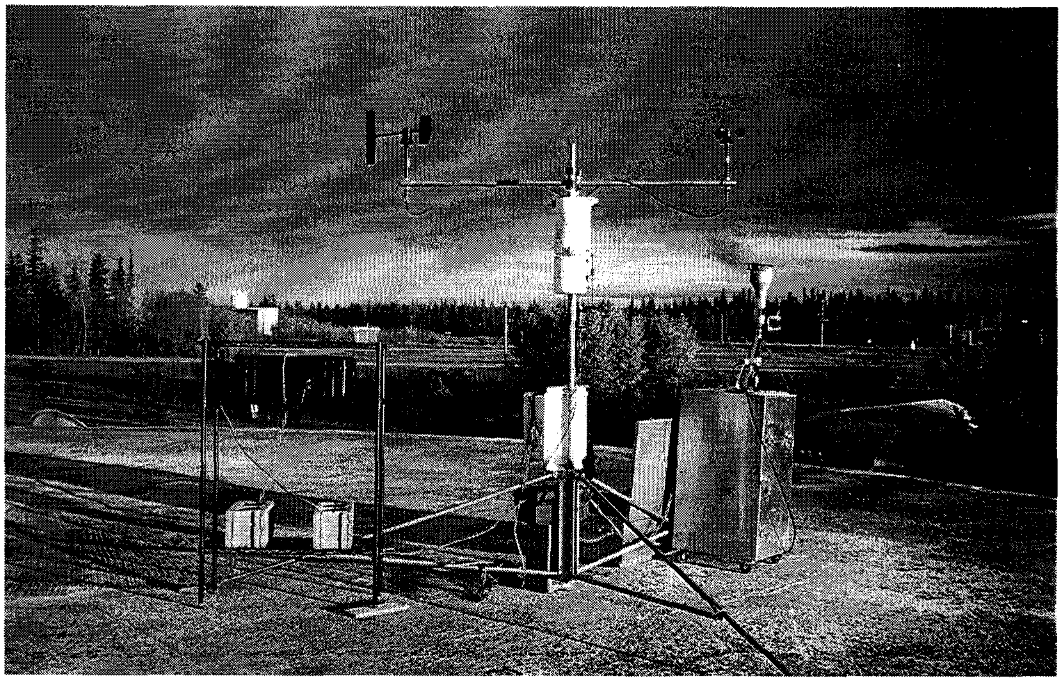


Figure 10. Photo – Water Treatment Plant Sampling Site

Figure 11. Hospital Sampling Site

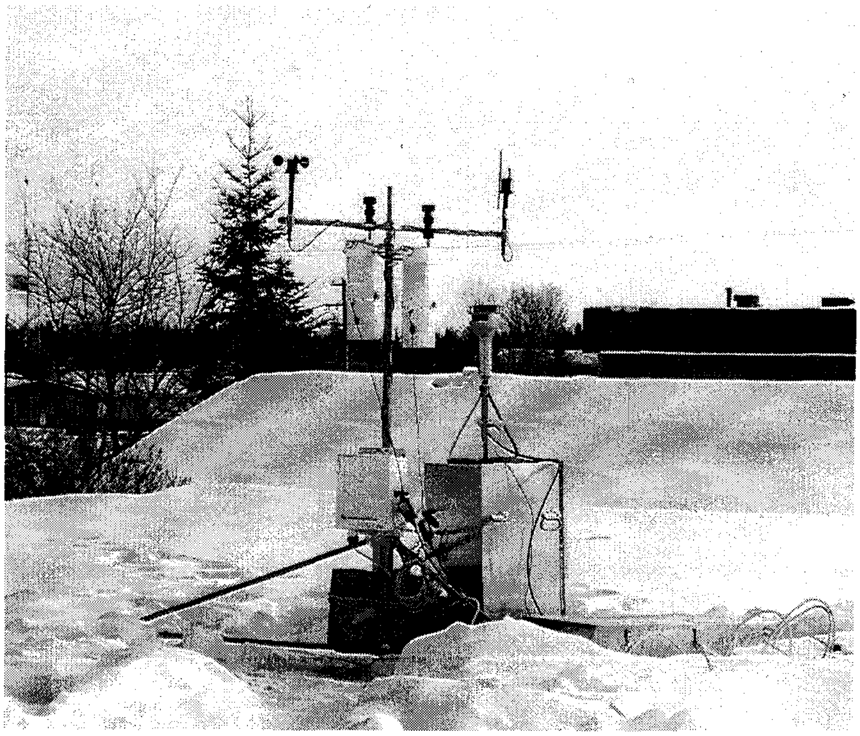


Figure 12. Photo – Hospital Sampling Site

Table 6. Seasonal Air Sampling Schedule for High Level, AB

Season	Date and Time				Location
	Start		End		
Winter	March 1,1999	Mon	March 11,1999	Thu	Hospital
	March 11,1999	Thu	March 19,1999	Fri	WTP
Spring	May 12,1999	Wed	May 21,1999	Fri	Hospital
	May 21,1999	Fri	May 31,1999	Mon	WTP
Summer	July 14,1999	Wed	July 23,1999	Fri	WTP
	July 23,1999	Fri	August 1,1999	Sun	Hospital
Fall	September 24,1999	Fri	October 3,1999	Sun	WTP
	October 12,1999	Tue	October 20,1999	Wed	Hospital

WTP – Water Treatment Plant.

4.10 Quality Assurance and Quality Control

It is most important to note, "*no chemical analysis method, no matter how accurate or precise can adequately represent atmospheric concentrations if the filters are improperly selected or handled – even the slightest contamination can bias these measurements.*" (Chow and Watson, 1998). To ensure proper quality assurance and quality control standards, actions were taken prior to and during both phases of research:

1. With a very limited number of people working on this project, compounded human error was kept to a very minimal level.
2. Prior to laboratory and field work a full review of measurement methods was done to ensure appropriate compliance was met with appropriate standards.
3. Prior to any extended sampling, equipment was setup and tested for approximately 48 hours to ensure no complications developed since equipment was previously used.

4. Equipment was periodically cleaned and re-calibrated to ensure operational success during sampling.
5. Only the primary researcher was responsible for setup and take down of equipment during sampling experiments, ensuring standard operating procedures were followed.

5. COMPILATION OF ELEMENTAL PROFILES FOR PARTICULATE MATTER

PM_{10} is typically associated with primary emissions (emitted directly) mixed with fugitive sources. Fugitive dust sources can vary based on numerous factors. For Alberta, PM_{10} fugitive dust accounts for approximately 55% to 65% of the total PM_{10} (Cheng et al., 1998), while approximately 89% of the United States total PM_{10} is fugitive dust (Chow and Watson, 1998). Geological material also varies greatly from site to site with levels varying from 20% to 80% (Chow and Watson, 1998).

PM_{10} includes material via mechanical processes such as crushing, grinding (abrasion), construction, demolition, wind erosion, agricultural, road dust and industrial activities. Generally there is a strong relationship with natural sources as contributors to particle size fraction (Rhebergen et al., 1999; Pryor and Barthelmine, 1996). From studies done in Edmonton and Calgary, Alberta, it was found that wind blown soil and road dust were the major source of PM_{10}, while contributions from industrial sources were minimal (Cheng et al., 1998).

$PM_{2.5}$ typically includes particles from process operations such combustion from industrial activities. Major sources of $PM_{2.5}$ can be broken into three types:

1. emitted directly in solid phase;
2. emitted in gas phase with subsequent ondensation into solid phase; and
3. secondary emissions that are particles formed by atmospheric reactions of precursor compounds.

Direct emissions include such sources as combustion (of gasoline or diesel), wood stoves, fireplaces (household heating), land clearing, agricultural prescribed burning, wild fires (forest fires), road dust, dust from ore processing / refining, construction, agricultural, compressor stations, gas processing plants, power plants, incinerators and furnaces (BC Ministry of Health, 1994; Pacific Environmental Services, Inc., 1999; EPA, 1997f; EPA, 1997c; Chow and Watson, 1998; West Central Airshed Society, 1997; Pryor and Barthelmine, 1996; Cheng et al., 1998).

Secondary emissions contributing to $PM_{2.5}$ include anions such as sulphates and nitrates (precursors of acid rain), cations such as sodium, and organic aerosols formed from primary emissions (Pacific Environmental Services, Inc., 1999; EPA, 1997f; EPA, 1997c; Chow and Watson, 1998; West Central Airshed Society, 1997; Watson et al., 1997). In general $PM_{2.5}$ tends to contain a higher fraction of tracer species such as acids, heavy metals and PAHs (Rhebergen, et at, 1999). From studies done in Edmonton and Calgary, Alberta, vehicle emissions and wood burning (from fire places, barbecues and forest fires) were reported as major sources of $PM_{2.5}$, whereas wind blown sources for $PM_{2.5}$ are only a minor fraction of $PM_{2.5}$ (Cheng et al., 1998).

A source profile analysis involves the characterization of elemental concentrations found from each source. These elemental signatures are required for specific sources in order to perform a detailed elemental tracer study. A detailed elemental signature profile was compiled by Chow (1995), however sources presented by Chow (1995) were limited and there was a need to identify elemental signatures for additional sources that may be relevant for this study.

A detailed summary of elemental signatures was compiled as part of this study based on a review of previous emission profile studies and source receptor studies. Sources were broken down into the following categories and summarized in Table 7:

motor vehicles, road dust, salts, crustal weathering (wind blown dust), agricultural soils, biomass burning (wood burning), refuse incineration, residual oil emissions, oil fired power plants, coal fired power plants, sulfates, industrial emissions (smelters), and construction emissions.

Table 7. Particulate Matter Elemental Profiles based on Source Contributions

Emission Source	$PM_{2.5}$ **Main (>1%)** [Trace (<1%)]	PM_{10} **Main (>1%)** [Trace (<1%)]	**Reference: Source**
Motor vehicles	**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]	2, 3, 4, 5, 6, 8, 9, 10, 11, 14, 15, 18, 20, 22, 24, 25, 28, 29, 30, 31, 43, 46, 47, 49
Road dust (paved and unpaved)	**K, Ca, Fe, Si, (Na, Cl)*** [S, Pb, Zn] * road salts	**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]	2, 6, 11, 13, 17, 19, 21, 24, 28, 29, 30, 31, 32, 33, 34, 39, 42, 44, 53
Salts	**Na, Cl** [Al, Si, K, Ca, Fe, Cu, Zn, Ba, La, Ti, V, Ni, Sr, Zr, Pb, Ag, Sn, Sb, Br]		6, 7, 9, 11, 12, 13, 15, 18, 28, 30, 43, 50
Crustal weathering (wind blown dust)	**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]	1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 14, 15, 18, 19, 27, 28, 29, 30, 31, 36, 37, 38, 40, 41, 42, 43, 47, 48, 50
Agricultural soils	**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]	11, 28, 30
Biomass-burning (wood burning)	**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]	5, 6, 11, 16, 23, 24, 26, 28, 30, 42, 43, 45, 52, 53
Refuse incineration	**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]	2, 4, 7, 11, 15, 18, 28, 30, 31, 42, 43, 50, 51
Residual oil and heating	**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]**	2, 5, 8, 9, 11, 14, 18, 19, 28, 29, 30, 31, 36, 43

Table 7. Particulate Matter Elemental Profiles based on Source Contributions (Continued)

Emission Source	$PM_{2.5}$ **Main (>1%)** [Trace (<1%)]	PM_{10} **Main (>1%)** [Trace (<1%)]	Reference: Source
Oil fired power plant	**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]	11, 15, 28, 30, 50, 51
Coal fired power plant	**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]	2, 7, 11, 18, 28, 29, 30, 31, 43, 50, 51
Sulfates	**S, Pb, Fe, Si** [Zn, Al]	**S, Al, Fe** [K, Pb, Mn]	3, 4, 5, 8, 9, 12, 28, 30, 47
Construction (asphalt, rock crushing, etc.)	**As, Cr, Pb, Si, Al, Fe, K, Ca** [S, Ti, Mn, V, Zn, Cl, Cu, Rb, Mg]	**As, Cr, Pb, Si, Al, K, Ca, Fe** [Mn, Zn, Sr, Ba, S, Ti, Mg, Na, V, Cu, Ni, Br]	11, 14, 15, 28, 29, 30, 42

(1) Alberta Health, 1997; (2) Alpert and Hopke, 1980; (3) Chang et al., 1988; (4) Alpert and Hopke, 1981; (5) Rojas et al., 1990; (6) Morales et al., 1990; (7) Van Borm et al., 1990; (8) Tuncel et al., 1985; (9) Pratsinis et al., 1988; (10) Stevens et al., 1984; (11) Chow, 1995; (12) Maenhaut and Cafmeyer, 1998; (13) Swietlicki et al., 1996; (14) Fung and Wong, 1995; (15) Huang et al., 1994; (16) Sexton et al., 1985; (17) Janssen et al., 1997; (18) Kowalczyk et al., 1982; (19) Cass and McRae, 1983; (20) Silva and Prather, 1997; (21) Fergusson and Ryan, 1984; (22) Liu et al., 1995; (23) Stevens, 1985; (24) Kulmala et al., 1986; (25) Linton et al., 1980; (26) Edward Aul & Associates, Inc. and E.H. Pechan & Associates, Inc., 1993; (27) Pacific Environmental Services, Inc., 1999; (28) Chow and Watson, 1998; (29) Cooper and Watson, 1980; (30) EPA, 2000a; (31) Harrison et al., 1996; (32) Yassoglou et al., 1987; (33) Albasel and Cottenie, 1985; (34) Johnston and Harrison, 1984; (35) Hubbard, 1995; (36) Schneider, 1987; (37) Crecelius et al., 1980; (38) Chow et al., 1990; (39) Chutke et al., 1995; (40) Romo-Kröger et al., 1994; (41) Chow et al., 1994; (42) Scheff et al., 1989; (43) EPA, 1994a; (44) de Miguel et al., 1997; (45) EPA, 1993; (46) Rokosz et al., 1985; (47) Koutrakis and Spengler, 1987; (48) Lowenthal et al., 1997; (49) Kitto, 1993; (50) Kleinman et al., 1980b; (51) Gao et al., 1996; (52) Rau, 1989; (53) Baisden et al., 1995.

5.1 Motor Vehicles

In Alberta the main tracers of vehicles (Pb and Br) have been dropped after the complete ban of leaded fuel in December 1990 (Cheng et al., 1998). Instead elemental tracers such as Ni, Zn, Cu, Cd, V and P usually indicate vehicle emissions (U.S. EPA, 1993; Chow, 1995; Chow and Watson, 1998). This is in combination with elemental tracers found in gasoline: Na, K, Ca, Fe, Zn, As *(greater than 1% mass fraction)* [Cr, Co, Se, Br, Ag, Sb, La, Ce, Au, Th *(less than 1% mass fraction)*] (Kitto, 1993). Whereas, analyses of paved road dust shows that the major chemical constituents include organic carbon compounds, Si, Fe, Al, Ca, K, S and elemental carbon (Rogge et al., 1993b, CEPA and FPAC, 1999) (Table 7). In addition to metals found in vehicle emissions, PAHs have also been found in the semi-volatile fraction of emissions in both vapour and particle phases (Mitra et al., 2002).

5.2 Road Dust

Relatively few studies in Canada have been conducted for on-road conditions and the contribution of airborne particles from vehicle emissions and roadside dust. Road side exposure to particulate matter can include: vehicle exhaust, worn tire flakes, brake and clutch lining particles, construction dirt, garden soil, leaves / plant material (molds, pollens and pollen fragments), animal dander, sand, salt, trace elements (roadsides can act as a sink for some heavy metals present in vehicle exhaust), as well as deposited atmospheric particles (CEPA and FPAC, 1999; Al-Chalabi and Hawker, 2000; Lamoree and Turner, 1999; Miguel et al., 1999, Glovsky et al., 1997). Vehicle emissions can vary with individual driving modes such as idling, accelerating, decelerating, or cruising

(Chow and Watson, 1998; Kleinman et al., 1980b). The roadside dust exposure is predominately in the PM_{10} size fraction, with the majority of the direct vehicle emissions being in the $PM_{2.5}$ size fraction (CEPA and FPAC, 1999). Primary and trace elements associated with road dust as reported by others are shown in Table 7.

5.3 Salts

The elements Na and Cl are very indicative of salt aerosols such as those found in road salt (Marcazzan, 1998; U.S. EPA, 1993). Salt is found more prevalent near sea coasts, however, in the absence of saline water salt is more prevalent after de-icing materials are applied (EPA, 1999c). In its raw form, salt is usually in the PM_{10} fraction and is classified as a geological material (EPA, 1999c). When water droplets containing sodium chloride evaporate, many of the “dry” core particles are below 2.5 μm in diameter ($PM_{2.5}$ fraction). Particles that originally contain sodium chloride may be neutralized by nitric or sulfuric acid; chloride is driven off and replaced by equivalent amounts of nitrate or sulfate (EPA, 1999c). In general salts found can include elements such as: Na, Cl, Mg, K and Ca (Table 7).

5.4 Crustal Weathering and Agricultural Soils

Geological materials (crustal material) are likely to retain chemical and elemental characteristics over a long time period and are therefore very good for elemental signatures (Chow et al., 1994). Crustal weathering or natural sources are important, as they are not pollutants; however the levels in the ambient air are not under control by humans. These levels may represent the “background” airborne particle concentration to which urban atmospheres can be achieved by imposed air quality standards (Stevens, 1985). Suspended geological material consists mainly of Al, Si, Ca, Ti, and Fe (Table 7).

The precise combination of these components depends on the geology and industrial processes of the surrounding area. Geological re-suspended dust typically consists of 20% $PM_{2.5}$ however, in summer months it can be as high as 40% (EPA, 1999c). Crustal markers that have been typically used, include Ti, Mn and Zn (Chow, 1995; Beceiro-Gonzalez et al., 1997). Typically crustal material contains clay particles which can be associated with a vast matrix of elements including; Si, Ca, Al, Mg, Fe, K, Zn, Ti and Mn (Beceiro-Gonzalez et al., 1997). Geological material can be also be comprised of wind blown agricultural soils. Elements typical of wind blown soil can include Si, Al, K and Mn (Stevens, 1985) (Table 7).

5.5 Biomass Burning

Biomass fuels (primarily wood) account for approximately 14% of the worldwide energy consumption (Kozinski and Saade, 1998). Biomass burning produces a number of air pollutants that include: particulate matter (smoke, soot and ash), un-burnt hydrocarbons, NO_X and CO (Kozinski and Saade, 1998). Wood is typically comprised of 5% extractives, 65 to 70% holocellulose and 25 to 30% lignin (of which contains aromatic structures) (Leppa and Saarni, 1982). When burnt, wood tends to produce a single particle size mode of 0.1 to 0.2 μm in diameter (Kleeman et al., 1999). However, particulates produced from combustion of wood vary substantially with the type of wood being burnt, moisture content, temperature and oxygen levels when the wood is combusted.

Elements present in smoke streams are at trace levels, but vary for wood type and include: for pine Ti, Fe, and Rb; and for oak Al, Fe, Zn, and Ba (Kleeman et al., 1999). The elements present in the smoke vary with those found in the ash. Wood ash contains Ca, Mg, K, Mn, S, with trace elements P, Na, Fe, Al, Si, Ti, and bark ash contains primarily Ca, Si, Al, K, Mg, with trace elements Na, P, S, Fe, Ti, Mn (Someshwar, 1996).

Direct samples collected from the stack of a wood burning facility may not represent the ambient particles present in the community, for direct samples do not allow the particles time to agglomerate, which is normally seen in the ambient levels around a facility (Hueglin et al., 1997). Depending upon impurities in the wood waste, soil may be introduced with wood, thus changing the elemental source profile slightly, such that wood ash mixed with soil can contain Mn, B, Cu, Pb, Zn, Cr with trace amounts of Ni, Mo, As, Co, Cd, and Hg (Edward Aul & Associates, Inc. and E.H. Pechan & Associates, Inc., 1993; Someshwar, 1996). Primary and trace elements associated with biomass burning as reported by others are shown in Table 7.

5.6 Refuse Incineration

In addition to wood burning and biomass burning, there is a component of refuse incineration. Elements typically found in the combustible components include Ca, Cu, Hg, K, and Mg; whereas elements found in the non-combustible components include Ag, Cd, Cr, Mn, Pb, Sn, and Zn (Kleinman, et al., 1980a). In addition to the elemental signatures from combustion of solid wastes, PAHs are reported to be associated with flyash and solid residue particles (Morawska and Zhang, 2002). Primary and trace elements associated with refuse incineration as reported by others are shown in Table 7.

5.7 Industrial Processes

Industrial process fingerprints can vary substantially, however there are some common components that are similar between processes. The similarities can be viewed through the fuel source, such as natural gas, oil or coal:

1. For natural gas fuels there is no known elemental tracer for emission related particles (Kleinman et al., 1980a). However, for natural gas powered motor vehicles some PAHs and oxyPAHs are emitted and therefore potential tracers (Mitra et al., 2002),
2. For oil, V tends to be a primary tracer element (Gao et al., 1996). In addition fuel oils used in combustion processes have elemental signatures including S, Na, Cl, V, Ca and trace Al, Ba, Br, Mn, Ni (Kleinman et al., 1980a; Kitto, 1993),
3. For coal combustion Se or As tends to be the primary tracers (Kitto, 1993; Gao et al., 1996). In addition, flyash associated with coal combustion has the primary elemental signature of Pb and As (Parekh and Husain, 1981; Fung and Wong, 1995; Alves et al., 1998),

Also associated with industrial emissions is the production of sulphates. The sulphate contribution comes from direct industrial and vehicular emissions with only a small fraction originating from secondary formation in Alberta (Cheng et al., 2000).

Other industrial emissions are associated with processes such as smelter activities. Industrial processes vary greatly from community to community, as does the processes involved in each industry. Industries such as smelters can represent a very well-defined point source with distinctive particulate composition (Kleinman et al., 1980). It is difficult to give generalized elemental fingerprints to such vast profiles. Common elemental profiles specific to selected industrial activities have been summarized in Table 7.

5.8 Construction Processes

Particulate matter emissions from construction activities are either direct or from fugitive wind blown sources. Fugitive dust is more common due to activities on a construction site including grading, excavating and general building construction. Elements associated with construction activities are typically that of crustal nature, such as Ca, Mg, Na, K and S (Gao et al., 1996). In addition with many construction activities using cement, cement dust can also be used as a signature source around construction sites, including Al, Ca, and Fe (Chueinta et al., 2000). Primary and trace elements associated with construction processes as reported by others are shown in Table 7.

Results from this summary identified common source profiles through elemental signatures of particulate matter emissions. These signature profiles can in turn be used to aid in identification of potential sources through relationships found between elemental abundances collected from ambient samples.

6. SEM-EDX BLANK FILTER ANALYSIS

With a goal of this study to collect a minimal amount of particles for individual particle analysis, the filter material used must be as clean or free of interferences as possible. A quantitative blank analysis was conducted using SEM-EDX under 10 torr of vacuum, at 20 keV for 30 and 60 second intervals. SEM was used to examine the filter surface in order to judge the ability of the filter to capture small particles without "short circuiting" (EPA, 1994a). EDX was used to quantify the elemental background of the filter material in order to judge whether elements present could interfere with elements being sought by analysis (EPA, 1994a).

The first two filter types analyzed were the Pall Gelman Quartz (Figure 13 and Figure 14) and the Whatman Quartz (Figure 15 and Figure 16). The Pall Gelman Quartz filter showed a major component of Si, with trace amounts of K, Al, Ca, Ba, Na and Zn (Figure 14). This would not be very functional in ambient studies as Si is a primary and trace element in several sources (Table 7). This was also the case for the Whatman Quartz filter which also showed a major component of Si with trace amounts of Na and Al (Figure 16). This filter would not be very functional for individual particle analysis due to interference with Si.

A second set of filters were analyzed: Gelman Teflon (Figure 17 and Figure 18) and Whatman Teflon (Figure 19 and Figure 20). Background elements detected in these filters were primarily comprised of F, with little to no trace elements. The Gelman filter had a primary elemental constituent of F (97.9% by weight), with trace amounts of Fe (1.1% wt), Si (0.1% wt), Ca (0.3% wt), K (0.1% wt), Mg (0.3% wt) and Mn (0.2% wt). Similar to the Gelman filter, the Whatman filter had a primary elemental constituent of F

(97.3% by weight), with trace amounts of Ca (1.4% wt), Na (0.5% wt) and Cl (0.7% wt). Both the Gelman and Whatman Teflon filters were deemed functional because of low interference with primary and trace elements of interest (e.g. Si). These Teflon filters would likely not cause false positives due to filter contamination or filter background.

The Ringed Teflon-membrane filters produced by Gelman and Whatman were judged acceptable for analysis using the SEM-EDX. Visually, it was easier to observe particles imbedded on the Gelman filter. However, the Whatman filters showed less trace contamination and had a unique stamp identifying each filter. These results indicated that the Teflon filters would be appropriate for use with low volume samplers and individual particle analysis for a variety of elements. For consistency, the same filter type - Whatman Teflon-membrane filters - was used for the entire sampling period and only between sampling periods, filter batches were changed. The choice of Teflon filters was further substantiated by EPA (1994b), who reported that Teflon filters used for elemental analysis have good results. In addition, EPA (1997d) stated that:

> *"Although Teflon may preclude certain chemical analyses (e.g., elemental and organic carbon), the EPA believes that Teflon filter material is the best overall choice to meet the objectives of compliance monitoring and to provide good measurement precision. Other filter media are likely to provide reduced gravimetric precision and preclude more types of subsequent chemical analysis."*

Based on SEM-EDX analysis, Teflon filters were found to be an excellent medium for collecting and analyzing individual particles. These filters provide very little background material that may interfere with predominant elements found from a variety of sources. With a goal of collecting minute sample sizes, cleaner filter material may allow for easier identification of individual ambient particles.

Figure 13. Pallflex Pure Quartz-fiber - Surface as Observed by SEM (1000x)

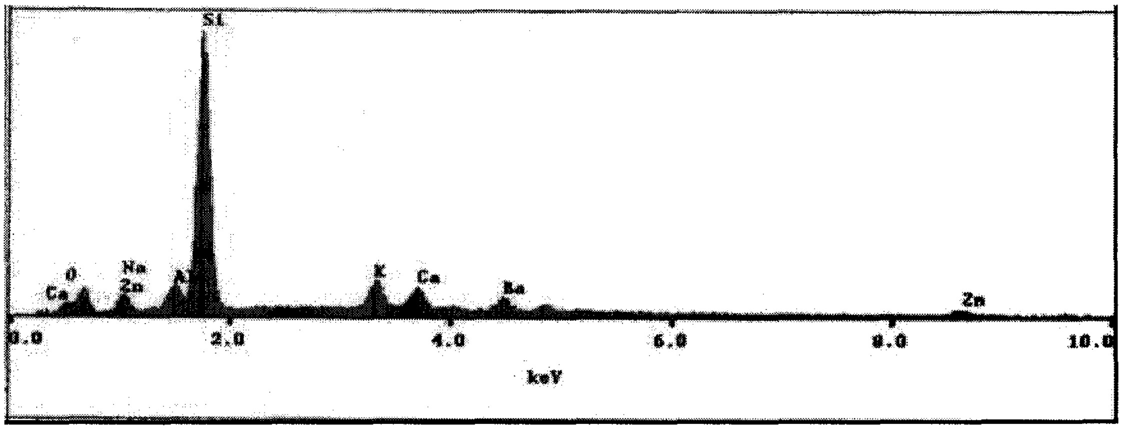


Figure 14. Pallflex Pure Quartz-fiber Filter EDX Scan

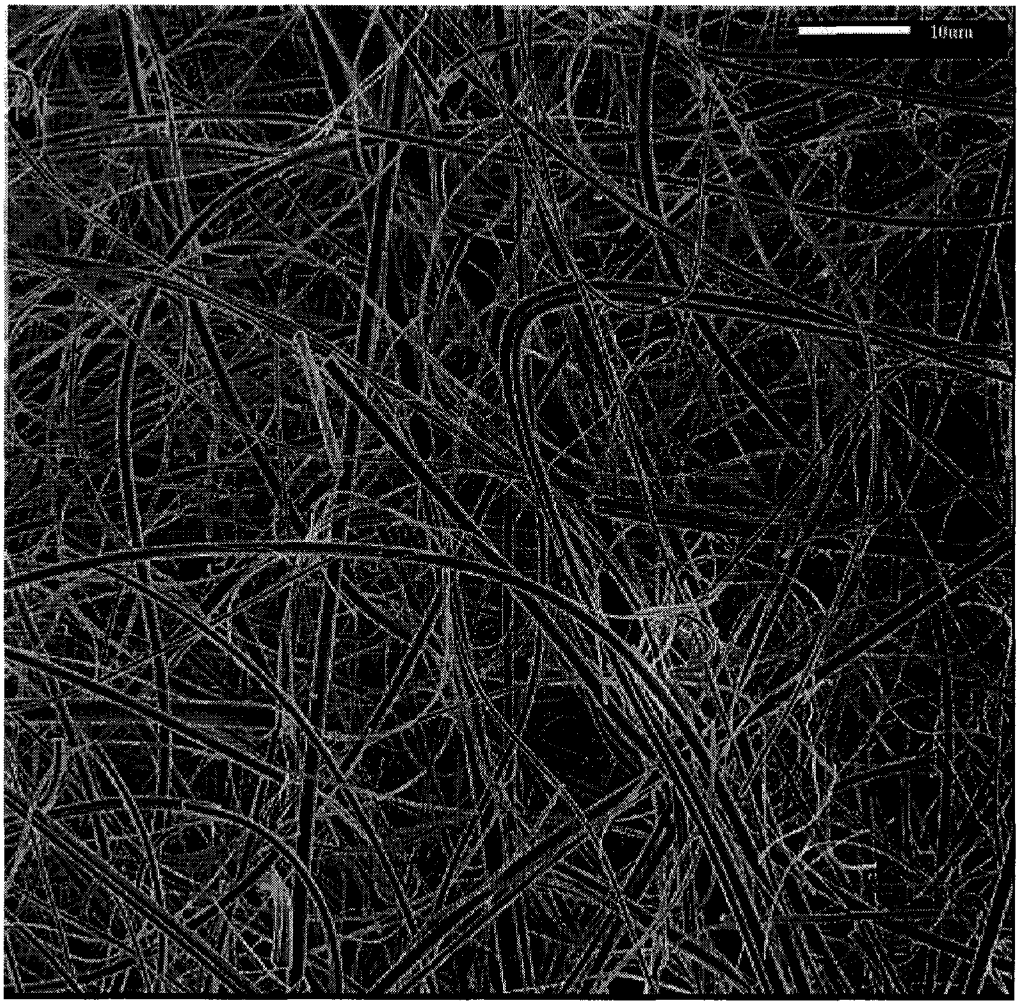


Figure 15. Whatman Quartz Filter - Surface as Observed by SEM (1000x)

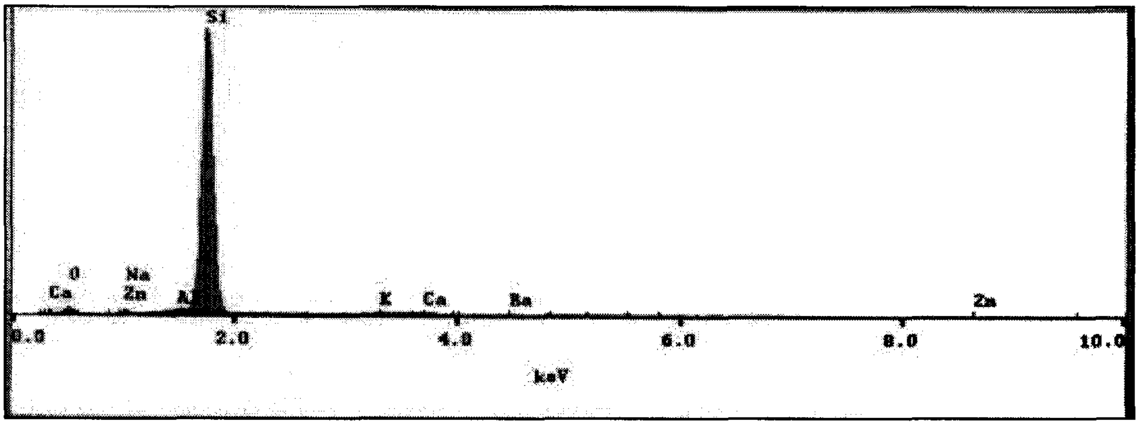


Figure 16. Whatman Quartz Filter EDX Scan

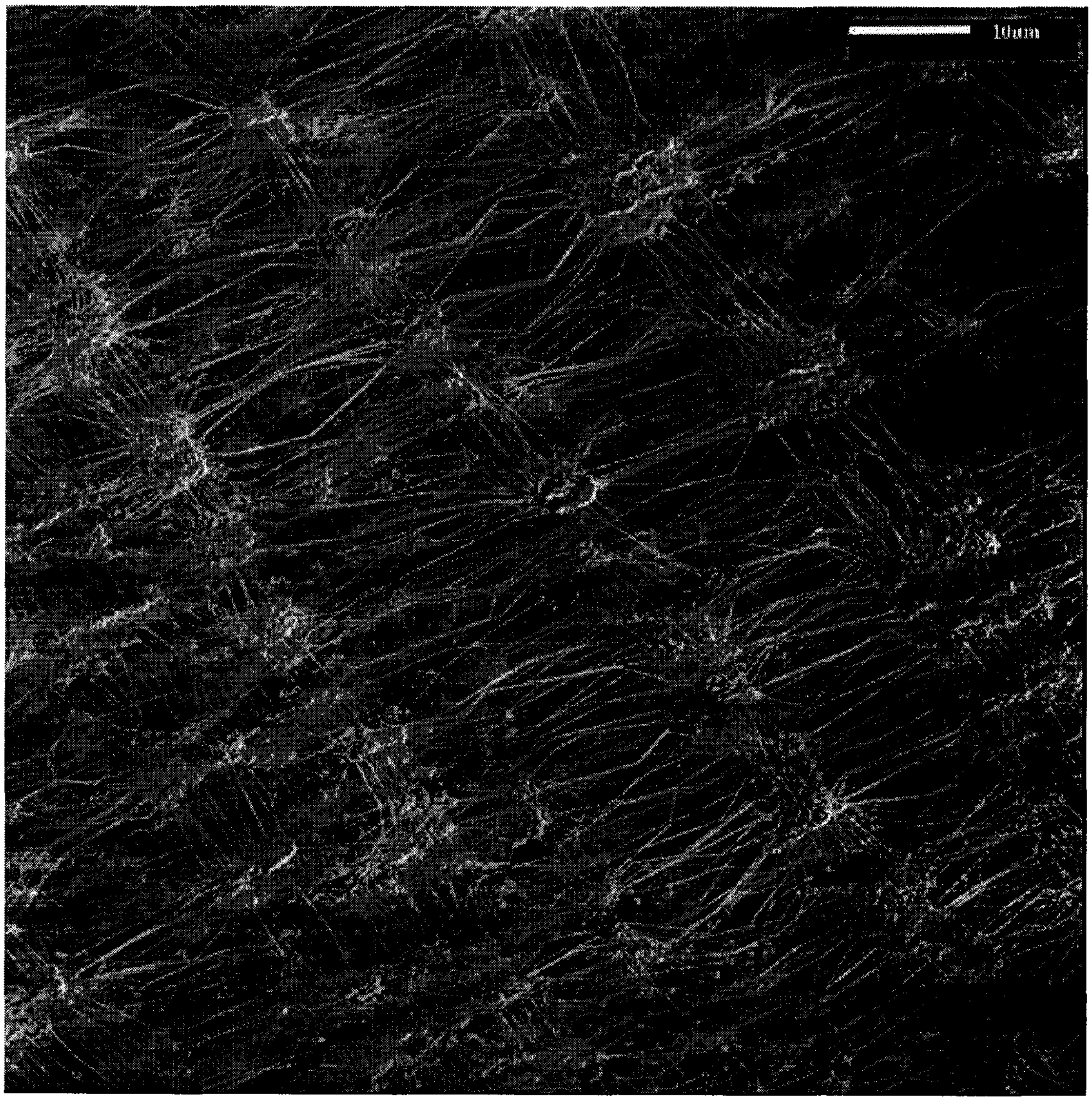


Figure 17. Gelman Ringed Teflon Filter –Surface as Observed by SEM (1000x)

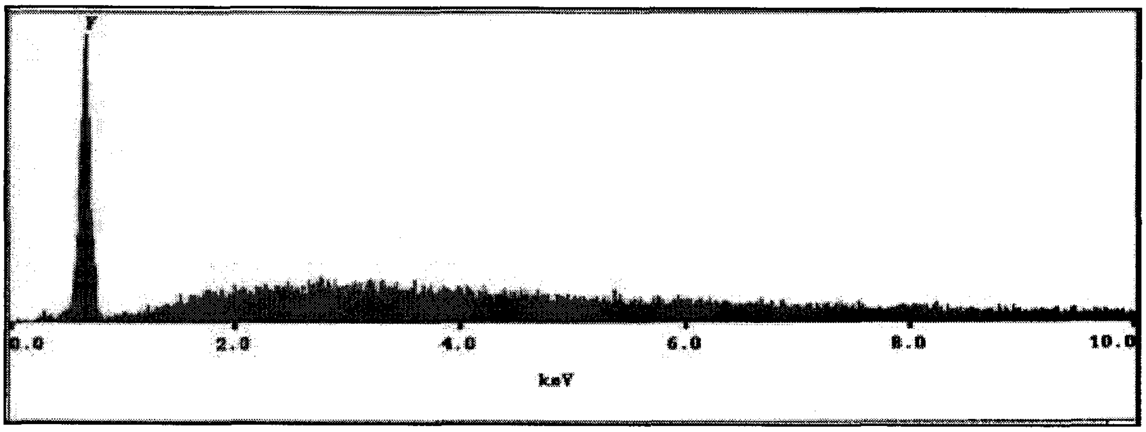


Figure 18. Gelman Ringed Teflon Filter EDX Scan

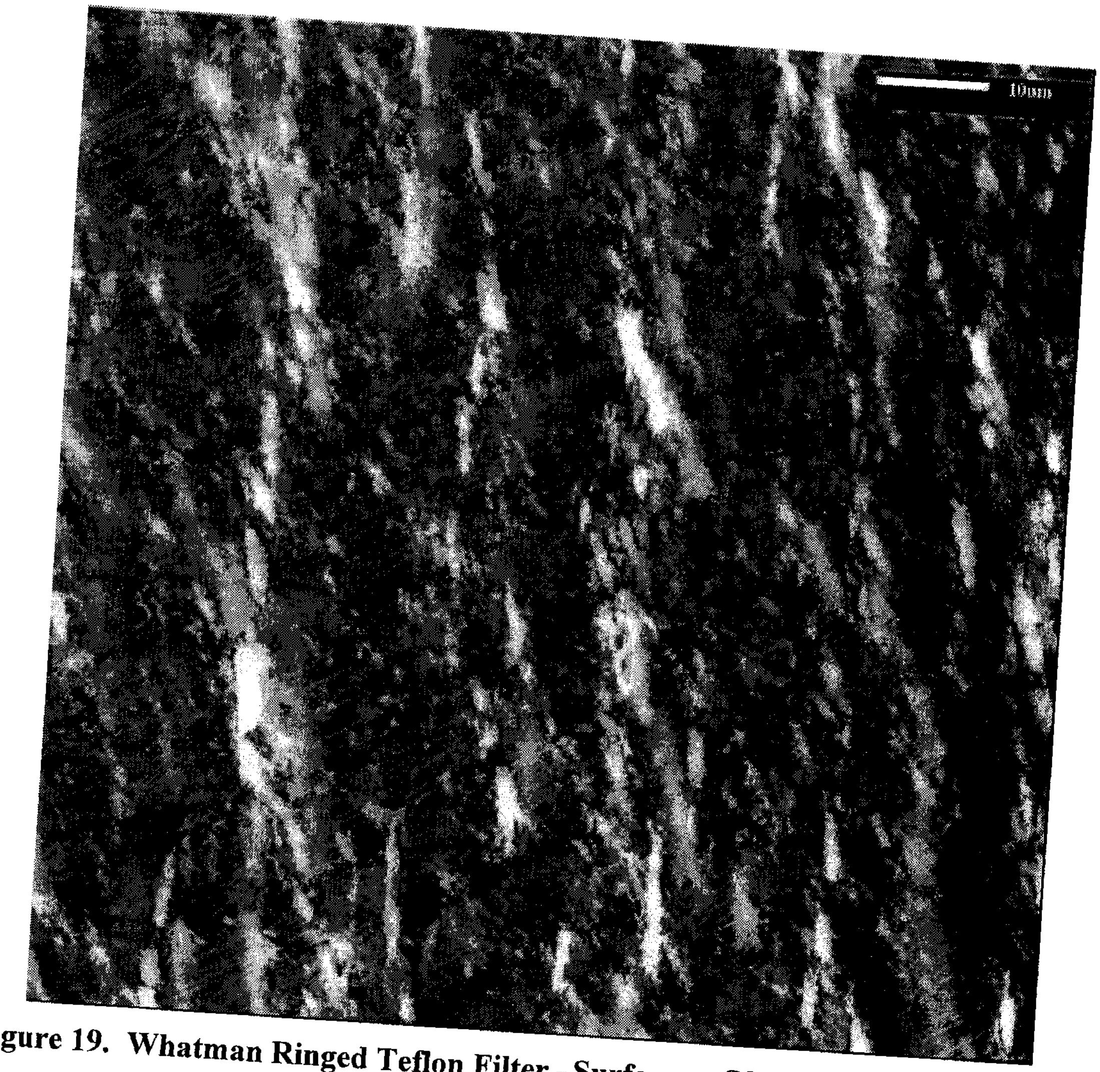


Figure 19. Whatman Ringed Teflon Filter –Surface as Observed by SEM (1000x)

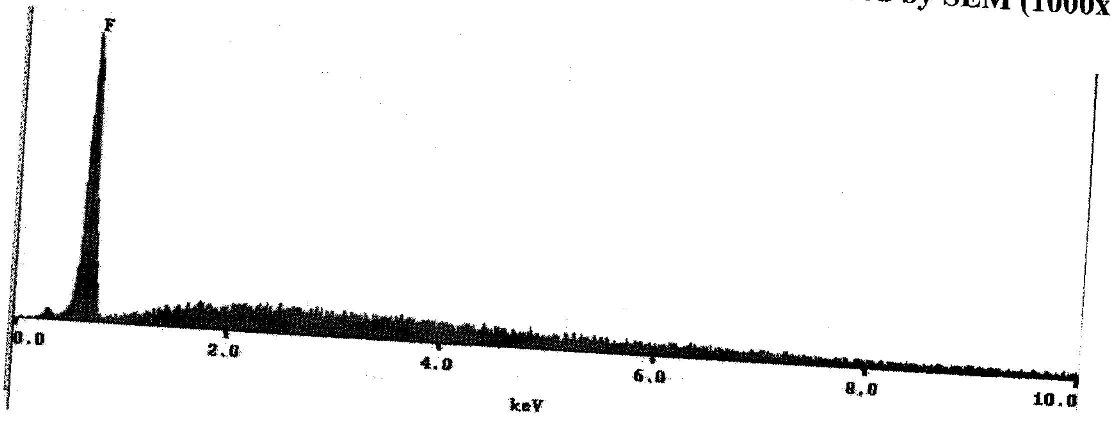


Figure 20. Whatman Ringed Teflon Filter EDX Scan

7. LABORATORY RESULTS

7.1 Chamber Injection Tests

The standard reference material (SRM) NIST-1648 was separated into eight vials containing varied mass for test injections, while adhering to the handling and preparation guidelines according to the Certificate of Analysis (NIST, 1998 – Appendix G). This allowed for individual injection tests into the sealed chamber. Tests included two "blank injections," two 100 mg injections, four 200 mg injections and two 300 mg injections. A sample schedule was drawn up for the tests and followed as per Table 8. Prior to the tests there were two "non-injection blanks" (Table 8) that were conducted to determine the background particulate matter levels inside the tank, and to ensure the water trap was adequately drawing air from outside the chamber to replace the air being drawn through the samplers. The "blank injections" were performed by injecting pressurized dry air into the chamber at 345 kPa (50 pounds per square inch, psi) (i.e. no SRM was introduced). The remaining injections (Table 8) were conducted by placing the SRM into the injection port, sealing the port, and injecting the dust under pressure at 345 kPa (50 psi) into the chamber.

From these twelve tests, a total of twenty-four filters were collected: sixteen filters were collected using PM_{10} sampling heads on the low volume MiniVols and eight filters were collected using $PM_{2.5}$ sampling heads on the MiniVols. In addition, the Grimm particle analyzer was used to measure background particle concentrations in the chamber, and to record real-time TSP, PM_{10} and $PM_{2.5}$ mass concentration levels from each injection.

The MiniVol samplers were set to collect SRM in the chamber over a 24-hour period. To ensure high resolution of real-time particle data, the Grimm particle analyzer was set to collect and store data at a rate of every six seconds.

Table 8. Injection Schedule for SRM-1648 – January to February 2001

Sample Type	Filters Needed	Injection (mg)	Start Date	End Date	Experiment Time
PM_{10}	2	*No-Injection Blank*	Jan 8, 2001	Jan 11, 2001	24 hours
$PM_{2.5}$	2	*No-Injection Blank*	Jan 30, 2001	Jan 31, 2001	24 hours
PM_{10}	2	Blank Injection	Jan 31, 2001	Feb 1, 2001	24 hours
$PM_{2.5}$	2	Blank Injection	Feb 1, 2001	Feb 2, 2001	24 hours
PM_{10}	2	100	Feb 2, 2001	Feb 3, 2001	24 hours
PM_{10}	2	100	Feb 3, 2001	Feb 4, 2001	24 hours
PM_{10}	2	200	Feb 5, 2001	Feb 6, 2001	24 hours
PM_{10}	2	200	Feb 6, 2001	Feb 7, 2001	24 hours
$PM_{2.5}$	2	200	Feb 7, 2001	Feb 8, 2001	24 hours
$PM_{2.5}$	2	200	Feb 9, 2001	Feb 10, 2001	24 hours
PM_{10}	2	300	Feb 10, 2001	Feb 11, 2001	24 hours
PM_{10}	2	300	Feb 12, 2001	Feb 13, 2001	24 hours

A water trap on the side of the chamber was constantly filled with de-ionized water throughout the sample injection period. The purpose of the water trap was to allow air from the laboratory room to enter the chamber only after it passed through the water, thereby scrubbing out any ambient particles. Thus during injections of SRM the water trap was used to ensure that only SRM particulate matter was in the chamber.

7.1.1 Particle Size Distribution of SRM

The particle size distributions of the SRM were unknown. This information was not available from certificate information (NIST, 1998). Monitoring data from the Grimm particle analyzer were used to determine the percent size distribution of $PM_{2.5}$

(fine particulate matter), particulate matter between 2.5 μm and 10 μm (coarse particulate matter), and >PM_{10} (TSP) fractions.

Resulting size distributions of the SRM for the eight injection tests are shown in Table 9. Based on the eight injection tests, approximately two-thirds (66%) of particles from the SRM were in the coarse fraction (between 2.5 μm and 10 μm), with only 12% in the fine fraction.

The dominance of SRM particle sizes in the coarse fraction (PM_{10}) was confirmed after injection tests which showed the low volume PM_{10} impactor heads were relatively clean compared to the low volume $PM_{2.5}$ impactor heads. This was observed in Figure 21, which showed darkened spots in the center of the $PM_{2.5}$ heads compared to the PM_{10} heads. The majority of the SRM (approximately 88%) was removed by the $PM_{2.5}$ impactor heads whereas only approximately 22% was removed by the PM_{10} impactor heads.

Table 9. Particle Size Distribution Based on Grimm Particle Analyzer Mass Concentration Results

Sample Test and Injection mass		Particle Size Distribution ≤ 2.5 μm	> 2.5 μm, ≤ 10 μm	> 10 μm
PM_{10}	100 mg	11.5%	65.9%	22.6%
PM_{10}	100 mg	11.8%	65.7%	22.5%
PM_{10}	200 mg	12.2%	66.6%	21.2%
PM_{10}	200 mg	11.3%	65.2%	23.5%
$PM_{2.5}$	200 mg	12.6%	66.8%	20.5%
$PM_{2.5}$	200 mg	12.7%	65.9%	21.4%
PM_{10}	300 mg	12.7%	65.5%	21.8%
PM_{10}	300 mg	12.6%	66.1%	21.4%
Mean Distribution		12.2%	66.0%	21.9%

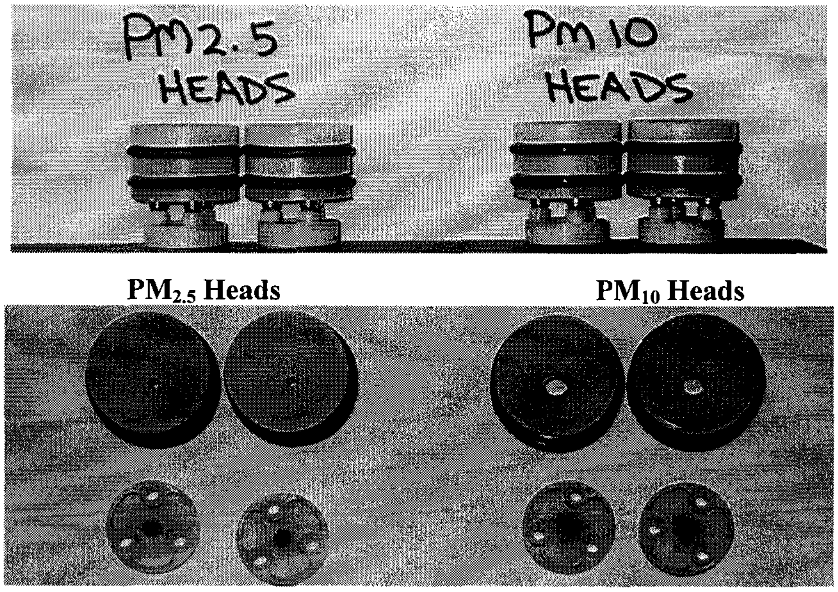


Figure 21. Example of MiniVol (Low Volume Integrated PM_{10} & $PM_{2.5}$) Air Sampling Impactor Heads after an Injection Test

7.1.2 SRM Mass Concentrations

Real-time data from the Grimm particle analyzer exhibited initial peak concentrations of SRM in the chamber followed by rapidly decreasing concentrations during injection tests. An example of a 200 mg injection test is shown in Figure 22. The total mass collected and corresponding 24-hour average mass concentrations for the low volume samplers were compared to the Grimm analyzer in Table 10 and Figure 23 based on eight injection tests with SRM. Figure 23 shows the agreement between the low volume samplers and the Grimm at the 100 mg and 200 mg SRM injection tests. However, there was not agreement between the low volume samplers and the Grimm analyzer for the 300 mg SRM injection test. Although unconfirmed, this discrepancy at the 300 mg level may have been a combination of incomplete mixing and rapid settling of SRM inside the chamber, with the addition of overloading the Grimm due to excessive particle counts (which are used to determine mass concentration). SRM that was not collected by the samplers accumulated on the sides and bottom of the chamber.

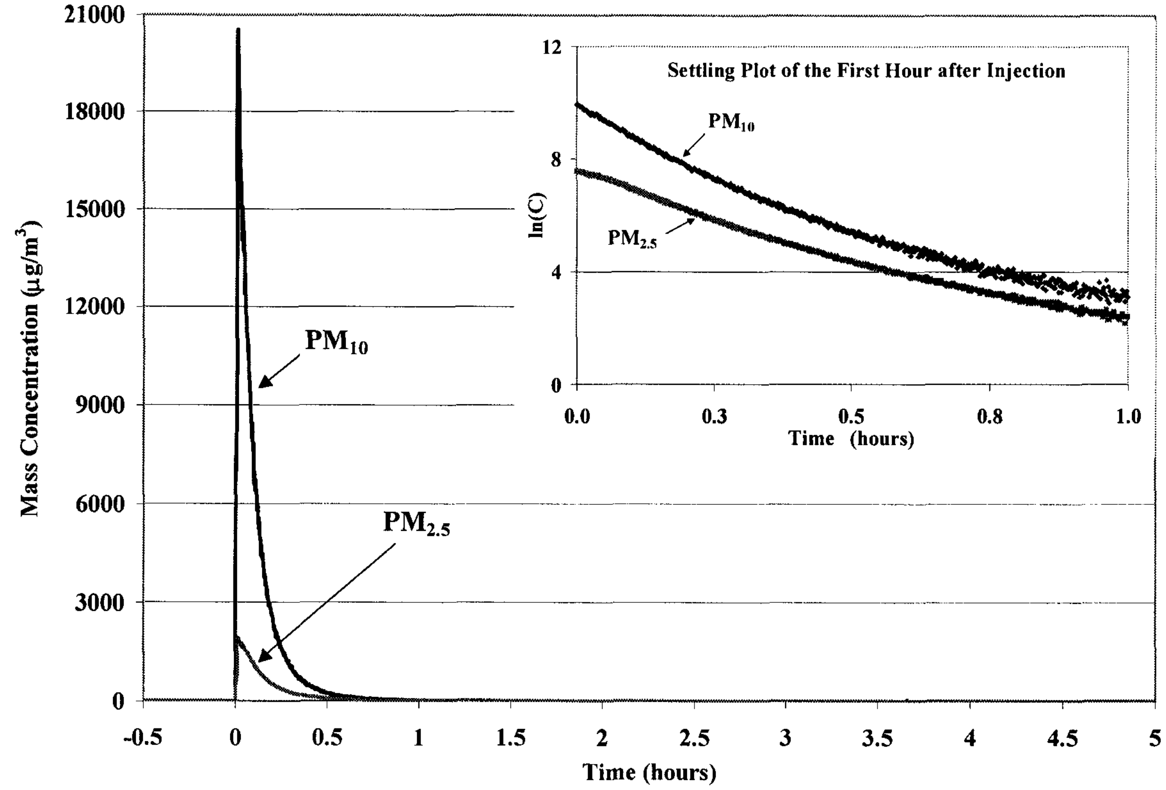


Figure 22. Example of Real-Time Particle Concentration from Injection of 200 mg, NIST-1648 as Recorded by a Grimm Analyzer

Table 10. Injection Results of SRM Inside the Chamber

		Mass Collected			Mass Concentration		
	True	Minivol	Minivol	Grimm	Minivol	Minivol	Grimm
Sample	Injection	2325	2324		2325	2324	
Type	(mg)	µg	µg	µg	µg/m^3	µg/m^3	µg/m^3
PM$_{10}$	100.1	215	197	68	30	28	38
PM$_{10}$	100.5	267	224	57	38	32	33
PM$_{10}$	200.5	634	524	148	90	74	84
PM$_{10}$	199.4	551	424	142	78	60	80
PM$_{10}$	300.6	961	771	270	137	110	153
PM$_{10}$	300.5	676	770	240	96	110	136
PM$_{2.5}$	200.2	194	102	44	28	14	13
PM$_{2.5}$	201.9	130	110	38	19	16	16

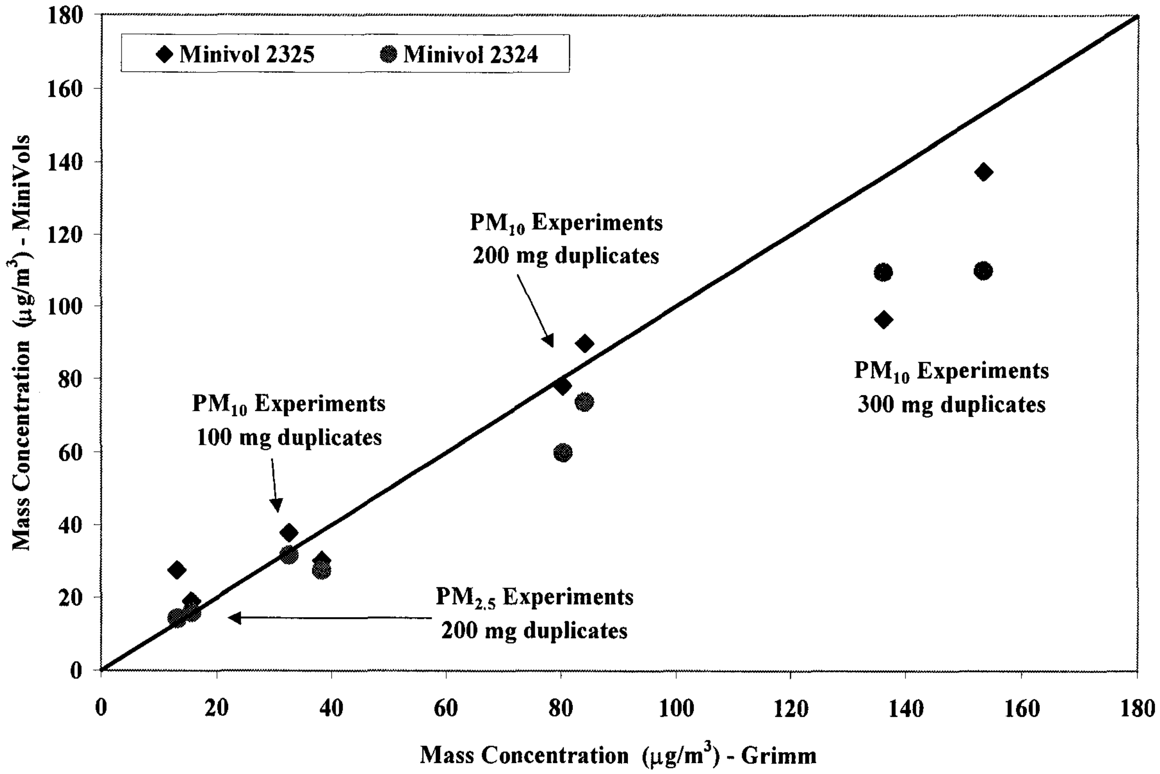


Figure 23. Comparison of Mass Concentrations from Low Volume Samplers and Grimm Particle Analyzer for Eight Injection Tests

The Grimm particle analyzer was one of only a few portable air sampling instruments that could provide an independent measurement of SRM airborne mass concentrations inside the chamber during the injection tests. Thus, there was interest in establishing whether SRM airborne mass concentrations were similar, measured by both the low volume samplers and the Grimm particle analyzer during the injection tests.

Regression analysis was completed to compare the 24-hour average airborne mass concentration data collected from all three samplers based on the 10 injection tests (not including the blank non-injections). These results are provided in Table 11. Coefficient of determination (r^2) values for comparison of each sampler ranged from 94 to 99%

indicating reasonable agreement among each sampler in measuring 24-hour average SRM airborne mass concentrations during the injection tests.

A paired t-test was performed on the measured 24-hour average SRM airborne mass concentrations for each individual sampler for the 10 injection tests (not including the blank non-injections). The results shown in Table 11 indicated no statistical difference in the collection ability of any of the samplers ($P \leq 0.05$). All three samplers measured comparable airborne mass concentrations in the enclosed chamber over a 24-hour period.

Table 11. Regression and Statistical Results from Sampler Comparison

Injections (n=10)		Y = mX + b		r^2	Paired t-test (at 5% significant level)
X	**Y**	**m (±SE)**	**b (±SE)**		**Ho: The means are equal** **Ha: The means are unequal** **reject if: |t stat| > t Critical two-tail**
MiniVol 2325	MiniVol 2324	0.89 (±0.08)	-1.72 (±5.59)	0.94	**|1.79| < 2.26** **do not reject the hypothesis**
MiniVol 2324	Grimm	1.36 (±0.05)	-6.44 (±3.21)	0.99	**|-1.98| < 2.26** **do not reject the hypothesis**
MiniVol 2325	Grimm	1.22 (±0.10)	-9.69 (±6.74)	0.95	**|-1.10| < 2.26** **do not reject the hypothesis**

The objective of these laboratory tests was not to try and recover the total mass of SRM injected into the chamber but to be able to collect sufficient comparable mass for subsequent elemental analysis regardless of the initial SRM mass injected. Filters from the low volume samplers were destined for elemental analysis to compare SEM-EDX with ICP-MS for similar SRM sampling conditions. One filter from one of the samplers was analyzed for elements using SEM-EDX and the filter from the second sampler was analyzed for elements using ICP-MS.

7.2 Elemental Analysis of SRM

7.2.1 Qualitative Information from Individual Particle Analysis

Bulk analysis methods such as ICP-MS are best suited for heavily loaded filters from FRM sampling in order to address higher detection limit requirements of individual elements posed by this technique. A drawback of FRM sampling methods is that filters may become too loaded for individual particle evaluation as was observed by Pinto et al. (1998). Individual particle analysis of filters from low volume sampler only requires a thin layer of particles. This was expected to be the case for the collected samples from the MiniVols from the injection tests over the 24-hour sampling period.

A further advantage of individual particle (SEM-EDX) analysis is that information about particle morphology (form or shape) can be obtained along with elemental composition. Using a categorical summary of particle properties based on homogeneity shape, surface texture, and elemental composition (summarized in Chapter 2), individual SRM particles studied can be classified. This information can aid in determination of particle origins during source apportionment based on elemental profiles.

Individual particle analysis (SEM-EDX) of the SRM matched fourteen primary elements: aluminum, iron, potassium, sodium, zinc, manganese, sulfur, magnesium, chloride, titanium, silica, calcium, phosphorus, and lead (Al, Fe, K, Na, Zn, Mn, S, Mg, Cl, Ti, Si, Ca, P, and Pb). These elements were matched based on comparison to the bulk elemental analysis and the certificate values of the SRM (Appendix G).

Although not shown, the morphological and elemental properties of most SRM particles analyzed by SEM-EDX appeared to be related to combustion and crustal sources.

7.2.2 Individual Particle Analysis versus SRM NIST-1648 Certified Quantities – Multiple Filter Comparison

An important aspect in demonstrating that low volume sampling/individual particle analysis is a viable alternative for airborne particulate matter source apportionment is the ability to quantify the abundance of elements present in particles collected. This was initially examined by comparing elemental quantities present in SRM particles as measured by SEM-EDX with SRM NIST-1648 certified quantities based on average results determined from analysis of filters from all the SRM injection tests.

Common elements that were measured by SEM-EDX and reported for the SRM included: aluminum, iron, sodium, zinc, sulfur, magnesium, chloride, titanium, potassium and manganese. These elements accounted for 17% mass fraction of the SRM (Certificate values - Appendix G) compared to 41% by weight (measured by SEM-EDX). The "average percent abundance of individual elements" was calculated and used to compare SRM certificate quantities with results from SEM-EDX (and ICP-MS for subsequent analysis) for common elements:

$$\%\,\text{Abundance SRM} = \frac{\text{Individual elemental component (mg/kg)}}{\sum \text{Total elemental component reported (mg/kg)}} \quad\text{........................}(19)$$

$$\%\,\text{Abundance SEM - EDX} = \frac{\text{Individual elemental weight \%}}{\sum \text{Total elemental weight \%}} \quad\text{..}(20)$$

$$\%\,\text{Abundance ICP-MS} = \frac{\text{Individual elemental concentration } (\mu\text{g/m}^3)}{\sum \text{Total elemental concentrations } (\mu\text{g/m}^3)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (21)$$

The "average percent abundance of individual elements" as determined by SEM-EDX was based on the following procedures:

- An assumption was made that SRM particles collected on the filter were uniformly distributed across the collection area.
- A small area of the filter, approximately 13 mm in diameter, was considered in which 10 particles within this area were randomly selected and subjected to SEM-EDX analysis (refer to Appendix C for protocols).
- The "average percent abundance of individual elements" was computed using equation 20.

Two additional elements identified by SEM-EDX but not reported on the NIST–1648 certificate values for the SRM were silica (Si) and calcium (Ca). SEM-EDX results indicated these were major elements present in the SRM at 30% to 35% by weight and 20% to 25% by weight for Si and Ca, respectively based on analysis from the eight injection tests of SRM.

Figure 24 and Table 12 illustrate average percent abundance of the 10 common elements detected in SRM by SEM-EDX compared to NIST–1648 certificate values. Average % abundance measured by SEM-EDX was regressed against NIST–1648 certificate values for the 10 elements in the SRM (Figure 25). An r^2 value of 97% indicates close agreement for all of the elements using the SEM-EDX method compared to NIST–1648 certified quantities. Average % abundance measured by SEM-EDX was based on an average of analysis of 10 individual particles on 10 filters collected from the 10 injection tests.

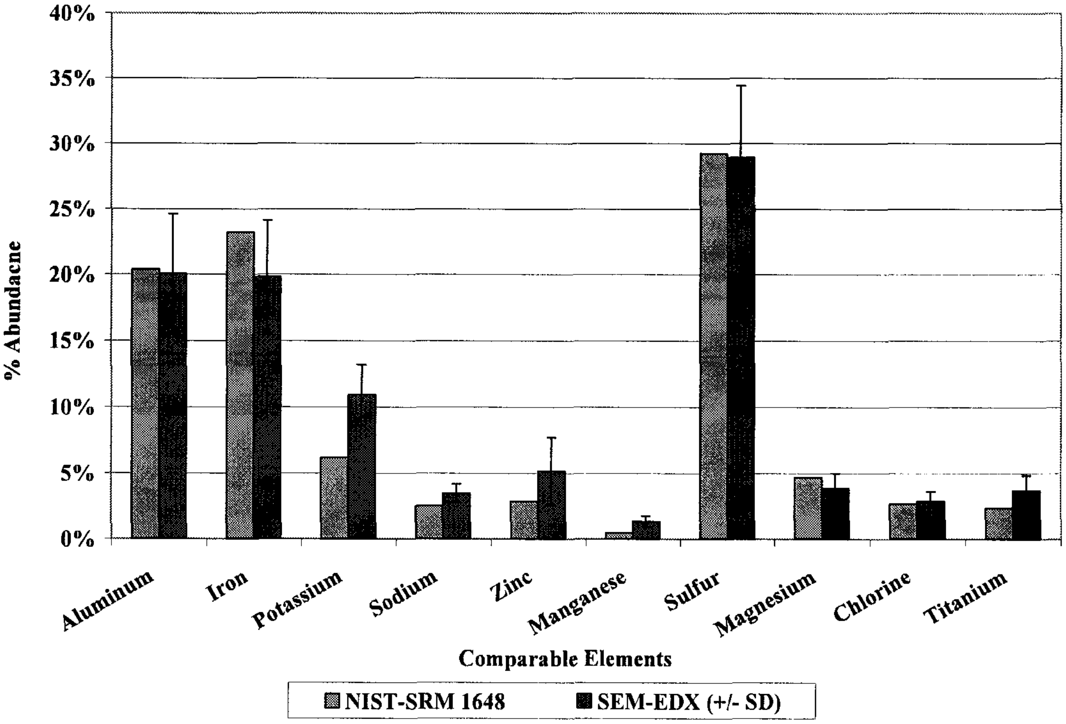


Figure 24. Average % Abundance of Individual Elements in SRM (certified amount) and SEM-EDX based on 10 Injection Tests

A paired t-test was performed to compare the average % abundance of individual elements measured by SEM-EDX and NIST–1648 certificate values for the 10 common elements in the SRM (Table 12). Results of the paired t-test concluded no difference in the average % abundance of individual elements as determined by SEM-EDX and NIST–1648 certificate values ($P \leq 0.05$):

Ho: The means are equal

Ha: The means are unequal

reject if: |t stat| > t Critical two-tail

|0.84| < 2.26 with 9 degrees of freedom $\therefore$ do not reject the hypothesis

Table 12. Average % Abundance of Individual Elements in SRM (certified amount) and SEM-EDX based on 10 Injection Tests

Comparable Element	SRM – Certificate Value (%)	SEM-EDX – analyzed value (%)	SRM %Abundance Eq. 19	SEM-EDX %Abundance Eq. 20
Aluminum	3.48	8.3	20%	20%
Iron	3.96	8.2	23%	20%
Potassium	1.06	4.5	6%	11%
Sodium	0.43	1.4	2%	3%
Zinc	0.48	2.1	3%	5%
Manganese	0.08	0.6	0.5%	1.3%
Sulfur	5.00	12.0	29%	29%
Magnesium	0.80	1.6	5%	4%
Chloride	0.45	1.2	3%	3%
Titanium	0.40	1.5	2%	4%

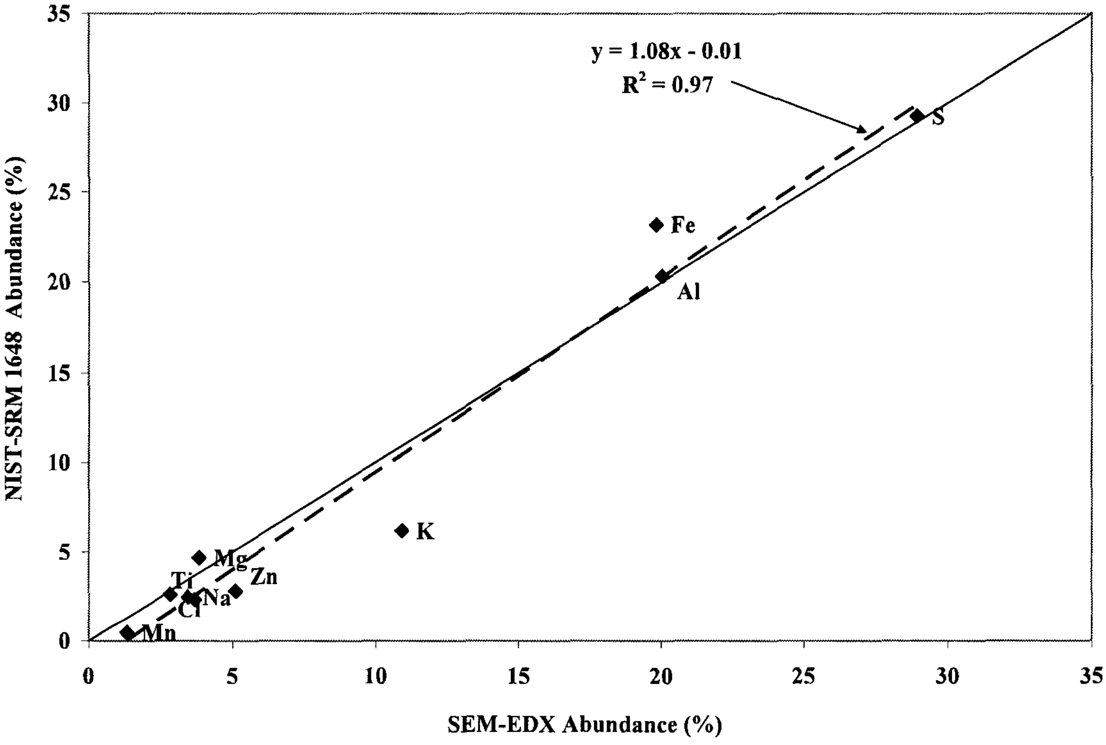


Figure 25. Regression of Average % Abundance for Individual Elements – SRM (certified amount) versus SEM-EDX based on 10 Injection Tests

7.2.3 Individual Particle Analysis versus SRM NIST-1648 Certified Quantities and ICP-MS – Filter-to-Filter Comparison

Another form of analysis that was undertaken was a "filter-to-filter" comparison of common elements present in SRM particles as measured by SEM-EDX: i) with those measured by ICP-MS; and ii) with those based on NIST–1648 certified quantities. This analysis was based on results determined from analysis of filters from the eight individual SRM injection tests. ICP-MS is an accepted bulk analytical method used in practice to characterize elemental profiles of airborne particulate matter. Thus it was considered important to demonstrate that SEM-EDX had an equivalent capability for measuring elemental quantities in the SRM compared to ICP-MS. This analysis was accomplished by performing paired t-tests of individual elemental concentrations for replicate filter samples for the following conditions:

- Elemental % abundance determined by SEM-EDX (Equation 20) versus elemental % abundance determined by ICP-MS (Equation 21).
- Elemental % abundance determined by SEM-EDX (Equation 20) versus elemental % abundance based on NIST–1648 certified quantities (Equation 19).
- Elemental % abundance determined by ICP-MS (Equation 21) versus equivalent elemental concentrations based on NIST–1648 certified quantities (Equation 19). This comparison was undertaken to verify ICP-MS as an accepted bulk analytical method.

SEM-EDX versus ICP-MS. Results from these paired t-tests are summarized in

Table 13 and discussed below. The first condition tested was elemental % abundances determined by SEM-EDX versus elemental % abundances determined by ICP-MS. This test was based on 10 common elements (aluminum, iron, potassium, sodium, zinc, sulfur, magnesium, titanium, silica, and calcium) measured by SEM-EDX and ICP-MS. From these tests, all of these elements except silica were not rejected ($P \leq 0.05$) indicating the SEM-EDX method quantified similar elemental abundances as the ICP-MS method (calculated by Equation 21).

The result observed for silica was expected. This element was used as an "internal check" due to an inability of the ICP-MS method to measure it. It was believed in advance that silica would fail the paired t-test because the digestive method used to prepare the SRM for ICP-MS analysis (SW-846 procedure 3050B) cannot solubilize silica. Thus the quantity reported by the ICP-MS method would not represent the actual quantity. Chloride and manganese were measured by SEM-EDX, however these elements could not be compared because they were not quantifiable by the ICP-MS method.

SEM-EDX versus NIST–1648 Certified Quantities. The second condition tested was elemental abundances measured by SEM-EDX versus equivalent elemental abundances based on NIST–1648 certified quantities. These paired t-tests were based on 10 common elements (aluminum, iron, potassium, sodium, zinc, sulfur, magnesium, titanium, chloride, and manganese).

However, all of the elements except potassium were not rejected ($P \leq 0.05$) indicating that the SEM-EDX method quantified similar elemental abundances as equivalent abundances based on NIST-1648 certified quantities. It was speculated that potassium failed due to the SEM-EDX method reporting higher abundances than what was indicated to be present in the SRM. The response for potassium in this chamber study was also believed to be an anomaly, due to both the laboratory and field samples (Chapter 8) demonstrating comparable findings between ICP-MS and SEM-EDX for potassium. The discrepancy of the potassium findings does pose further research potential regarding low abundances and trace metal analysis with SEM-EDX.

ICP-MS versus NIST–1648 Certified Quantities. The final condition tested was a check on the capabilities of the ICP-MS as an accepted bulk analytical method. This was done for eight common elements including; aluminum, iron, potassium, sodium, zinc, sulfur, magnesium, and titanium. All eight of the elements were not rejected ($P \leq 0.05$) indicating the ICP-MS method quantified similar elemental abundances as those based on NIST-1648 certified quantities.

Table 13. t-test Comparison of % Abundance of Elements Determined by SEM-EDX, ICP-MS, and Equivalent % Abundance based on NIST-1648 Certified Quantities

Paired t-test

(SEM-EDX results are based on average of 10 random particles per filter)

Ho: The means are equal; Ha: The means are unequal

reject if: $|t_{calculated}| > t_{critical}$ (using a two-tail test)

$t_{critical}$ at 5% significance level = 2.26; $t_{critical}$

8 tests	SEM-EDX to ICP-MS	SEM-EDX to SRM	ICP-MS to SRM
	$t_{calculated}$	$t_{calculated}$	$t_{calculated}$
Al	|-1.40| < 2.26, do not reject	|0.07| < 2.26, do not reject	|0.51| < 2.26, do not reject
Fe	|-1.64| < 2.26, do not reject	|1.14| < 2.26, do not reject	|0.12| < 2.26, do not reject
K	|-2.14| < 2.26, do not reject	|5.82| > 2.26, cannot accept	|1.20| < 2.26, do not reject
Na	|2.16| < 2.26, do not reject	|1.36| < 2.26, do not reject	|2.24| < 2.26, do not reject
Zn	|1.63| < 2.26, do not reject	|0.93| < 2.26, do not reject	|1.76| < 2.26, do not reject
S	|-1.03| < 2.26, do not reject	|1.72| < 2.26, do not reject	|0.01| < 2.26, do not reject
Mg	|1.34| < 2.26, do not reject	|0.51| < 2.26, do not reject	|1.92| < 2.26, do not reject
Ti	|-0.21| < 2.26, do not reject	|1.67| < 2.26, do not reject	|2.24| < 2.26, do not reject
Si	|-3.38| > 2.26, cannot accept (Si not reported by ICP-MS)	not applicable (Si not reported in NIST-1648 SRM)	not applicable (Si not reported in NIST-1648 SRM)
Ca	|2.14| < 2.26, do not reject	not applicable (Ca not reported in NIST-1648 SRM)	not applicable (Ca not reported in NIST-1648 SRM)
Cl	not applicable (Cl not quantified by ICP-MS)	|0.37| < 2.26, do not reject	not applicable (Cl not quantified by ICP-MS)
Mn	not applicable (Mn not quantified by ICP-MS)	|2.07| < 2.26, do not reject	not applicable (Mn not quantified by ICP-MS)

7.3 Determination of Minimum Number of Individual Particles to Analyze using SEM-EDX

Another key aspect in demonstrating that low volume sampling/individual particle analysis method is a viable alternative for airborne particulate matter source apportionment was establishing the minimum number of particles collected on a filter to be subjected to SEM-EDX. Ideally all particles should be analyzed to adequately represent elemental quantities on a filter. However this would be costly and time-consuming to accomplish. Assuming that particles are distributed across a filter surface, analyzing a minimum number of randomly-selected particles within a defined area of a filter sample, would be efficient. This would be the case if average elemental quantities determined from analysis of a minimum number of particles were similar to those quantities for all particles on a filter.

Two filters from the 300 mg injection test (Table 8) were used to investigate this further whereby SEM-EDX was used to analyze up to 40 randomly selected particles within a defined 13 mm diameter section of each filter:

- The upper limit of 40 randomly-selected particles was arbitrarily set as a maximum number of particles to analyze for determination of representative average % abundance of elements on a filter.
- Average % adundance of elements were then calculated for successively larger numbers of particles in groupings of five, e.g. 5, 10, 15, 20, 25, 30, 35, and 40 particles.
- To ensure averaging was unbiased, each particle was assigned a random number and selected accordingly into each grouping.
- Average % abundance of elements for each of these groupings were compared to average % abundance of elements computed from 40 particles (the arbitrary upper limit).

This resulted in a total of eighty particles analyzed at random by SEM-EDX, forty on each filter – a very time-consuming process.

Figure 26 (Filter 19) and Figure 27 (Filter 14) present the results of this comparison. Twelve elements measured by SEM-EDX included: aluminum, iron, sodium, zinc, sulfur, magnesium, chloride, titanium, silica, calcium, potassium, and manganese.

A two-tailed t-test under an assumption of equal variance was used to compare the average % abundance of an individual element for each particle grouping to the average % abundance based on the total of 40 particles. This involved 84 tests for each filter (7 particle groupings x 12 elements). Results of the t-test are provided in Appendix H for each filter. For both filters, no differences were indicated in average % elemental abundance for each of the particle groupings (e.g. 5, 10, 15, 20, 25, 30, and 35 particles) compared to average % elemental abundance based on 40 particles ($P \leq 0.05$). This suggests that the average % abundance of the twelve elements detected by SEM-EDX based on five randomly-selected particles was comparable to average % abundance of the twelve elements based on 40 randomly selected particles. There was a greater inconsistency with averaging five particles (as seen from r^2 in Tables 14 and 15) compared to averaging 10 particles, therefore the minimum average of 10 particles represented better agreement with the SRM. Further evaluation of non-homogenous SRM was conducted in the field study in Chapter 8.

Further statistical testing was undertaken to compare the average % elemental abundance for each particle grouping, including the grouping of 40 particles, with the SRM NIST–1648 certified quantities. Only 10 elements were included in these tests: aluminum, iron, sodium, zinc, sulfur, magnesium, chloride, titanium, potassium, and manganese. Silica and calcium were not reported in the SRM (Section 7.2.2). Regression analysis was undertaken to compare average % abundance of individual elements for each particle grouping, including the grouping of 40 particles, to SRM NIST–1648 certified quantities. These results are provided in Table 14 for Filter 19. As shown in Table 14, r^2 value for the smallest group of five particles was only 47%, whereas r^2 values for groupings of $\geq$ 10 particles ranged from 76 to 92%. Whereas for Table 15 (results for Filter 14), the r^2 value for the smallest group of five particles was 96% and r^2 values for groupings of $\geq$ 10 particles ranged from 88 to 96%.

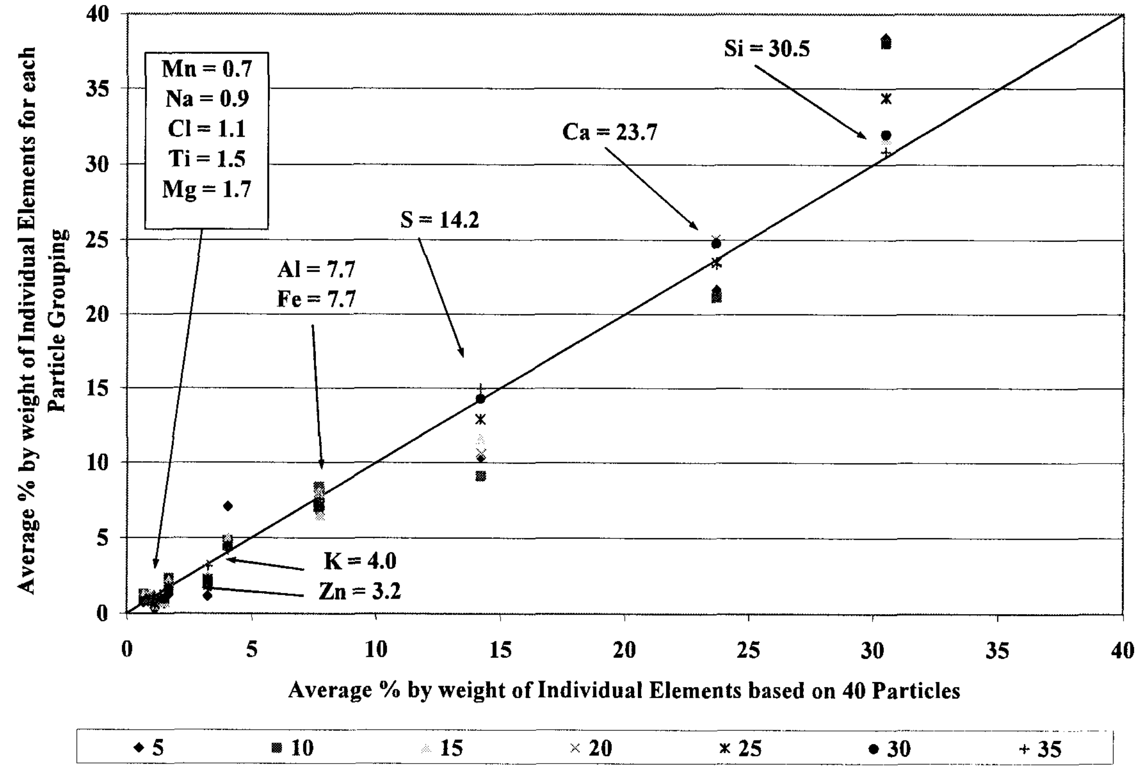


Figure 26. Comparison of Average % Abundance of Individual Elements for each Particle Grouping to Average % Abundance based on 40 Particles (Filter 19 from a 300 mg Injection SRM Test)

Although it is unknown what produced inconsistent r^2 results for the smallest group of five particles, 47% (Table 14) versus 96% (Table 15), greater consistency was observed for groupings of $\geq$ 10 particles. Another observation of Table 14 and Table 15 was that r^2 values determined for higher particle groupings (e.g. 30, 35, and 40 particles) were not consistently higher than r^2 values determined for the lower particle groupings (e.g. 10, 15, and 20 particles). This suggests that groupings of 10 to 20 particles provide similar quantitative data on elements detected by SEM-EDX as groupings of 30 to 40 particles.

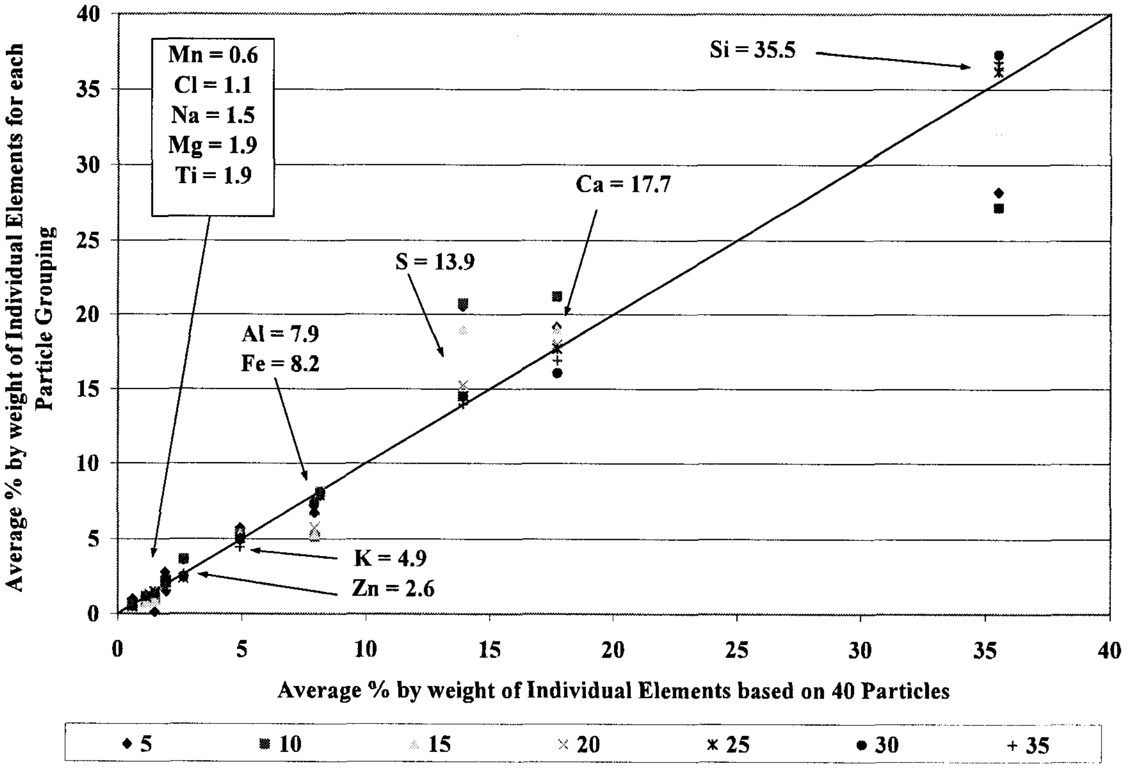


Figure 27. Comparison of Average % Abundance of Individual Elements for each Particle Grouping to Average % Abundance based on 40 Particles (Filter 14 from a 300 mg Injection Test)

While not exact, the above results support that SEM-EDX analysis of a minimum of 10 randomly-selected particles within a filter area can be used to represent elemental quantities (i.e. % abundance) of up to 40 randomly-selected particles within the filter area for particulate matter collected by low volume samplers. Further, SEM-EDX analysis of a minimum of 10 randomly-selected particles within a filter area can be used to represent quantities (i.e. % abundance) in the SRM collected by low volume samplers based on NIST–1648 certified quantities.

Table 14. Computed Regression Equations and Paired t-test Results for Comparison of Average % Abundance of Individual Elements for Each Particle Grouping as Determined by SEM-EDX with SRM NIST–1648 Certified Quantities (Filter 19)

<table>
<tr><th colspan="2">Samplers (n=10)</th><th colspan="2">Y = mX + b</th><th>r^2</th><th>Paired t-test (P≤0.05)</th></tr>
<tr><th>Y
NIST-1648</th><th>X
Groups of randomly selected particles</th><th>m (±SE)</th><th>b (±SE)</th><th></th><th>Ho: The means are equal
Ha: The means are unequal
reject if: |t stat| > t Critical two-tail</th></tr>
<tr><td>SRM</td><td>5</td><td>1.08 (±1.92)</td><td>1.35 (±0.50)</td><td>0.47</td><td>|-1.61| < 2.26, do not reject Ho</td></tr>
<tr><td>SRM</td><td>10</td><td>-1.10 (±1.37)</td><td>1.32 (±0.24)</td><td>0.89</td><td>|-0.40| < 2.26, do not reject Ho</td></tr>
<tr><td>SRM</td><td>15</td><td>-0.62 (±0.85)</td><td>1.31 (±0.15)</td><td>0.90</td><td>|-1.02| < 2.26, do not reject Ho</td></tr>
<tr><td>SRM</td><td>20</td><td>0.16 (±1.03)</td><td>1.03 (±0.16)</td><td>0.84</td><td>|-0.42| < 2.26, do not reject Ho</td></tr>
<tr><td>SRM</td><td>25</td><td>0.82 (±1.20)</td><td>0.82 (±0.16)</td><td>0.76</td><td>|0.05| < 2.26, do not reject Ho</td></tr>
<tr><td>SRM</td><td>30</td><td>0.22 (±1.04)</td><td>0.95 (±0.15)</td><td>0.83</td><td>|0.06| < 2.26, do not reject Ho</td></tr>
<tr><td>SRM</td><td>35</td><td>0.07 (±0.93)</td><td>1.00 (±0.14)</td><td>0.87</td><td>|-0.09| < 2.26, do not reject Ho</td></tr>
<tr><td>SRM</td><td>40</td><td>-0.24 (±0.74)</td><td>1.08 (±0.11)</td><td>0.92</td><td>|-0.25| < 2.26, do not reject Ho</td></tr>
</table>

Table 15. Computed Regression Equations and Paired t-test Results for Comparison of Average % Abundance of Individual Elements for Each Particle Grouping as Determined by SEM-EDX with SRM NIST–1648 Certified Quantities (Filter 14)

Samplers (n=10)		Y = mX + b		r^2	Paired t-test ($P \leq 0.05$)
Y NIST-1648	**X Groups of randomly selected particles**	**m (±SE)**	**b (±SE)**		**Ho: The means are equal** **Ha: The means are unequal** **reject if: |t stat| > t Critical two-tail**
SRM	5	-1.06 (±0.59)	1.73 (±0.13)	0.96	**|-1.81| < 2.26, do not reject Ho**
SRM	10	-0.71 (±0.57)	1.56 (±0.12)	0.96	**|-1.82| < 2.26, do not reject Ho**
SRM	15	-0.51 (±0.78)	1.49 (±0.16)	0.91	**|-1.71| < 2.26, do not reject Ho**
SRM	20	-0.55 (±0.93)	1.41 (±0.18)	0.88	**|-1.37| < 2.26, do not reject Ho**
SRM	25	-0.46 (±0.94)	1.44 (±0.19)	0.88	**|-1.50| < 2.26, do not reject Ho**
SRM	30	-0.57 (±0.90)	1.46 (±0.18)	0.89	**|-1.49| < 2.26, do not reject Ho**
SRM	35	-0.47 (±0.73)	1.41 (±0.14)	0.93	**|-1.60| < 2.26, do not reject Ho**
SRM	40	-0.59 (±0.69)	1.45 (±0.14)	0.93	**|-1.61| < 2.26, do not reject Ho**

7.4 Findings

Based on the experimental analysis from the laboratory injection tests, the following findings are presented:

1. Standard reference material (SRM NIST–1648 Urban Particulate Matter) was injected into the chamber and sampled at three points using two low volume MiniVols and one real-time Grimm particle analyzer. The resulting sampling demonstrated close agreement between the real-time particle analyzer mass concentration and the low

volume mass concentration over a 24-hour period ($r^2 = 0.94$ between low volume samplers and $r^2 = 0.95$ to 0.99 between low volume samplers and Grimm). The total mass of SRM injected was not fully collected in the chamber likely due to incomplete mixing and rapid settling. Most importantly, similar amounts of SRM were collected by each low volume sampler during the injection tests.

2. An important aspect in demonstrating that low volume sampling/individual particle analysis is a viable alternative for airborne particulate matter source apportionment is its ability to quantify the abundance of elements present in particles collected:
    a. Filter samples of the SRM collected with the low volume samplers in the chamber experiments were analyzed by individual particle analysis (SEM-EDX). Average elemental quantities (% abundance) based on this analysis were compared to certificate values of the SRM. Results showed that SEM-EDX analysis of 10 randomly selected particles on a filter could detect comparable elemental quantities compared to SRM certificate values.
    b. Filters sample of SRM collected with the low volume samplers were analyzed by individual particle analysis (SEM-EDX) and bulk analysis (ICP-MS), respectively. Average % abundance of individual elements based on SEM-EDX analysis of 10 randomly selected particles on a filter and ICP-MS measurements were shown to be comparable.

These findings support that the individual particle analysis method can provide representative quantitative data on elements (i.e. % abundance) when combined with low volume sampling of airborne particulate matter.

3. Another important aspect in demonstrating that low volume sampling/individual particle analysis is a viable alternative for airborne particulate matter source apportionment was establishing the minimum number of particles collected on a filter to be subjected to individual particle analysis. Results supported that SEM-EDX analysis of a minimum of 10 randomly selected particles within a filter area adequately represented elemental quantities of up to 40 randomly selected particles within the filter area for SRM collected by low volume samplers. Further, SEM-EDX analysis of a minimum of 10 randomly selected particles within a filter area could adequately represent elemental quantities of the SRM injected into the chamber.

Based on these findings it was recommended that no less than 10 randomly selected particles should be analyzed within a 13 mm diameter filter area for low volume sampling/individual particle analysis applications.

8. FIELD ELEMENTAL STUDY

8.1 Field Collection Tests in Edmonton

Duplicate ambient PM_{10} samples were collected over 24-hours using a PM_{10} sampling head on low volume MiniVols according to Table 16. From these tests, a total of twenty filters were collected. Two additional blank samples were also collected one from each sampler. These samples were collected based on an ongoing sampling program at an industrial site in northwest Edmonton, AB. Samples were collected from this site to aid the understanding of source influences at the location and to further test low volume sampling and SEM-EDX analysis protocols in the field.

Table 16. PM_{10} Mass Concentration Results from Field Study

Sample Date	Minivol 2127 µg/m^3	Minivol 2201 µg/m^3
July 19, 2002	9.3	9.7
July 31, 2002	10.6	14.5
August 12, 2002	16.0	15.2
August 24, 2002	10.6	15.1
September 5, 2002	15.4	18.4
October 12, 2002	2.7	3.0
November 10, 2002	9.1	10.4
November 16, 2002	25.3	26.1
November 28, 2002	25.3	24.8
December 22, 2002	40.4	36.9

8.1.1 Ambient Mass Concentrations

The mass concentrations from the 10 24-hour average tests of low volume samplers are compared in Table 16. Figure 28 shows the relative agreement with 24-hour average mass concentrations for the low volume samplers. Similar to the laboratory tests, a filter from each low volume sampler was destined for elemental analysis to examine how well the SEM-EDX technique would compare with an accepted analysis technique (ICP-MS) under ambient conditions. Initially, there was interest in establishing whether similar mass concentrations were measured by each low volume sampler during the analysis.

Regression analysis was undertaken to compare the 24-hour average mass concentration data collected from both samplers based on 10 field tests. These results are provided in Table 17. The coefficient of determination (r^2) value from this comparison was 96% suggesting good agreement among each sampler for measuring 24-hour average mass concentrations.

This was further confirmed by performing a paired t-test of measured 24-hour average mass concentrations determined from each sampler for all 10 field samples. Results shown in Table 17 indicated no statistical difference in the collection ability of each sampler ($P \leq 0.05$).

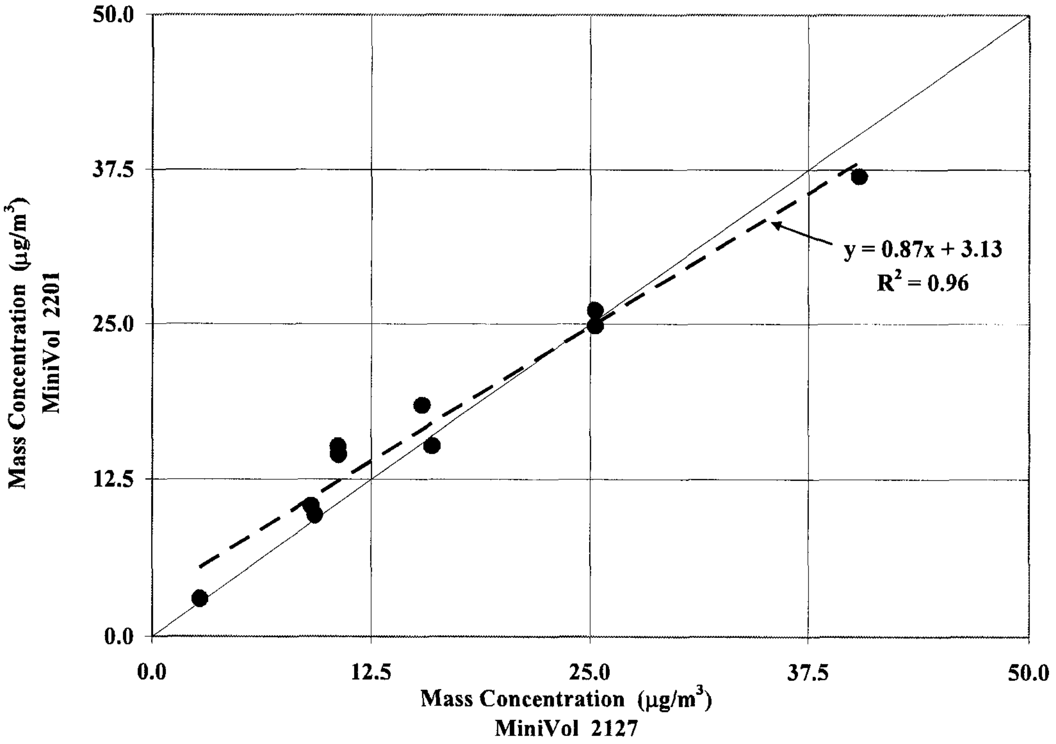


Figure 28. Comparison of Mass Concentrations from Low Volume Samples collected with Low Volume Samplers in the Field Study

Table 17. Regression and Paired t-Test Results from 10 Field Samples collected with Low Volume Samplers in the Field Study

Samples (n=10)		Y = mX + b		r^2	Paired t-test ($P \le 0.05$)
X	Y	**m (±SE)**	**b (±SE)**		**Ho: The means are equal** **Ha: The means are unequal** **reject if: $\lvert t \text{ stat}\rvert > t$ Critical two-tail**
MiniVol 2127	MiniVol 2201	0.87 (±0.06)	3.13 (±1.15)	0.96	**$\lvert 1.25\rvert < 2.26$** **do not reject the hypothesis**

8.2 Elemental Analysis

8.2.1 Qualitative Information from Individual Particle Analysis

A categorical summary of particle properties was derived based on shape and surface texture (morphology), and elemental composition using descriptors described in Chapter 2. This information was used to aid in classifying non-homogeneous PM_{10} samples collected at the Edmonton industrial site. Information obtained from SEM (i.e. shape and surface texture properties) can provide additional information that chemical analysis alone cannot. For example, this information can be used to distinguish between biological particles (e.g. spores, plant fragments, insect fragments) and non-biological particles (e.g. combustion soot). SEM pictures of each type of classified particle are presented in Figure 29 to Figure 43 and corresponding EDX results are presented in Table 18 to Table 30.

Similar to the multiple particle tests conducted in Chapter 7, a minimum of 40 particles were analyzed per filter, with which only 10 with a valid EDX trace (e.g. not biological) were randomly selected to obtain an overall elemental average. From this analysis a total of 441 particles were analyzed by SEM-EDX from the 10 duplicate field samples collected over six months (July to December 2002) at the industrial site.

Using shape and surface texture properties (morphology) obtained from examination of SEM results and elements identified through EDX, particles were classified based on sources. This exercise would not be possible using analytical techniques alone. These particle classification results are summarized in Table 31. This classification was based solely on individual particles identified and classified through SEM-EDX.

As this classification was based solely on identification of individual particles based on SEM-EDX, it is proposed that it would not be necessary to analyze a large number of filters to arrive at this classification. Ideally, thorough analysis of one representative filter sample should be able to provide a preliminary indication of source types provided that enough individual particles are considered in the analysis.

In terms of what was observed during this exercise, it was noted that at times there were large numbers of oil droplets covering a vast majority of the filter (>50% of the surface covered). These oil droplets would contribute substantially to the total number of individual particles present on the filter and they were typically present in much higher quantities than what is indicated in Table 31. This was also found with biological particles, in which more biological particles (>25% of the surface covered) were present than what was analyzed and indicted in Table 31.

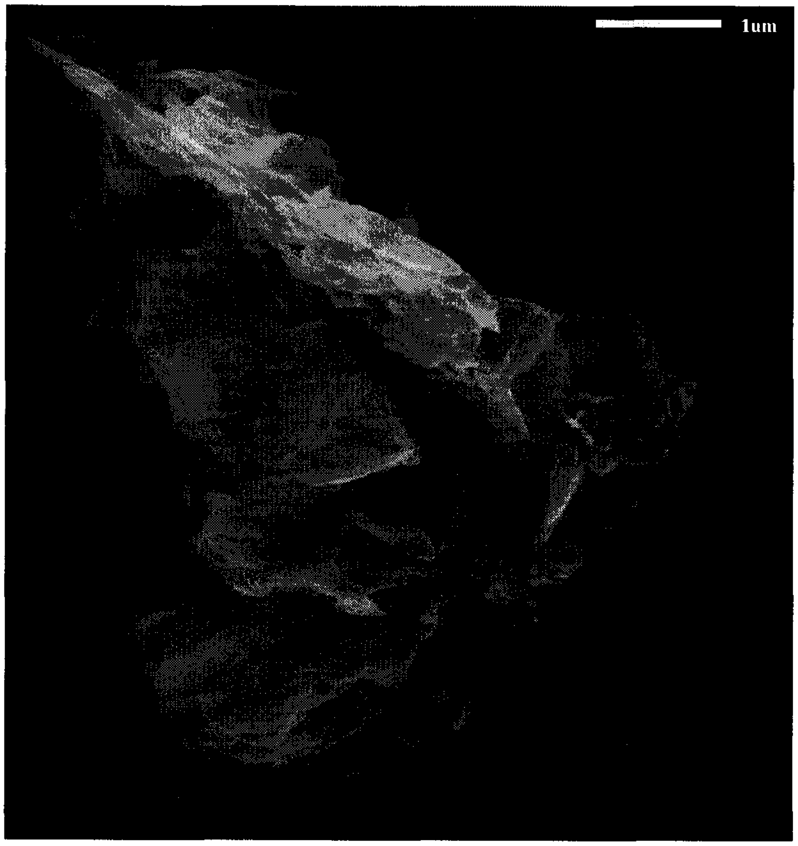


Figure 29. SEM Picture of an Agglomerated Crustal Silica Particle

- Agglomerated crustal silica particle which is non-spherical, ridged, and primarily comprised of Si, with varying amounts of other crustal elements.

Table 18. Corresponding EDX Elemental Scan of an Agglomerated Crustal Silica Particle

Library Standards: /imix/spectra/system standards (LDL 0.1%)
Accelerating Voltage 20 keV
Takeoff Angle 56.8 degrees

Elements	wt%
Si	82.6
Ca	2.1
K	2.7
Mn	0.8
Fe	1.9
Ni	2.5
Zn	3.9
Al	1.7
Cd	1.8

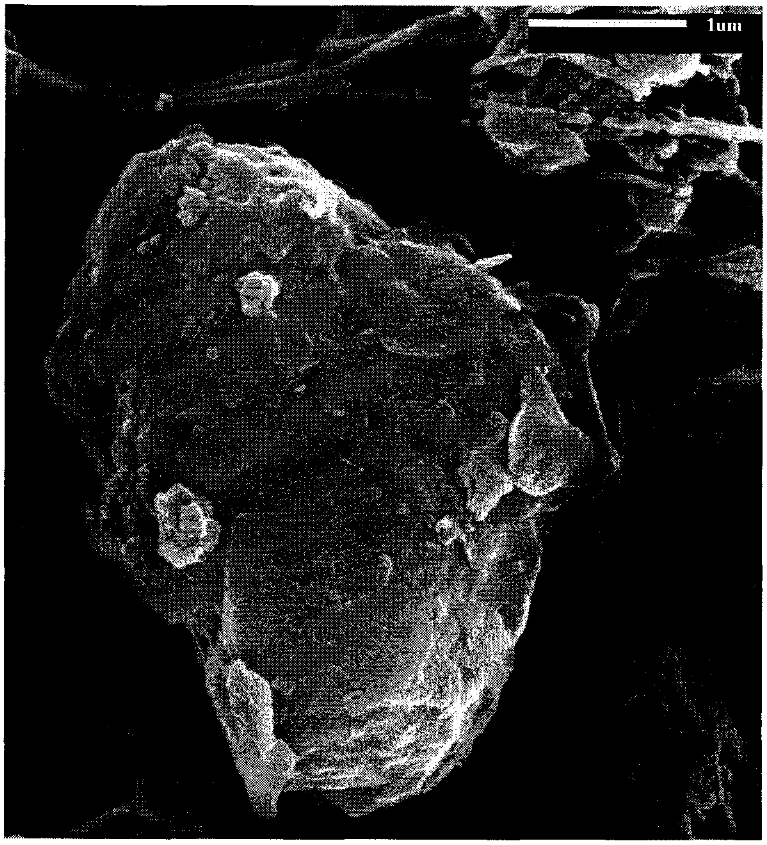


Figure 30. SEM Picture of a Crustal Silica Particle

- Crustal silica particle which is non-spherical, ridged, and primarily comprised of Si, with varying amounts of other crustal elements.

Table 19. Corresponding EDX Elemental Scan of a Crustal Silica Particle

Library Standards: /imix/spectra/system standards (LDL 0.1%)

Accelerating Voltage	20 keV
Takeoff Angle	56.8 degrees

Elements	wt%
Si	91.1
Mg	1.2
Ca	0.6
K	1.1
Mn	0.5
Fe	2.2
Cu	1.7
Al	1.3
Cl	0.3

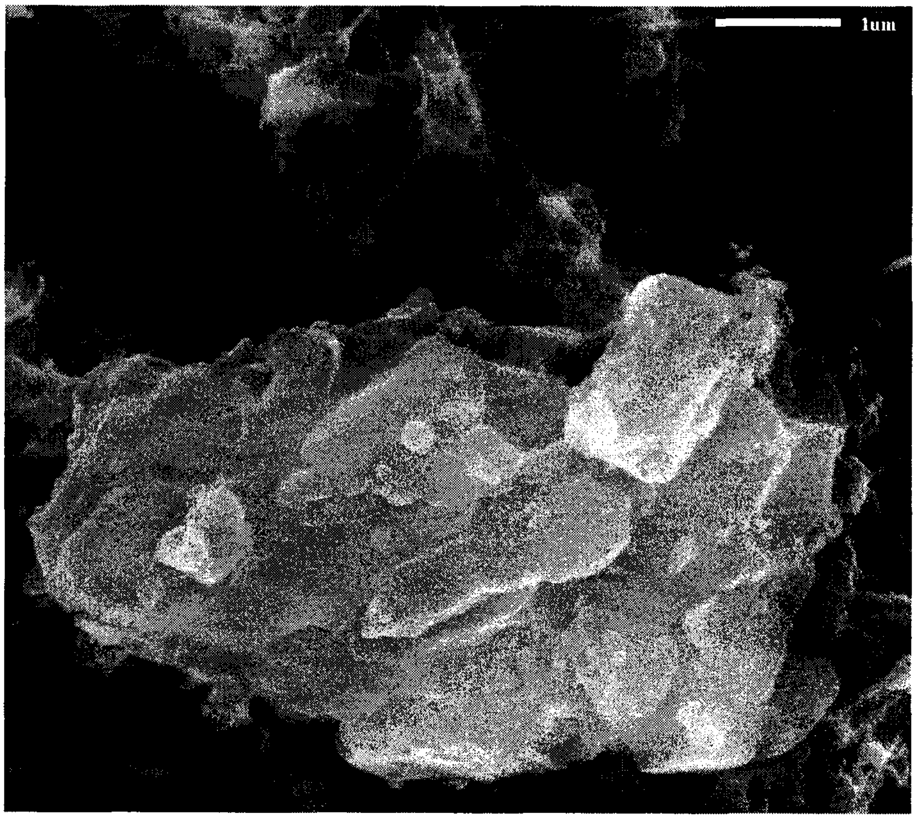


Figure 31. SEM Picture of a Crustal Clay Particle – Primarily Ca

- Crustal clay particle which is non-spherical, platy, and primarily comprised of Si and Ca with varying amounts of other crustal elements.

Table 20. Corresponding EDX Elemental Scan of a Crustal Clay Particle (Ca)

Library Standards: /imix/spectra/system standards (LDL 0.1%)

Accelerating Voltage	20 keV
Takeoff Angle	56.8 degrees

Elements	wt%
Si	16.5
Na	2.6
Mg	2.6
Ca	64.6
K	0.6
V	0.7
Cr	0.6
Fe	2.1
Co	0.6
Cu	0.7
Al	1.2
Pb	6.9

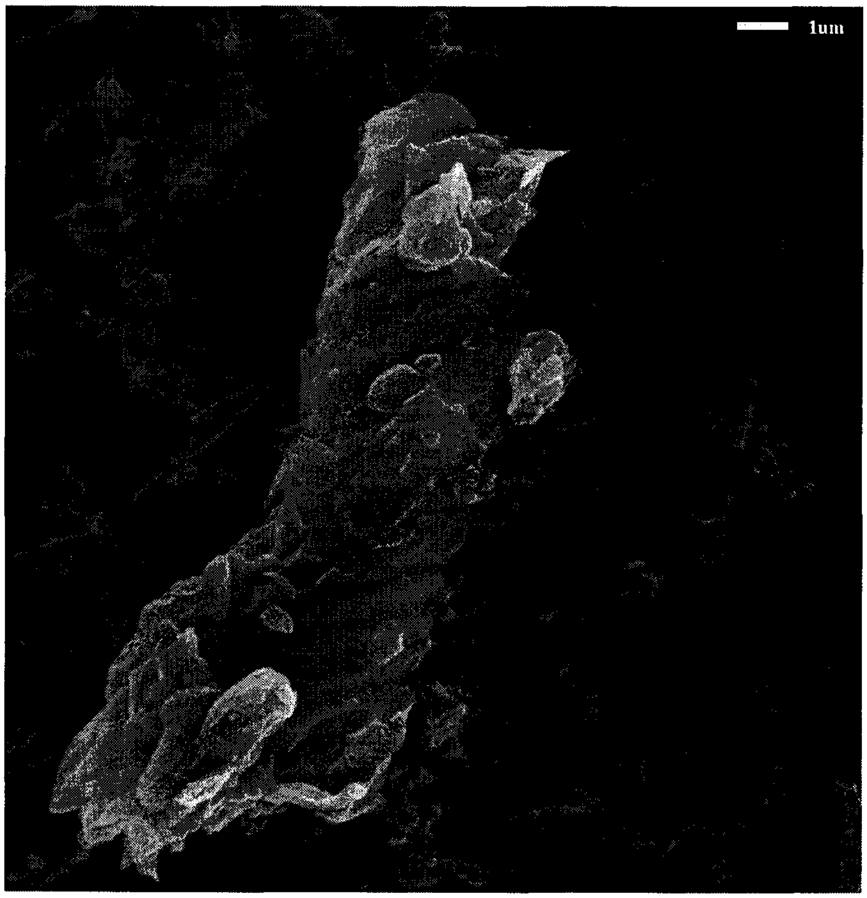


Figure 32. SEM Picture of a Crustal Clay Particle – Primarily Si

- Crustal clay particle which is non-spherical, platy, and primarily comprised of Si and Ca with varying amounts of other crustal elements.

Table 21. Corresponding EDX Elemental Scan of a Crustal Clay Particle (Si)

Library Standards: /imix/spectra/system standards (LDL 0.1%)

Accelerating Voltage	20 keV
Takeoff Angle	56.8 degrees

Elements	wt%
Si	47.0
Mg	2.9
Ca	8.2
K	4.0
Fe	13.0
Ni	0.6
Cu	3.3
Al	16.0
Cd	2.6
Cl	1.2

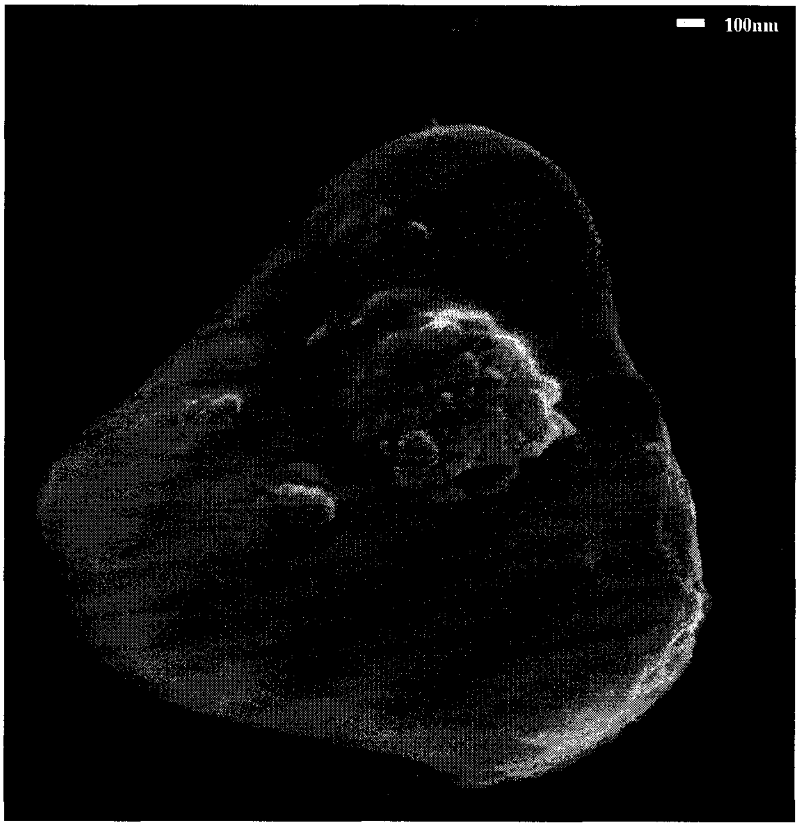


Figure 33. SEM Picture of a Salt Particle (November Sample)

- Salt particles appear as a non-specific shape, and are primarily comprised of Na and Cl with minor amounts of other crustal elements.

Table 22. Corresponding EDX Elemental Scan of a Salt Particle in November

Library Standards: /imix/spectra/system standards (LDL 0.1%)

Accelerating Voltage	20 keV
Takeoff Angle	56.8 degrees

Elements	wt%
Na	38.7
Mg	4.3
Ca	0.9
K	1.6
Cu	2.6
Al	0.3
Pb	3.1
Cd	1.7
Cl	46.3

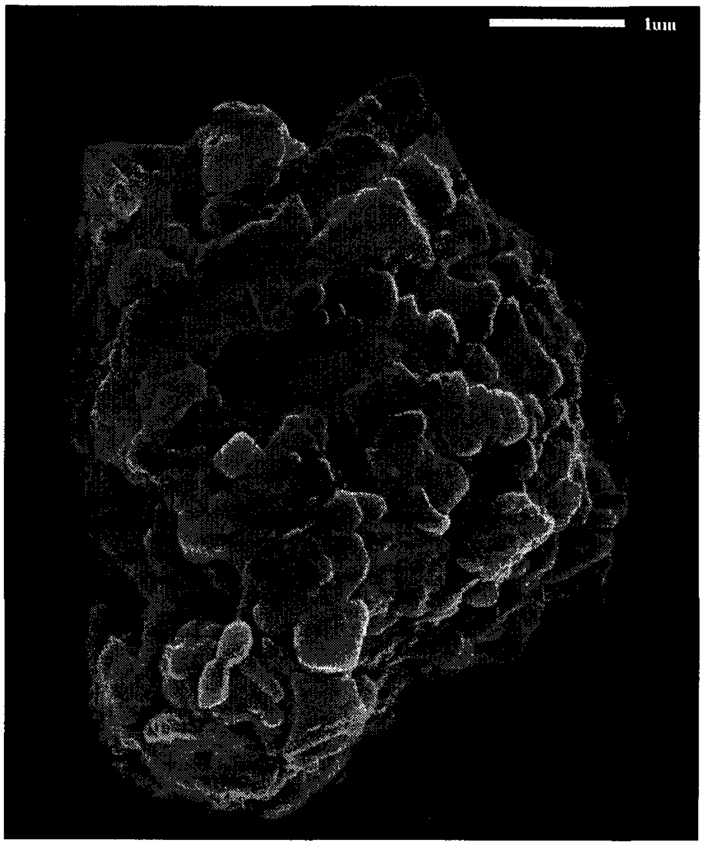


Figure 34. SEM Picture of a Salt Particle (December Sample)

- Salt particle mixed with silica, primarily comprised of Na and Cl with varying amounts of other crustal elements.

Table 23. Corresponding EDX Elemental Scan of a Salt Particle in December

Library Standards: /imix/spectra/system standards (LDL 0.1%)
Accelerating Voltage 20 keV
Takeoff Angle 56.8 degrees

Elements	**wt%**
Si	22.0
Na	28.2
Ca	2.0
K	1.7
Fe	6.4
Cu	2.4
Zn	0.9
Al	5.4
Pb	7.7
Cl	20.5

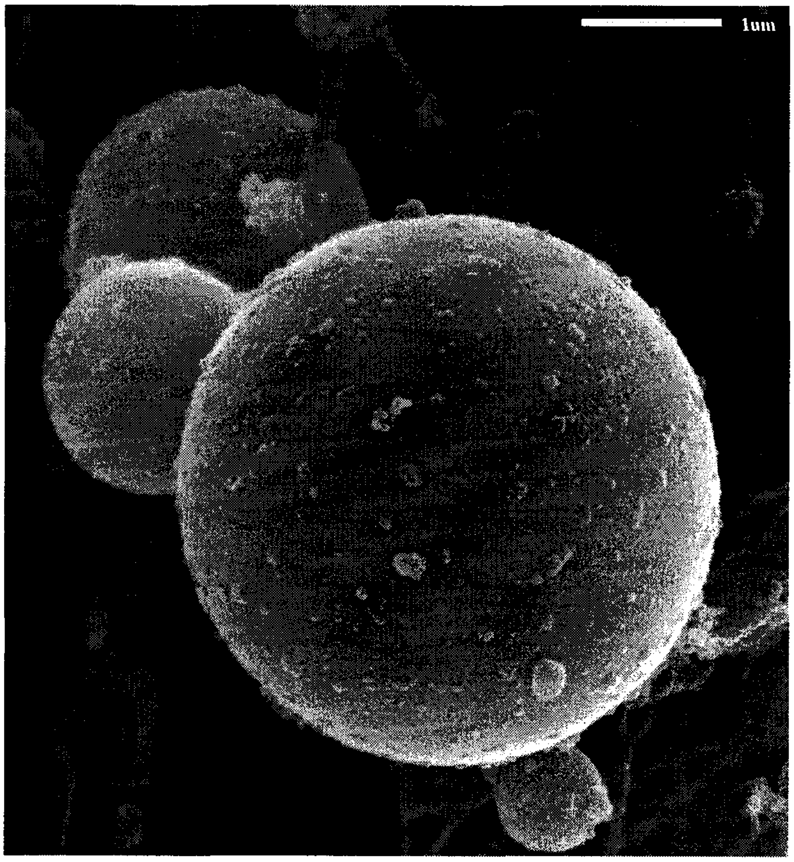


Figure 35. SEM Picture of Industrial Exhaust - Flyash

- Flyash particles that are very small, smooth, and round (excellent tracers from industry); and primarily comprised of Si and Al with trace amounts of As and Pb.

Table 24. Corresponding EDX Elemental Scan of Industrial Exhaust - Flyash

Library Standards: /imix/spectra/system standards (LDL 0.1%)

Accelerating Voltage	20 keV
Takeoff Angle	56.8 degrees

Elements	wt%
Si	55.3
Na	6.7
Mg	1.4
Ca	1.5
K	3.5
Ti	0.8
Fe	3.9
As	1.7
Al	20.3
Pb	3.0
Cd	0.9

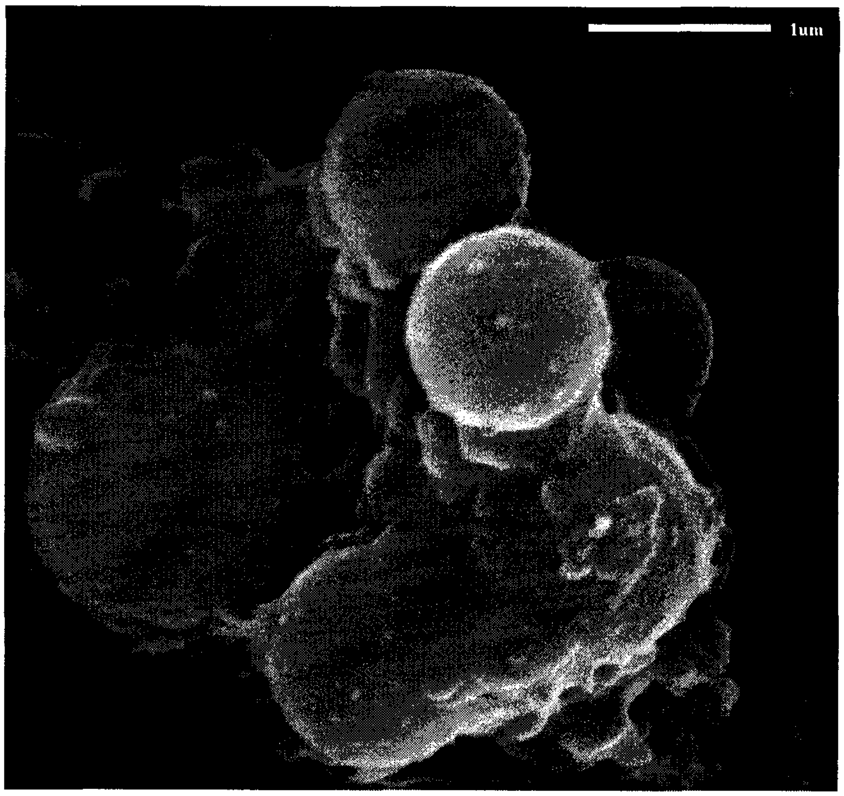


Figure 36. SEM Picture of Industrial Exhaust – Sintered Particle

- Industrial exhaust of a sintered particle appears as a cluster of melted particles with varying elemental signatures depending upon industrial source.

Table 25. Corresponding EDX Elemental Scan of Industrial Exhaust – Sintered Particle

Library Standards: /imix/spectra/system standards (LDL 0.1%)
Accelerating Voltage 20 keV
Takeoff Angle 56.8 degrees

Elements	wt%
S	21.1
Si	33.9
Na	0.8
Mg	1.4
Ca	17.8
K	3.0
Ti	0.6
Mn	0.6
Fe	4.4
Al	15.8
Cu	0.7

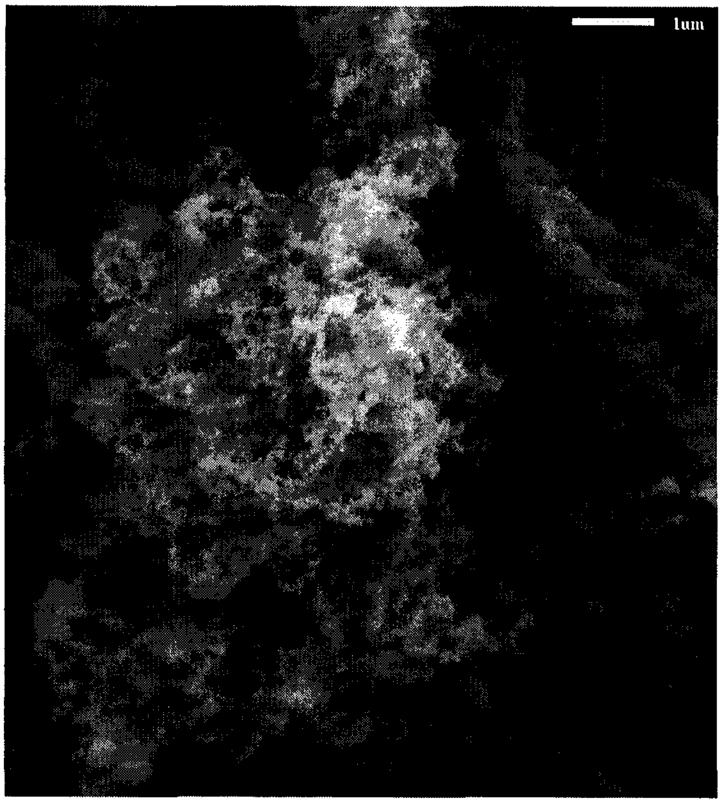


Figure 37. SEM Picture of a Combustion Particle (July Sample)

- Combustion particles with small loose porous structures (these particles can be difficult to scan with EDX due to their weak and porous structure).

Table 26. Corresponding EDX Elemental Scan of a Combustion Particle in July

Library Standards: /imix/spectra/system standards (LDL 0.1%)

Accelerating Voltage	20 keV
Takeoff Angle	56.8 degrees

Elements	wt%
Mg	15.1
K	1.2
Ti	2.1
Mn	4.0
Fe	3.0
Ni	2.7
Cu	24.7
As	46.9

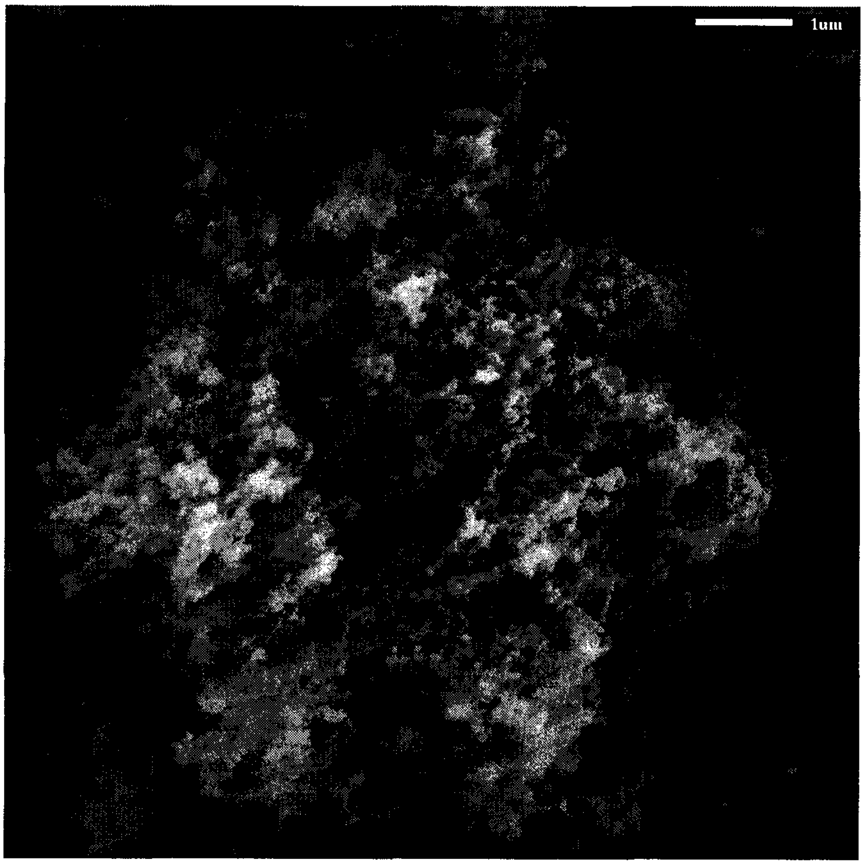


Figure 38. SEM Picture of a Combustion Particle (August Sample)

- Main constituents included Mg, K, Ti and Mn.

Table 27. Corresponding EDX Elemental Scan of a Combustion Particle in August

Library Standards: /imix/spectra/system standards (LDL 0.1%)

Accelerating Voltage	20 keV
Takeoff Angle	56.8 degrees

Elements	wt%
Mg	14.2
Ti	11.4
V	17.6
Mn	16.8
Fe	0.9
Ni	18.0
Cd	8.6
Cu	1.5
Pb	10.5

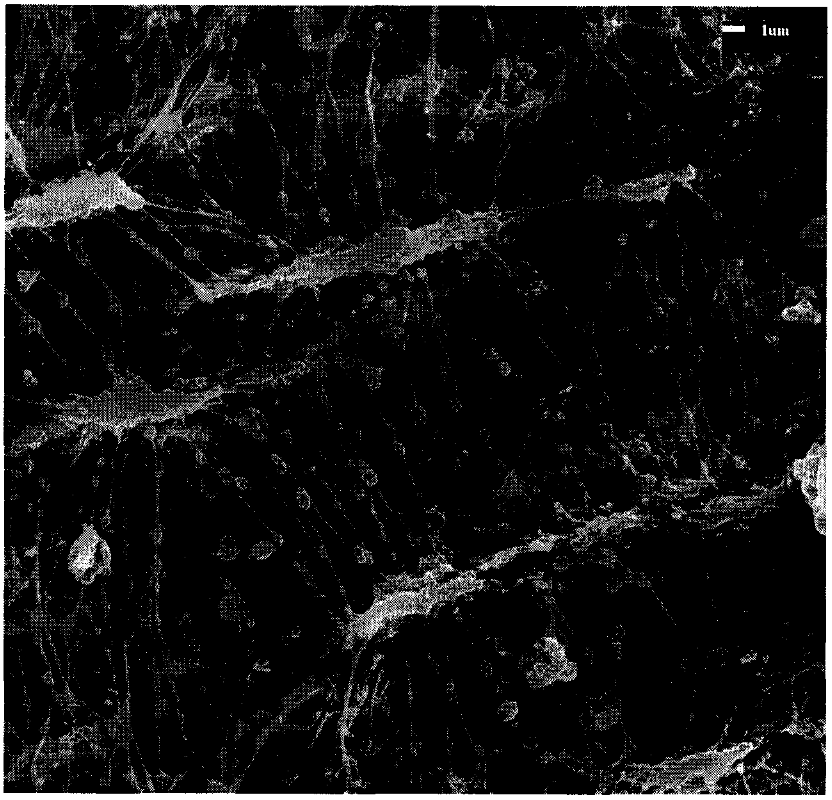


Figure 39. SEM Picture of Oil Droplets (November Sample)

- Oil droplets are small and smooth in appearance; these particles are extremely difficult to scan with EDX, based on minute sizes and tendency to deform when examined. These particles have been found to be related to vehicle emissions (Kindzierski et al, 2003; Braybrook, 2003)

Table 28. EDX Elemental Scan of an Oil Droplet in November

Library Standards: /imix/spectra/system standards (LDL 0.1%)
Accelerating Voltage 20 keV
Takeoff Angle 56.8 degrees

Elements	wt%
Mg	62.6
Ca	3.2
K	10.9
Ti	0.8
V	1.0
Cr	0.6
Mn	1.3
Fe	2.3
Cu	5.4
Cd	5.7
Cl	6.3

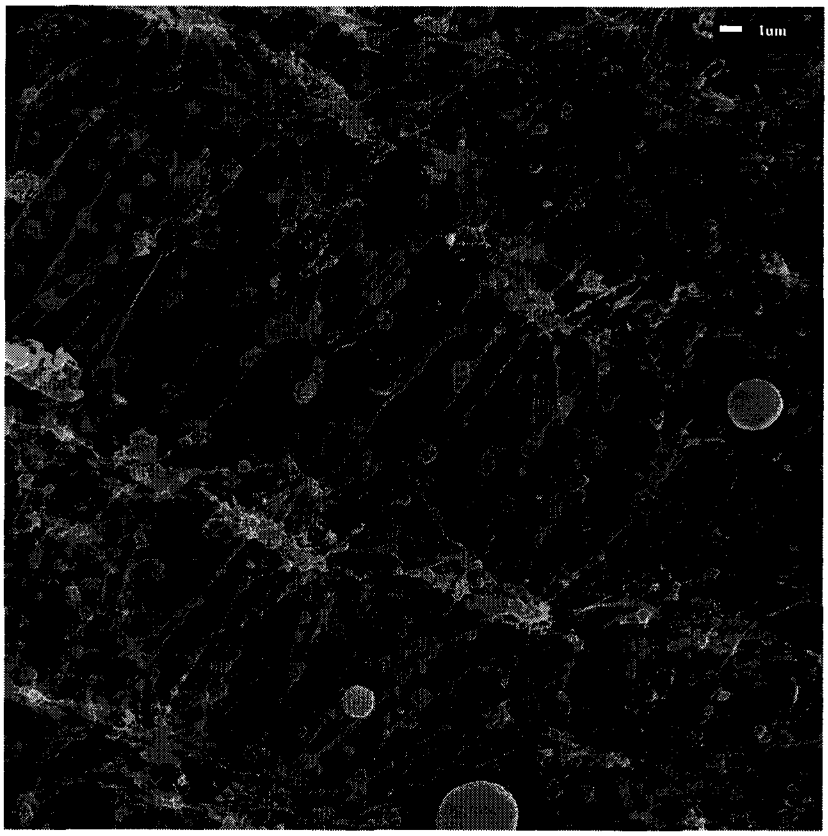


Figure 40. SEM Picture of Oil Droplets (December Sample)

- Main constituents included Carbon (not recorded), Mg, K, Cl, Cu, Ti and V.

Table 29. EDX Elemental Scan of an Oil Particle in December

Library Standards: /imix/spectra/system standards (LDL 0.1%)

Accelerating Voltage	20 keV
Takeoff Angle	56.8 degrees

Elements	wt%
Mg	20.4
Ti	7.1
Cr	7.1
Mn	1.7
Co	2.1
Cu	53.5
Cl	8.2

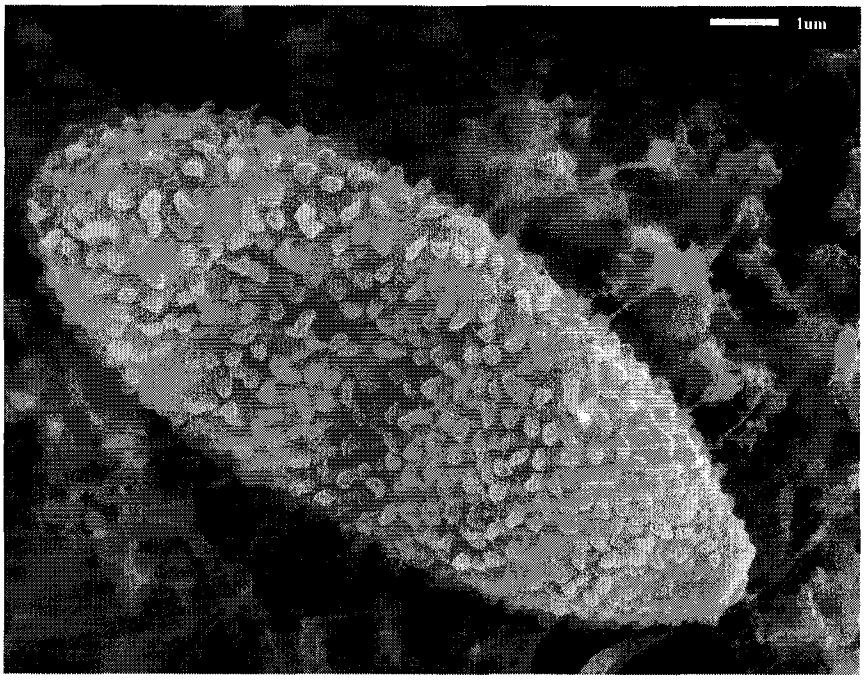


Figure 41. SEM Picture of an Organic Particle

- Biological particles are identifiable from their distinct shape and form. Elementally, the EDX is unable to quantify the composition of biological particles (EDX scan of organic particles appear with the same signature as the filter background).

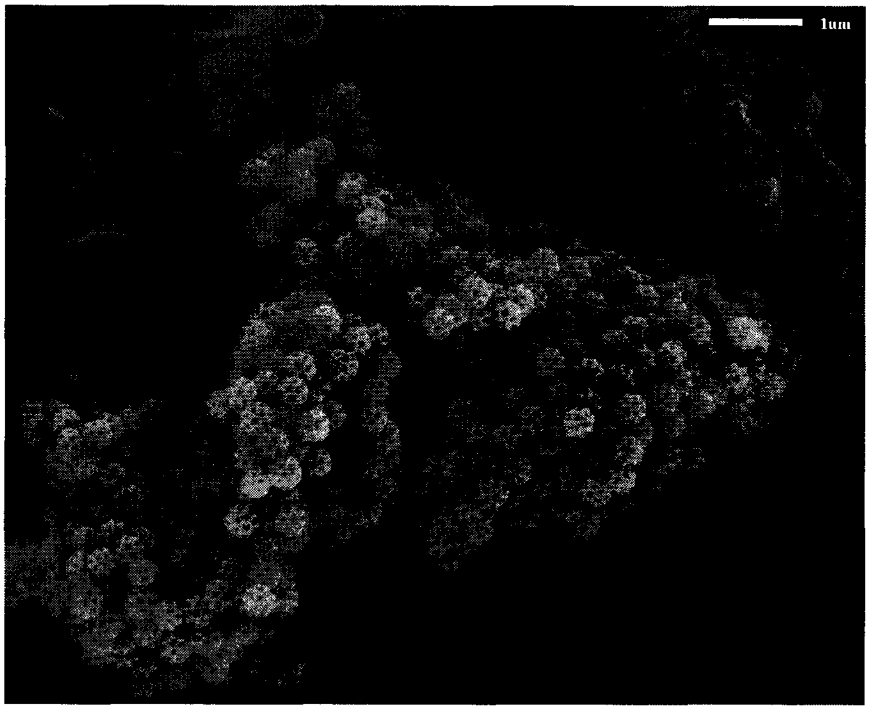


Figure 42. SEM Picture of Organic Particles

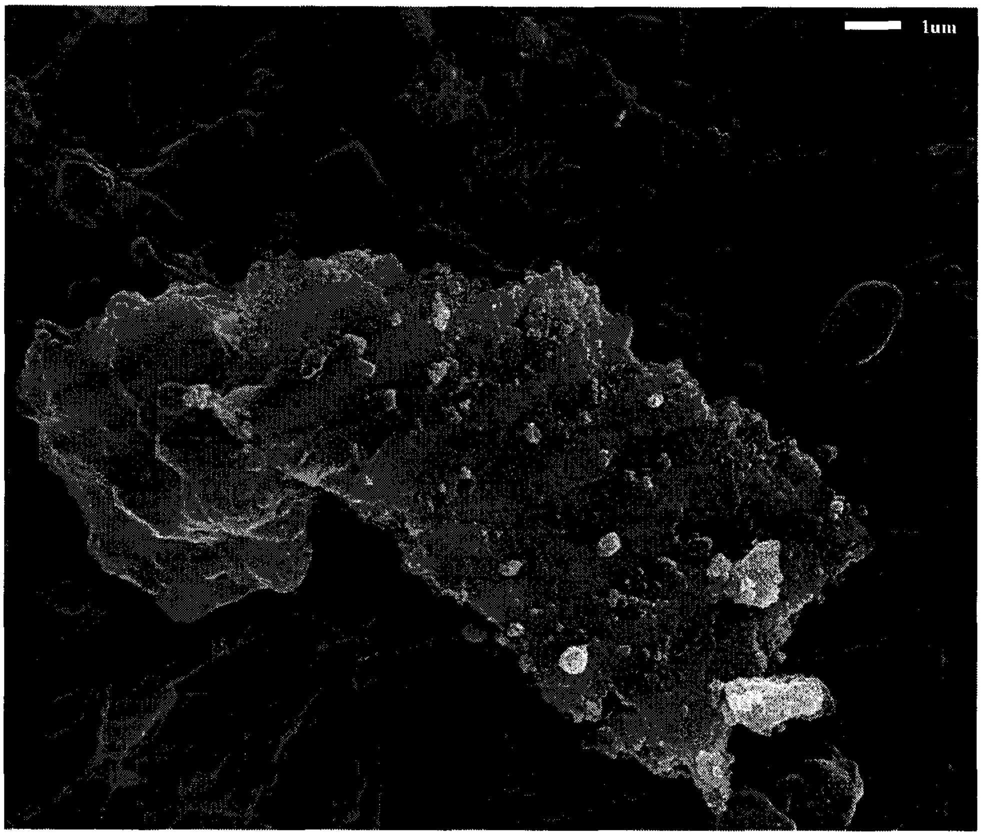


Figure 43. SEM Overview Picture of Rust Particle

- Most common type of particles classified as "other" found at this industrial site was rust particles that are comprised primarily of Fe.

Table 30. EDX Elemental Scan of a Rust Particle

Library Standards: /imix/spectra/system standards (LDL 0.1%)

Accelerating Voltage	20 keV
Takeoff Angle	56.8 degrees

Elements	wt%
Si	2.7
Mg	4.1
K	0.3
Ti	1.1
Mn	0.8
Fe	87.6
Co	1.4
Cu	1.0
Zn	0.3

Table 31. Summary of Particle Classifications based on SEM-EDX Analysis of 441 Particles collected during the Field Study

Particle Type	Descriptive Properties	July – September 5 filters	October – December 5 filters
Crustal	Silica	77	92
	Clay	76	53
	Salt	-	13
Industrial exhaust	Fly ash	3	8
	Sintered	2	-
Exhaust	Soot	16	6
	Oil droplets	12 (b)	28 (a)
Biological	Pollen, spores	34 (b)	4 (c)
	Fibrous	5	-
Other		3	9
TOTAL		228	213

(a) – particles analyzed by EDX only, however >50% surface area covered
(b) – particles analyzed by EDX only, however >25% surface area covered
(c) – only October sample contained organic particles, <25% surface area covered

The first detail noted from Table 31 was that crustal particles (silica, clay, salt) dominated and accounted for ~70% of particles identified at the industrial site over the sampling period (35% during July to September and 36% during October to December). Crustal silica and clay particles analyzed were the same in warmer months (17% silica and 17% clay) with no salt particles identified. Whereas in cooler months silica particle counts (21%) were greater than clay particle counts (12%). The presence of salt particles in cooler months was likely the result of localized sanding material being placed on roadways in the vicinity of the sampling site. The presence of crustal material on the filters was expected due to the dominance of open crustal material near the sampling location. This included open fields, dust piles, construction activities, road dust, and gravel dust.

Biological particles accounted for ~9% of the particles identified during July to September. During this time frame there were five filters analyzed and it was noted that the biological fraction in two of the filters had over 50% of the filter surface covered with biological particles, with the remaining three having over 25% of the surface covered with biological particles. Based on sampling in warmer periods this was an expected finding as other studies have also found that during warmer periods a large fraction of particulate matter sampled is comprised of biological materials (Hopke, 1985). During sampling in the cooler months (October to December) it was noted that the biological particles accounted for less than 1% of the total particles classified (by count), of which all were collected during the October sampling. The higher biological loading found during the warmer periods is primarily a result of biological activity from plants and insects compared to virtually no plant and insect activity in cooler months.

Another detail noted from Table 31 was the large numbers of small oil particles (droplets). During classification several oil droplets were analyzed in attempts to determine an elemental profile. During the cooler months these fine oil droplets tended to cover well over 50% of the filter surface (as can be seen in Figure 39 and Figure 40). After further investigation with site personnel, the high level of oil droplets were likely due to a greater frequency of localized (on-site) traffic during cooler months compared to warmer months at the industrial site where monitoring was conducted. In the warmer months the oil droplets and soot (vehicle combustion products) tended to cover ~6% of the filter surface, compared to in the cooler months the oil droplets and soot tended to cover ~8% of the filter surface. With the discrepancy between the combustion particles during the warmer and cooler periods it is believed that the combustion particles were more prevalent from increased localized traffic, during cooler periods.

The final classes of particles noted from the analysis are likely the most important particles types considering their anthropogenic origins. However, as can be observed in Table 31, they are only present in low counts relative to other particle classes described. These particles included flyash, industrial sintered particles, and rust fragments. Flyash particles are ideal tracers from industrial activities based on their unique and "un-natural" morphology, but these particles possess similar chemical properties as that of crustal mineral particles. Given such low counts of the particles (Table 31), a blind analysis technique (e.g. ICP-MS) would not necessarily be able to detect the presence of these flyash particles. This is not the case using SEM-EDX, which was clearly capable of identifying and classifying the presence of these particle types.

In addition to the flyash particles, sintered particles are also good tracers from industrial activities based on their morphology. The count of flyash and sintered particles identified was very low (1% in the warmer months and 2% in the cooler months). The importance of this finding is that SEM-EDX classification of these particles types (i.e. flyash and sintered particles) can potentially be used so that they may serve as tracers for activities at the industrial site where sampling was performed (cement manufacturing facility).

The rust fragments found during the analysis fell into the "other" category. These metal or rust fragments were more prevalent in the cooler months (2%) compared to warmer months (< 1%). Although unconfirmed, it was postulated that these fragments were more prevalent during cooler months based on increased local (on-site) traffic in the vicinity of the sampling site during this period.

8.2.2 Percent Weight of Elements from Individual Particle Analysis

Elemental quantities present in ambient samples collected and measured by SEM-EDX were compared to ICP-MS. This was done for elements that were recorded for both methods. These elements included: aluminum, iron, potassium, sodium, zinc, manganese, magnesium, chloride, titanium, silica, calcium, lead, chromium, copper, nickel, arsenic, vanadium, cobalt, and cadmium.

The mass concentration data reported by the ICP-MS method were transformed in order to compare the results by % abundance (equation 21). Figure 44 illustrates the average % abundance of 19 elements detected by both SEM-EDX and ICP-MS. Average % abundance shown in this figure was determined in a similar manner as the laboratory study:

- An assumption was made that ambient particles collected on the filter were distributed across the collection area.
- A small section of the filter, approximately 13 mm in diameter was considered in the analysis, of which a minimum of 10 particles within this area were randomly selected and subjected to SEM-EDX analysis.
- Average % abundance measured by SEM-EDX was based on an average of 10 randomly analyzed individual particles from each test. The wt% was transformed according to equation 20.
- The % abundance for ICP-MS was calculated according to equation 21.

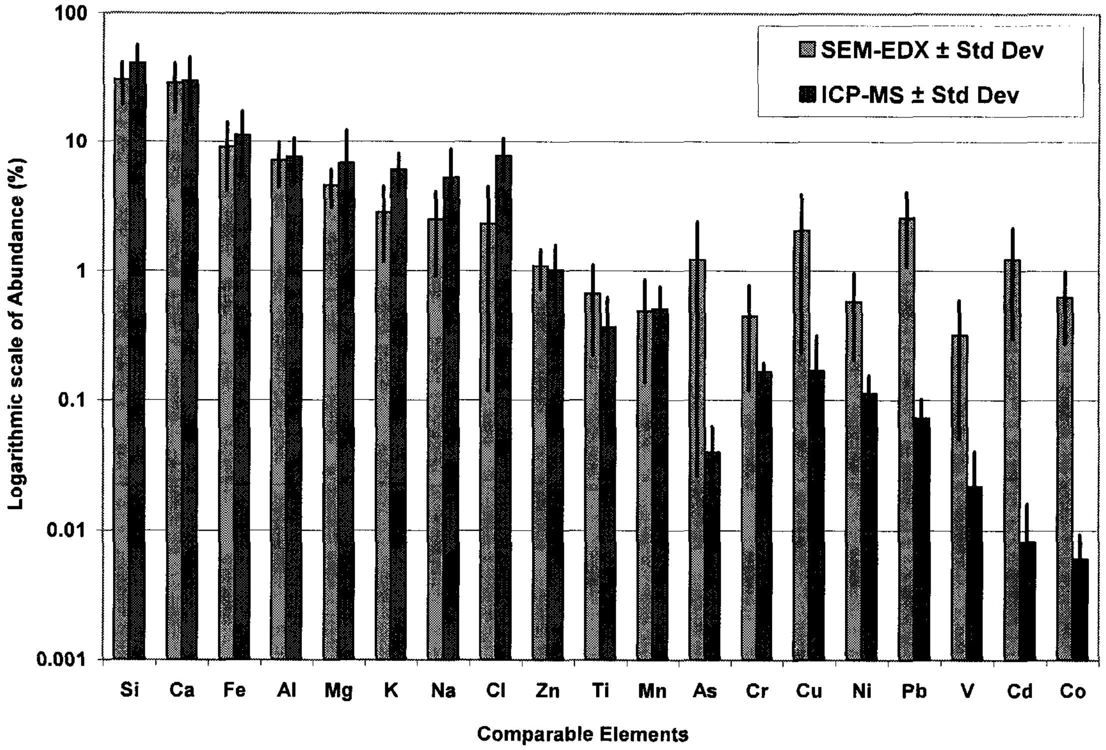


Figure 44. Comparison of Elemental Quantities by % Abundance from ICP-MS and SEM-EDX (average of 10 filter samples)

Average % abundance measured by SEM-EDX was regressed against % abundance measured by ICP-MS (Table 32). The coefficient of determination (r^2) ranged from 66% to 97% with the exception of one sampling event having an r^2 = 18%. These filter samples were collected in October yielding a 24-hour mass concentration of 3.0 μg/m^3 (MiniVol 2201) and 2.7 μg/m^3 (MiniVol 2127). These corresponding low particle loadings on the filters may have resulted in detection limitations with ICP-MS analysis. Results of the regression analysis (Table 32) indicated reasonable agreement between filter samples analyzed using the SEM-EDX method compared to ICP-MS method for the remaining nine filter samples. In addition, a paired t-test was performed to examine the extent of agreement between average % abundance measured by SEM-EDX and ICP-MS

Table 32. Computed Regression Equations and Paired t-test Results for Comparison of Average % Abundance from ICP-MS with SEM-EDX (average of 10 randomly selected particles)

		Y = mX + b Y = ICP-MS X = SEM-EDX		r^2	Paired t-test (at 5% significant level)
test	**Comparable elements**	**m (±SE)**	**b (±SE)**		**Ho: The means are equal** **Ha: The means are unequal** **reject if: |t stat| > t Critical two-tail**
1	Si, Ca, Al, Mg, Fe, K, Ni, Zn, As, V, Mn, Co, Cr, Cd, Pb, Cu, Ti	1.00 (±0.18)	-0.38 (±1.91)	0.68	|0.24| < 2.12, do not reject
2	Ca, Si, Al, Fe, Cl, K, Mg, Na, Ti, Mn, Cr, Zn, Pb, Cu, V, Co, As	0.89 (±0.16)	0.65 (±1.86)	0.66	|0.03| < 2.11, do not reject
3	Si, Ca, Fe, Al, K, Na, Mg, Mn, Zn, Ti, Cr, Cu, Pb, As, V, Co	1.40 (±0.14)	-2.26 (±1.72)	0.87	|0.03| < 2.12, do not reject
4	Si, Ca, Fe, Al, K, Mg, Na, Mn, Zn, Ti, Ni, Cu, Pb, As, Cr, V, Co, Cd	1.06 (±0.05)	-0.35 (±0.54)	0.97	|0.12| < 2.10, do not reject
5	Si, Ca, Al, Fe, K, Mg, Na, Ti, Mn, Zn, Cr, Pb, Cu, V, Ni, Co, As, Cd	1.03 (±0.05)	-0.15 (±0.60)	0.96	|0.03| < 2.10, do not reject
6	Mg, K, Na, Fe, Al, Zn, Mn, Cu, As, V, Cd	1.04 (±0.70)	4.28 (±3.57)	0.18	|1.73| < 2.20, do not reject
7	Ca, Si, Fe, Na, Cl, Al, Mg, K, Zn, Mn, Ti, Cu, Pb, Ni, As, V, Cd, Co	0.95 (±0.08)	0.30 (±0.81)	0.91	|0.02| < 2.11, do not reject
8	Ca, Mg, Fe, K, Al, Zn, Na, Ti, Mn, Cu, Pb, Ni, V, Co, Cd	1.14 (±0.11)	1.28 (±1.34)	0.90	|1.50| < 2.11, do not reject
9	Si, Ca, S, Cl, Na, Fe, Al, K, Mg, Zn, Mn, P, Ti, Cr, Cu, Pb, Ni, As, V, Co, Cd	0.84 (±0.12)	0.72 (±1.04)	0.73	|0.03| < 2.11, do not reject
10	Ca, Fe, Al, K, Mg, Zn, Ti, Mn, Cu, Pb, As, V	1.31 (±0.12)	0.20 (±1.41)	0.92	|1.43| < 2.11, do not reject

for all comparable elements. Results of the paired t-test found no differences between the two methods ($P \leq 0.05$). Results from this comparison between % abundances of SEM-EDX and ICP-MS demonstrated that comparable findings were possible with analysis of non-homogeneous substances collected from ambient field studies.

A further analysis was performed to compare individual % elemental abundances found from SEM-EDX and ICP-MS (Table 33). This was accomplished by performing paired t-tests of individual % elemental abundances found on each of the filter and based on the following conditions:

- Elemental concentrations determined by SEM-EDX versus elemental concentrations determined by ICP-MS.
- Percent abundance for SEM-EDX determined by equation 20
- Percent abundance for ICP-MS determined by equation 21

Comparison of Individual % Abundances for SEM-EDX versus ICP-MS. Results for these tests are summarized in Table 33 and discussed below. Nineteen elements were measured by SEM-EDX and ICP-MS for comparison analysis (aluminum, iron, potassium, sodium, zinc, manganese, magnesium, chloride, titanium, silica, calcium, lead, chromium, copper, nickel, arsenic, vanadium, cobalt, and cadmium).

Results (Table 33) indicated that % abundances for the elements silica, calcium, iron, aluminum, magnesium, potassium, sodium, zinc, titanium, and manganese were not significantly different ($P \leq 0.05$). However, it was found that % abundances for eight trace elements (arsenic, chromium, cadmium, lead, copper, nickel, vanadium, and cobalt) were significantly different ($P \leq 0.05$). Several elements (chloride, phosphorus and sulfur) were not compared due to ICP-MS inability to quantify these elements in more than three filter samples.

Table 33. Paired t-test Comparison of % Elemental Abundances Determined by ICP-MS and SEM-EDX (average of 10 randomly selected particles)

Paired t-test

SEM-EDX comprised of an average of 10 random particles

Ho: The means are equal; Ha: The means are unequal

reject if: $|t_{calculated}| > t_{critical}$ (using a two-tail test)

10 tests	SEM-EDX to ICP-MS
	$t_{critical}$ at 5% significance level
Si (n=7)	|1.60| < 2.45, do not reject
Ca (n=9)	|0.01| < 2.31, do not reject
Fe (n=10)	|0.93| < 2.26, do not reject
Al (n=10)	|0.76| < 2.26, do not reject
Mg (n=10)	|0.79| < 2.26, do not reject
K (n=10)	|1.65| < 2.26, do not reject
Na (n=9)	|1.53| < 2.31, do not reject
Zn (n=10)	|0.08| < 2.26, do not reject
Ti (n=9)	|1.31| < 2.31, do not reject
Mn (n=10)	|0.12| < 2.26, do not reject
As (n=9)	|2.84| > 2.31, cannot accept
Cr (n=6)	|2.64| > 2.57, cannot accept
Cd (n=7)	|3.41| > 2.45, cannot accept
Cu (n=10)	|3.40| > 2.26, cannot accept
Ni (n=7)	|3.99| > 2.45, cannot accept
Pb (n=9)	|4.70| > 2.31, cannot accept
V (n=10)	|3.53| > 2.26, cannot accept
Co (n=8)	|6.39| > 2.36, cannot accept
Cl (n=3)	Only 3 samples quantified by ICP-MS, comparison not applicable
S (n=1)	Only 1 sample quantified by ICP-MS, comparison not applicable
P (n=1)	Only 1 sample quantified by ICP-MS, comparison not applicable

These findings indicate that SEM-EDX and ICP-MS quantified similar % abundances for the 10 most dominant elements (e.g. refer to Figure 44). However, SEM-EDX analysis was reporting higher % abundances for eight trace elements compared to % abundances reported by ICP-MS. This was considered an important finding as these trace elements are considered to be key markers in relating airborne particulate matter to anthropogenic (man-caused) sources such as residual oil (V, Ni) and oil fired power plants (Pb) (Table 7).

This deficiency was further investigated to identify the cause of the discrepancy between the analytical results from each method. The first item investigated was whether there were insufficient sample masses collected with the MiniVols for ICP-MS analysis. This was investigated by examining one years worth of NAPS PM_{10} data collected in Edmonton at the Odyssium (112 Avenue - 142 Street) with a FRM sampler (Partisol, Rupprecht & Patashnick Co., Inc., Albany, NY) during 1993 and analyzed for elements using ICP-MS by the Alberta Research Council. The purpose of this investigation was to identify whether the trace elements arsenic, chromium, cadmium, lead, copper, nickel, vanadium, and cobalt were present in sufficient quantities in Edmonton's airshed to enable detection by the ICP-MS method.

Amounts of Mass Collected

From the 10 field samples collected and analyzed by ICP-MS, five filter samples had mass gains of less than 0.1 mg collected over 24-hours of sampling. Four additional filter samples had mass gains of less than 0.2 mg, and one filter sample had a mass gain of less than 0.3 mg, all collected over 24-hours.

The ICP-MS is reported to be ideal for quantification of elemental masses typically in the range of 0.1 to 1 mg per filter (Feng, 2004). Although unconfirmed, what may have occurred is that the MiniVol filter samples did not accumulate sufficient particle masses to reliably exceed the ideal sample collection mass range needed for ICP-MS analysis of these eight trace elements. Whereas, these small masses (i.e. 0.1 to 1 mg per filter) are more than sufficient for SEM-EDX – which requires as little as 1 pg of elemental material for analysis (JEOL, 1997). In addition, small masses collected on a filter correspond to low loadings of individual particles and large spaces between these particles – allowing for easier morphological identification through SEM.

Based on the above premise that limited masses collected through low volume sampling may have been inadequate for ICP-MS analysis, the NAPS PM_{10} sample dataset were further reviewed. These results are derived using FRM sampling equipment that draws air at a rate of 16.67 litres per minute (24 m^3 of air over 24-hours at 25°C and 1 atm). The objective of this review was to determine if these samplers collected sufficient particle masses (ng/filter) for ICP-MS analysis of the eight trace elements, and to identify whether low volume sampling rates (5 litres per minute or 7.2 m^3 of air over 24-hours at 25°C and 1 atm) would be able to similarly collect sufficient particle masses (ng/filter) for ICP-MS analysis.

This latter objective was determined by using the following relationship to estimate theoretical mass collected (equation 22) using low volume sampling based upon the FRM NAPS sampling results and making comparisons with the reported detection limit for ICP-MS (Table 34).

theoretical elemental mass concentration in ng / filter (at 5 Lpm) =

$$\left(\text{elemental mass concentration in ng / filter (at 16.67 Lpm)} \times \frac{5\ \text{Lpm}}{16.67\ \text{Lpm}}\right) \quad \ldots\ldots\ldots(22)$$

Table 34. ICP-MS Detection Limits for Selected Trace Elements

Trace Elements (ng/filter)	As	Pb	V	Cd	Cu	Ni	Cr	Co
Method Detection Limits (MDL)	0.4	4	0.2	1	8	5	5	1

Based on analysis of the NAPS PM_{10} sample dataset (n=62), the following results were observed from the FRM sampling (Table 34):

- As, Pd, and V results indicated 23% of samples (14 of 62) had filter loadings (ng/filter) less than the method detection limits for these elements,
- Cd results indicated 24% of samples (15 of 62) had filter loadings (ng/filter) less than the method detection limit,
- Cu results indicated 26% of samples (16 of 62) had filter loadings (ng/filter) less than the method detection limit,
- Ni results indicated 37% of samples (23 of 62) had filter loadings (ng/filter) less than the method detection limit,
- Cr results indicated 39% of samples (24 of 62) had filter loadings (ng/filter) less than the method detection limit, and
- Co results indicated 53% of samples (33 of 62) had filter loadings (ng/filter) less than the method detection limit.

The sampling results from all 62 filters were converted using the theoretical sampling efficiency of the MiniVol based on an assumed relationship between low volume samplers (5 Lpm) and FRM samplers (16.67 Lpm) (equation 22). Results from this analysis indicated that of the 62 filter samples from the NAPS PM_{10} data set, only 11 filter samples would likely have had enough particle mass gains for analysis of the eight trace elements. From the theoretical dataset (n=62 generated from equation 22), the following results may be found if MiniVol sampling was used (Table 34):

Table 35. Trace Elemental Levels of Non-Detections from 62 NAPS Samples Collected with a FRM Sampler in Edmonton during 2003

Trace Elements	As	Pb	V	Cd	Cu	Ni	Cr	Co
FRM sampling <MDL	23%	23%	23%	24%	26%	37%	39%	53%
Theoretical Low volume sampling <MDL	82%	88%	92%	97%	85%	92%	82%	84%

- As and Pd results indicated 82% of samples (51 of 62) had filter loadings (ng/filter) less than the method detection limits for these elements,
- V results indicated 84% of samples (52 of 62) had filter loadings (ng/filter) less than the method detection limit,
- Cu results indicated 85% of samples (53 of 62) had filter loadings (ng/filter) less than the method detection limit,
- Cd results indicated 89% of samples (55 of 62) had filter loadings (ng/filter) less than the method detection limit,

- Ni and Cr results indicated 92% of samples (57 of 62) had filter loadings (ng/filter) less than the method detection limits for these elements, and
- Co results indicated 97% of samples (60 of 62) had filter loadings (ng/filter) less than the method detection limit.

This analysis clearly showed that low volume sampling coupled with ICP-MS analysis was flawed in that not enough particle masses were collected on the Minivol filters to reliably quantify the eight trace elements of interest. Results of the ICP-MS analysis were not providing a true representation of elemental quantities in ambient PM_{10} in the field study. Thus the objective of demonstrating that low volume sampling coupled with SEM/EDX can provide comparable trace elemental quantities remains unproven.

The eight trace elements of interest (As, Cr, Co, Cu, Pb, V, Ni, and Cd) are important tracers related to anthropogenic emissions including such activities as mining, smelting, combustion, and industrial processes (Table 7). A single particulate matter emission source that may contain all these elements is a facility that uses coal. The greatest occurrence of these elements in coal is predominantly in sulphides. These sulphides occur as follows; As (arsenopyrite), Cd (sphalerite), Cu (chalcopyrite), and Pb (galena) which are believed to be directly associated with coal combustion (Torrey, 1978). Nickel (Ni) may also occur as a sulphide, however there is uncertainty about the mode of occurrence, for it is found both in the coal and ash (DTI, 2004). The three remaining trace elements Cr, Co and V are thought to be inorganically bound, and released in combustion processes of coal (Torrey, 1978).

This has also been confirmed by SEM-EDX analysis studies that have been used for detecting several trace elemental species in coal (Karayigit et al., 2001; Zhang et al., 2002; Ren et al., 2003). These studies were able to detect trace elements in both the coal samples and the flyash samples being investigated. Specifically the study by Ren et al. (2003) used SEM-EDX to identify trace elements of Ni, Cu, and Cr in coal and flyash samples. Data reported from each study is summarized in Table 36.

Table 36. SEM-EDX Abundance for Selected Trace Elements (Figure 44) and Reported Abundance of Trace Elements from others

Trace Elements	As	Pb	V	Cd	Cu	Ni	Cr	Co
% Abundance (Figure 44) SEM-EDX average of 10 samples (ranges)	1.2% (0.2 to 3.6%)	2.6% (0.2 to 4.7%)	0.3% (0.1 to 0.8%)	1.2% (0.4 to 3.1%)	2.1% (0.1 to 5.4%)	0.6% (0.2 to 1.3%)	0.4% (0.1 to 1.1%)	0.6% (0.1 to 1.4%)
SEM-EDX % Abundance reported by others	2.45%[b]	c	no reference	c	0.02 to 0.2%[a]	0.01 to 0.08%[a]	0.01 to 0.18%[a]	c

a Samples reported by Ren et al., 2003 using SEM-EDX for trace elements in coal.
b Samples reported by Zhang et al., 2002 using SEM-EDX for trace elements in coal.
c Samples reported by Karayigit et al., 2001 using SEM-EDX for micron-mineral search in coal, several trace elements detected, levels not reported.

From these results and based on the abundances detected in the samples collected in Edmonton (Figure 44 and Table 36) indicates that likely the SEM-EDX was not limited in quantifying the amount of trace elements in the particulate matter found in the 10 ambient samples collected. In order to prove the SEM-EDX is capable of providing representative trace elemental measurements, further laboratory and field research is recommended to study these trace elements.

Laboratory Research

As the initial objective of demonstrating that low volume sampling coupled with SEM-EDX provides representative trace elemental measurements remains unproven, a recommendation for further analysis with higher loading periods in a sealed chamber can be performed. With the trace elements of interest more prevalent in coal and coal flyash, NIST standards were reviewed for a SRM of coal or coal flyash that has sufficient trace elements for an experiment. The NIST 1633b – Coal Flyash was found to contain all of the trace elements of interest specifically with elements (As, V, Cu, Ni, Cr, and Co) present at a larger mass compared to NIST 1648 – Urban Particulate Matter (Table 37). The NIST 1633b standard package contains 75 g of material for experiments, compared to the standard package of 2 g for NIST 1648. With more mass present for testing, injection mass could be increased to 1 g in a single injection allowing for much more loading of trace elements onto filters. In addition fans could be added into the chamber to aid in dust re-suspension allowing for more material to remain suspended and be collected by the samplers over a 24-hour period. With more material loaded onto filters, the duplicates can once again be analyzed by ICP-MS and SEM-EDX. These samples would likely contain enough material for analysis with ICP-MS and ultimately be compared to the SEM-EDX individual particle analysis.

Table 37. NIST Mass of Trace Elements from SRM 1648 and SRM 1633b

Trace Elements	As	Pb	V	Cd	Cu	Ni	Cr	Co
NIST SRM 1648 – Urban Particulate Matter (mg of trace element)	0.23	13.10	0.25	0.15	1.22	0.16	0.81	0.04
NIST SRM 1633b – Coal Flyash (mg of trace element)	10.20	5.12	22.18	0.06	8.46	9.05	14.07	3.75

Field Research

In addition to the laboratory phase, a field test could also be conducted to further evaluate the trace elements in ambient samples. Trace elements could be evaluated by performing duplicate tests using low volume samplers along with duplicate FRM samplers. Duplicates could then be analyzed by individual particle analysis (SEM-EDX) and bulk analysis (ICP-MS). Aside from the standard 24-hour samples, to ensure enough sample material is collected, the sampling period could be extended to 48-hours, 72-hours, and up to one week (168 hours). This sampling would likely allow for enough material to be collected on both the FRM samplers and low volume samplers ensuring an adequate comparison between the two methods (SEM-EDX and ICP-MS). In addition it would likely identify a maximum loading for SEM-EDX analysis from FRM sampling, such that individual particle analysis is unable to be completed due to large number of particles intermingled and undistinguishable.

8.3 Findings

Based on the analysis from the field study, the following findings are presented:

1. Ambient air was collected with two low volume MiniVols. The resulting airborne sampling demonstrated close similarity between the low volume mass concentration data, with an $r^2 = 0.96$ and a paired t-test result indicated no statistical difference in the collection ability of each sampler ($P \leq 0.05$).
2. Individual particle analysis (SEM-EDX) allowed additional qualitative information about particle morphology (form and shape) to be obtained. Combined with elemental information (% abundance), this provided valuable information for preliminary classification of origins of the particles. This exercise would not be possible using analytical techniques alone. As this classification was based solely on

identification of individual particles based on SEM-EDX, it would not be necessary to analyze a large number of filters to arrive at this classification. Ideally, one representative filter sample should be able to provide a preliminary indication of source types provided that enough individual particles are considered in the analysis.

3. Morphological observations allowed clear identification of organic materials (e.g. fungal spores and pollen fragments) and oil particles (droplets). Distinct size and shape of these particles allows for an identification of how much this class of particles cover the surface area of a filter in comparison to other particles. In cases where the loading of organic or oil particles may be excessive on a filter, these types of particles may have the ability to bias source apportionment applications based on measurement of elemental quantities using bulk analysis techniques.
4. Another promising aspect in demonstrating that low volume sampling/individual particle analysis is a viable alternative for airborne particulate matter source apportionment is its ability to quantify the abundance of elements present in particles collected:
    a. 10 filter samples of ambient particulate material collected with the low volume samplers were analyzed by individual particle analysis (SEM-EDX) and bulk analysis (ICP-MS), respectively. Corresponding average % abundance based on SEM-EDX and ICP-MS measurements were not shown to be statistically different for dominant elements that included: silica, calcium, iron, aluminum, magnesium, potassium, sodium, zinc, titanium, and manganese ($P \leq 0.05$). These findings indicated that comparable results were possible with averaging 10 individual particles

(SEM-EDX) and bulk ICP-MS results of non-homogeneous substances collected from ambient field studies.

b. There were discrepancies with the trace elements arsenic, chromium, cadmium, lead, copper, nickel, vanadium and cobalt. Corresponding average % abundance based on SEM-EDX and ICP-MS measurements were shown to be statistically different for these trace elements ($P \leq 0.05$). Further investigation indicated that the likely reason for this finding was that not enough particle masses were collected on the Minivol filters to reliably quantify the eight trace elements of interest using ICP-MS. Thus results of the ICP-MS analysis were not providing a true representation of elemental quantities in ambient PM_{10} in the field study. This leads to a recommendation that further comparative analysis of these trace elements under defined (e.g. laboratory or field controlled) conditions are necessary to demonstrate that low volume sampling coupled with SEM-EDX can provide comparable measurements of trace elemental quantities.

c. Notwithstanding results observed above, Ren (et al. 2003) and Zhang (et al., 2002) reported SEM-EDX detection limits for analysis of coal particles that were less than quantities (i.e. average % abundance) reported in this research for the trace elements chromium, copper, and nickel in ambient PM_{10}. In addition, average % abundance of other trace elements of interest ambient PM_{10} (arsenic, lead, vanadium, cadmium, and cobalt) were of similar magnitudes to that measured for chromium, copper, and nickel.

9. FIELD RECEPTOR STUDY

9.1 Field Collection Tests

Ambient PM_{10} samples collected during the field sampling conducted in High Level, Alberta resulted in 33, 24-hour samples, with the addition of 8 blank samples collected with low volume samplers (MiniVols). These samples were collected to quantify source contributions of PM in the ambient air of High Level through morphological identification and receptor-modeling using data from individual particle analysis (SEM-EDX).

Receptor modeling techniques have become an important tool for identifying source influences on receptor locations. By using the receptor modeling approach, samples are collected at a measurement (receptor) site and PM contributions are inferred back to potential sources (Friedlander 1981, Blanchard 1999). These potential sources are identified by using a multivariate (statistical) approach such as a principle component analysis (PCA) to unravel seemingly unrelated data into "source fingerprints" or source profiles. PCA has been well demonstrated by Thurston and Spengler (1985), Harrison et al. (1996, 1997), and Biegalski et al. (1998).

9.1.1 Ambient Mass Concentrations

Ambient data were collected over a period of seven months and included wind speed, wind direction, PAH and PM_{10}. Meteorological measurements (wind speed and wind direction) were set to collect data on a one-minute sampling interval and averaged over 30 minutes (to match PM_{10} measurements with a TEOM). Two Minivol samplers were set to collect integrated PM_{10} samples over 12-hour and 24-hour periods.

The basis for these sampling durations was to capture changes in PM_{10} levels in response to changes in diurnal patterns and meteorology. However, for comparison purposes only the 24-hr samples were considered. The results of the seasonal sampling overall averages are summarized in Table 38. Data collected from each site was grouped for comparison purposes based on seasonal sampling collected from elevated locations. Results from the sampling tests are further explained for each season of sampling.

Table 38. PM_{10} 24-hour Mass Concentration Results from 33 Field Samples collected with MiniVols and corresponding TEOM average

Sample Date	MiniVol $\mu g/m^3$	TEOM $\mu g/m^3$
Winter 1999 (n=7)	7.7	7.0
Spring 1999 (n=6)	5.8	5.2
Summer 1999 (n=8)	9.3	7.5
Fall 1999 (n=12)	6.9	6.4

Winter Sampling

Winter sampling was performed during March 1999. During this sampling period winds prevailed from an easterly direction approximately 55% of the time. Precipitation during winter sampling was recorded at 4.6 mm (7.8 cm snow) (Environment Canada, 2000). Results from the 24-hr average low volume (MiniVol) sampling during this period were 8 $\mu g/m^3$ (n =7). The continuous TEOM data had a comparable time average (only the data during the time periods of sampling) of 7 $\mu g/m^3$ during this period. TEOM and precipitation data are presented in Appendix I.

Spring Sampling

Spring sampling was performed during May 1999. During this sampling period winds were predominately from an easterly direction approximately 38%, with occurrences of extended wind gusts from a southeasterly (18%) and northwesterly (12%) direction. Precipitation during the spring sampling was recorded at 31.7 mm (of rainfall) (Environment Canada, 2000). Results from the 24-hr average low volume sampling were 6 $\mu g/m^3$ (n =6). The continuous TEOM data had an overall average of 5 $\mu g/m^3$ during this period. TEOM data along with precipitation data are presented in Appendix I. In addition, total PAH concentrations were collected for this period. The average total PAH concentration was 5 ng/m^3 for the sampling period (Appendix I).

Summer Sampling

Summer sampling was performed during July and August of 1999. During this sampling period winds prevailed from a southerly direction approximately 28% of time, and an easterly direction approximately 27% of time. There were additional occurrences of sustained wind gusts from a southeasterly (8%) and northwesterly (13%) direction. Precipitation during sampling was recorded at 90.2 mm, with 39.4 mm falling over a twenty-four hour period (Environment Canada, 2000). Results from the overall 24-hr average low volume sampling during this period were 9 $\mu g/m^3$ (n =8). The continuous TEOM data had an overall average of 8 $\mu g/m^3$ during this period. TEOM data along with precipitation data are presented in Appendix I. The average total PAH level was 6 ng/m^3 for the sampling period (Appendix I).

Fall Sampling

Fall sampling was performed during September and October of 1999. During this sampling period winds prevailed from an easterly direction approximately 32% of time, and a westerly direction approximately 21% of time. There were additional periods of extended wind gusts from a southeasterly (7%), southwesterly (8%), and northwesterly (7%) direction. Precipitation during fall sampling was recorded at 15.9 mm, of which 5.6 mm fell as rain and 13.6 cm fell as snow (Environment Canada, 2000). Results from the overall 24-hr average low volume sampling during this period were 7 $\mu g/m^3$ (n = 12). The continuous TEOM data had an overall average of 6 $\mu g/m^3$ during this period. TEOM data along with precipitation data are presented in Appendix I. The average total PAH level was <3 ng/m^3 for the sampling period (Appendix I).

Throughout the sampling period the TEOM continuously recorded PM_{10}, whereas MiniVol samples were collected over integrated periods of 24-hours. With the TEOM recognized as an equivalent reference sampler (PM_{10} EPA Designation No. EQPM-1090-079, R&P, 1996), there was interest in establishing whether similar mass concentrations were measured by MiniVols and the TEOM. Simultaneous data from each sampler were compared to determine if there were differences based on 33, 24-hour field using a regression analysis and t-test ($P \leq 0.05$).

The regression curve is shown in Figure 45. The coefficient of determination (r^2) value from this comparison was 87% suggesting a reasonably good agreement between sampling methods for collection of 24-hour average mass concentrations. The differences in the mass concentration results could be related to the TEOM using a heated sampling column at 40°C, whereas the MiniVol sample is collected at ambient temperatures. Mass concentrations were also compared using a t-test to determine if the means were equal (rejecting if: |t stat| > t Critical two-tail). Results of the test, |1.24| < 2.04, indicated that the means were equal ($P \leq 0.05$). Results indicated no difference in 24-hour average mass concentrations as measured by the Minivol or TOEM.

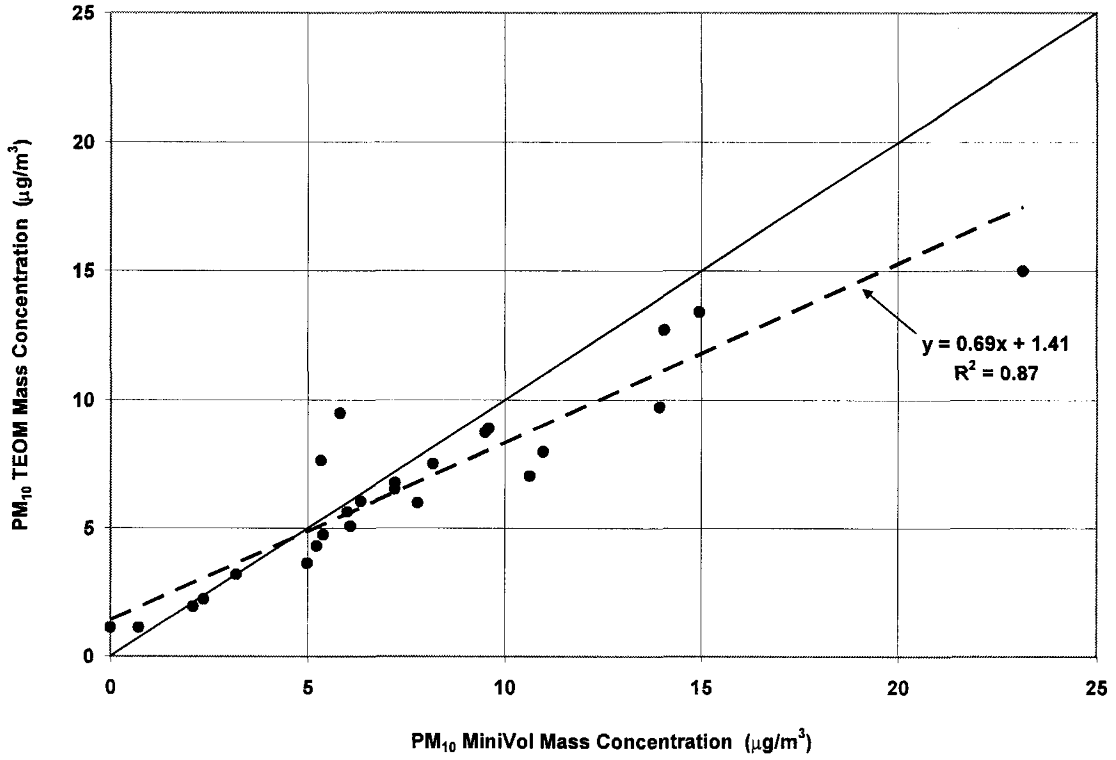


Figure 45. Comparison of Mass Concentrations from Field Study using Low Volume Samples and TEOM

9.1.2 Summary of Elemental and Morphological Analysis

9.1.2.1 EDX Analysis

A particle-by-particle micro-quantification was performed on the filters with SEM-EDX using methods outlined in Appendix C. Based on the presence of combustion and organic particles on the filters, more than 10 particles per filter were required for analysis. As the particle was brought into magnification, the particle would be scanned (by EDX) and classified. If the particle was unable to be scanned, as in the case with many organic and combustion particles, the particle type was noted and an additional particle was analyzed. This resulted in more than 10 individual particles analyzed per filter for a total of 403 particles being analyzed. The average % abundances, however, were based on 10 random particles from each filter for all four seasons of sampling (summarized in Figure 46). Average % abundances shown in this figure was determined in a similar manner as the laboratory study (as described in Appendix C):

- An assumption was made that ambient particles collected on the filter were uniformly distributed across the collection area.
- A small section of the filter, approximately 13 mm in diameter was considered in the analysis, of which a minimum of 10 particles within this area randomly selected and subjected to SEM-EDX analysis.
- Average % abundance measured by SEM-EDX was based on an average of 10 randomly analyzed individual particles from each test. The wt% was transformed according to equation 20.

Winter Sampling

From the winter analysis there were a total of seven 24-hour PM_{10} filters analyzed. The dominant elements seen during this period appeared to be directly associated with crustal sources which include silica, calcium, iron and aluminum. In addition, there was evidence of elements associated with road de-icing activities (sodium and chloride). The presence of the salts during winter sampling was expected. Chow and Watson (1998) found that even though salt is applied for de-icing as a course material, after evaporating from a suspended water droplet the salt becomes more abundant as fine particulate matter.

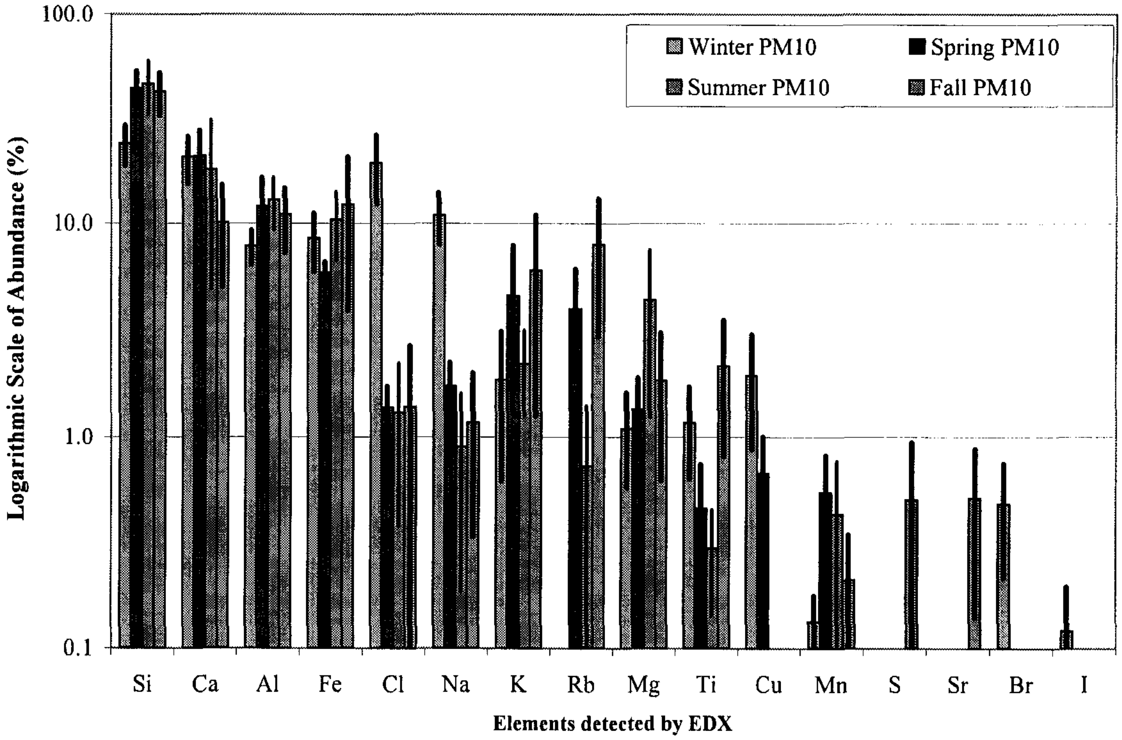


Figure 46. Elemental Summary from 33 Low Volume Filter Samples Collected over Four Seasons (based on an average of 10 particles per filter)

Spring Sampling

From the spring sampling a total of six 24-hour PM_{10} filters were analyzed. Elemental analysis of PM_{10} samples indicated that the most dominant elements found were directly related to crustal sources silica, calcium, iron and aluminum. During spring sampling, major and minor trace elements were found to be more prevalent compared to winter sampling. This would be expected due to snow cover that had melted exposing more ground base material for re-suspension. In addition, there was more evidence of elements associated with combustion, which include calcium, potassium, manganese and rubidium (Chapter 5).

Summer Sampling

From the summer sampling a total of eight 24-hour PM_{10} filters were analyzed. The abundant elements seen in the analysis appeared to be directly associated with crustal sources which include silica, calcium, iron, aluminum and trace magnesium. During the summer sampling there was also a noticeable increase in the organic particle fraction seen on the filters (discussed further in the SEM analysis).

Fall Sampling

From the fall sampling a total of 12 PM_{10} filters were analyzed. The dominant elements seen in the analysis also appeared to be directly associated with crustal sources, including silica, calcium, iron, aluminum, magnesium and trace titanium. There was also increased evidence of combustion particles relating to calcium, potassium, and rubidium. With lack of permanent snow cover in the fall, the most abundant elements found were related to crustal sources. Additional information regarding morphological properties of each particle class is further evaluated through SEM analysis.

9.1.2.2 SEM Analysis

Particle morphology along with elemental analysis was characterized consistent with the categorical summary (shape, surface texture, and elemental composition) summarized in Chapter 2. A total of 403 particles were analyzed individually by SEM-EDX from the 33, 24-hour field samples collected over seven months. Examples of each type of particle are presented in Figure 47 to Figure 63 (shape and surface texture) and Table 39 to Table 47 (weight % of elements).

Overall particle classification results are summarized in Table 48. This classification was based on 403 individual particles identified and analyzed. Similar to the field study performed in Edmonton, AB, it was noted that on some filters the oil droplets covered a vast majority of the filter, and would contribute substantially to the total number of particles present on the filter. This was also found for biological particles, in which there were many more biological particles present than what was indicted in Table 48 during the summer sampling period.

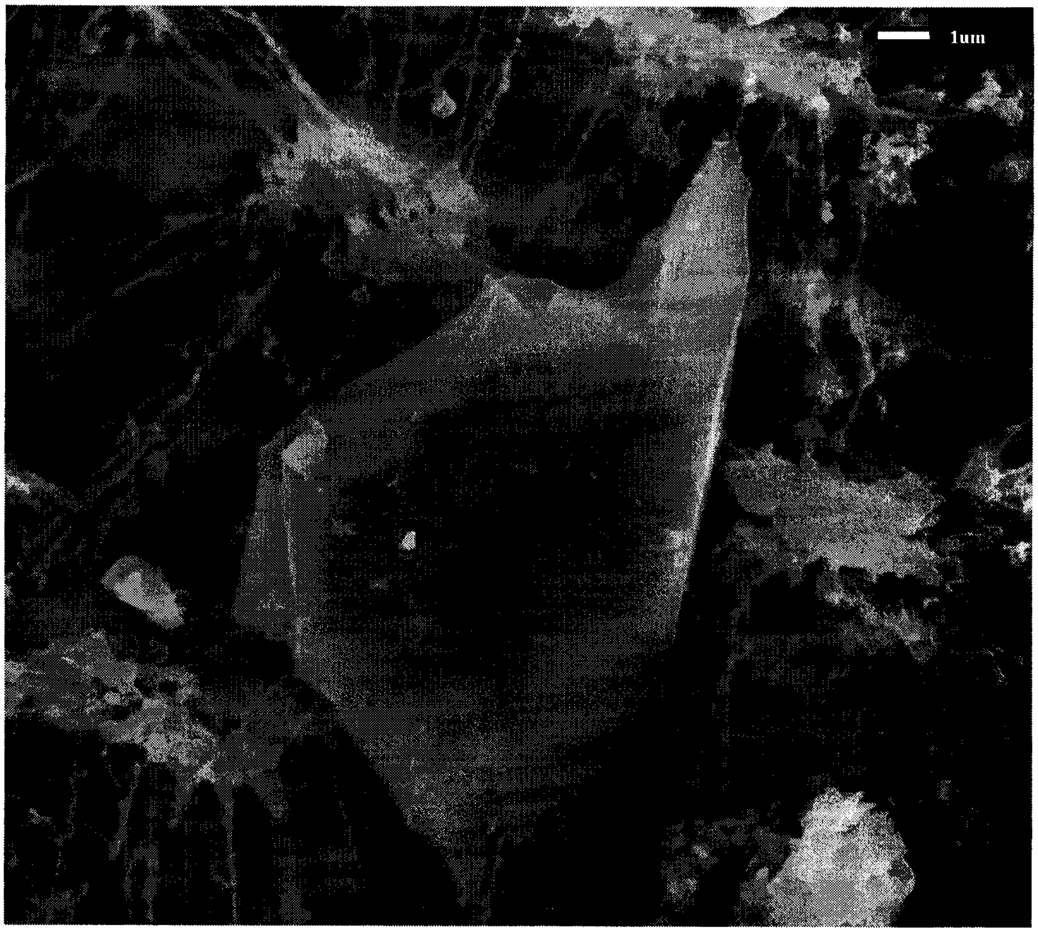


Figure 47. SEM Picture of Crustal Silica Particle (High Level, AB)

- Crustal silica particle which is non-spherical, sharp, ridged, and primarily comprised of Si, with varying amounts of other crustal elements.

Table 39. EDX Elemental Scan of Crustal Silica Particle (High Level, AB)

Library Standards: /imix/spectra/system standards (LDL 0.1%)

Accelerating Voltage	20 keV
Takeoff Angle	56.8 degrees

Elements	wt%
Si	97.2
Mn	0.3
Ni	0.2
Cu	0.3
Pb	1.0
Cd	0.2
Cl	0.4

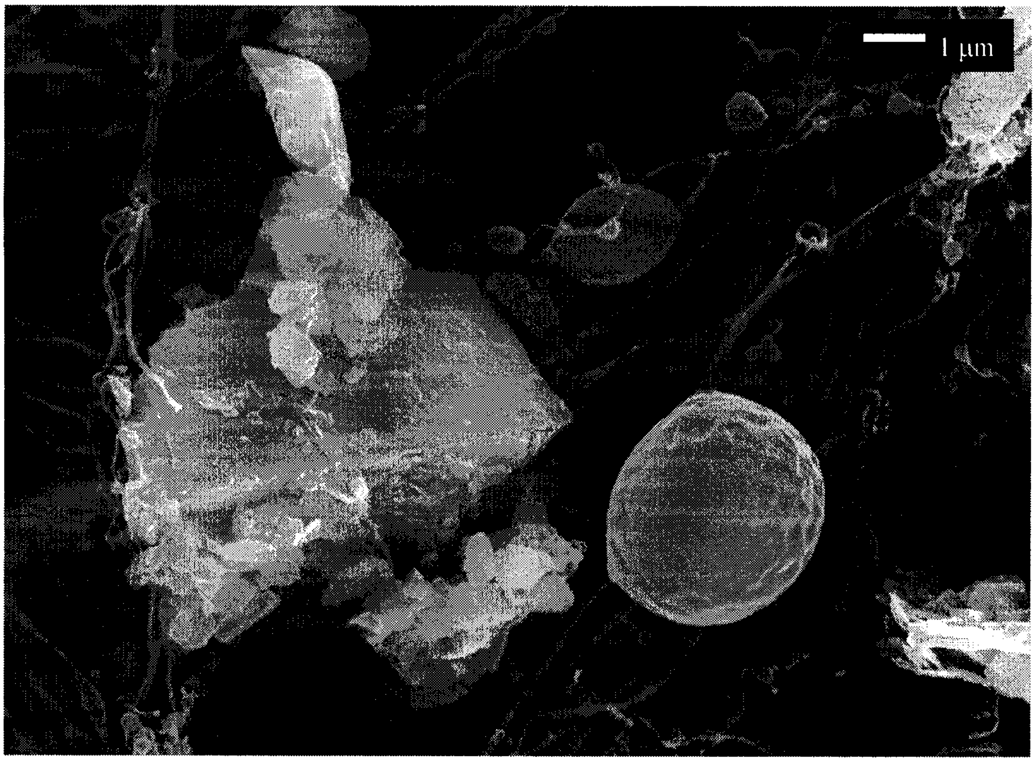


Figure 48. SEM Picture of Crustal Silica Particle with Oil Droplets (High Level, AB)

- Crustal Silica block with spherical oil droplets.

Table 40. EDX Elemental Scan of Crustal Silica Particle (High Level, AB)

Library Standards: /imix/spectra/system standards (LDL 0.1%)

Accelerating Voltage	20 keV
Takeoff Angle	56.8 degrees

Elements	wt%
Si	53.8
Ca	17.5
Fe	3.9
Al	16.8
K	1.2
Ti	0.2
Na	1.8
Mg	4.1
Cl	0.6
Mn	0.2

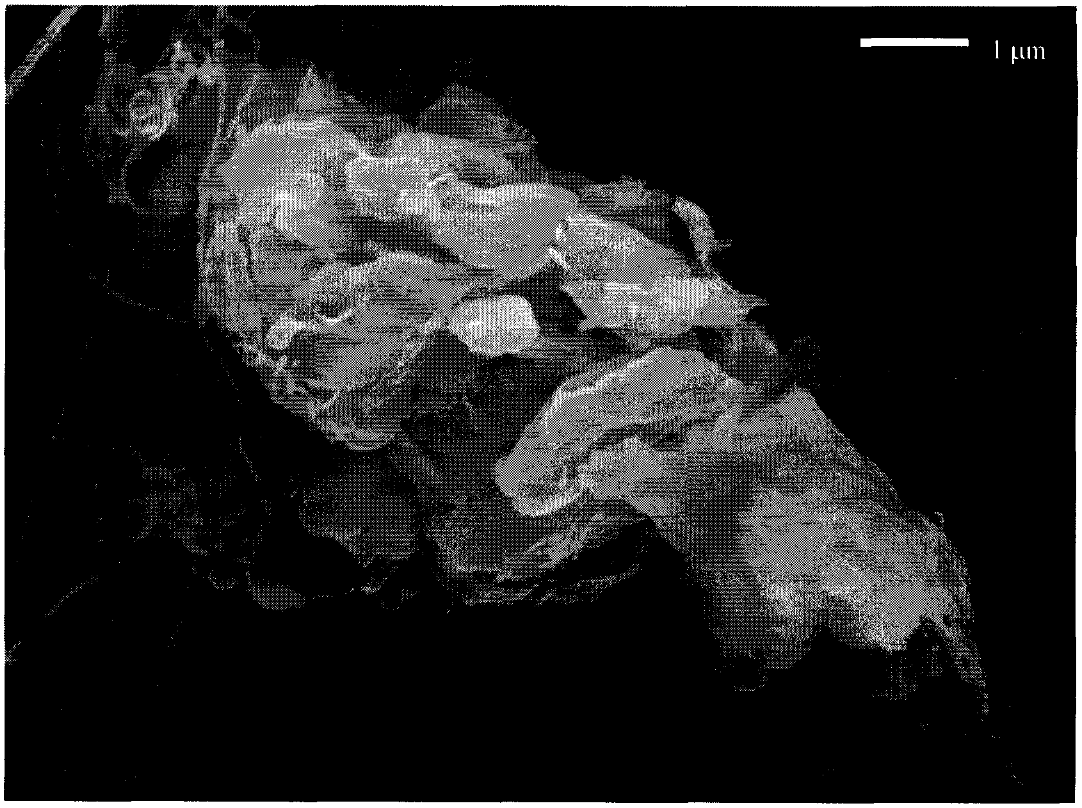


Figure 49. SEM Picture of Crustal Clay Particle (High Level, AB)

- Crustal clay particle which is non-spherical, platy, and primarily comprised of Si and Ca with varying amounts of other crustal elements.

Table 41. EDX Elemental Scan of Crustal Clay Particle (High Level, AB)

Library Standards: /imix/spectra/system standards (LDL 0.1%)

Accelerating Voltage	20 keV
Takeoff Angle	56.8 degrees

Elements	wt%
Si	51.7
Ca	5.1
Fe	17.3
Al	17.9
K	1.3
Ti	0.4
Na	2.1
Mg	2.4
Cl	0.7
Mn	0.3
P	0.7

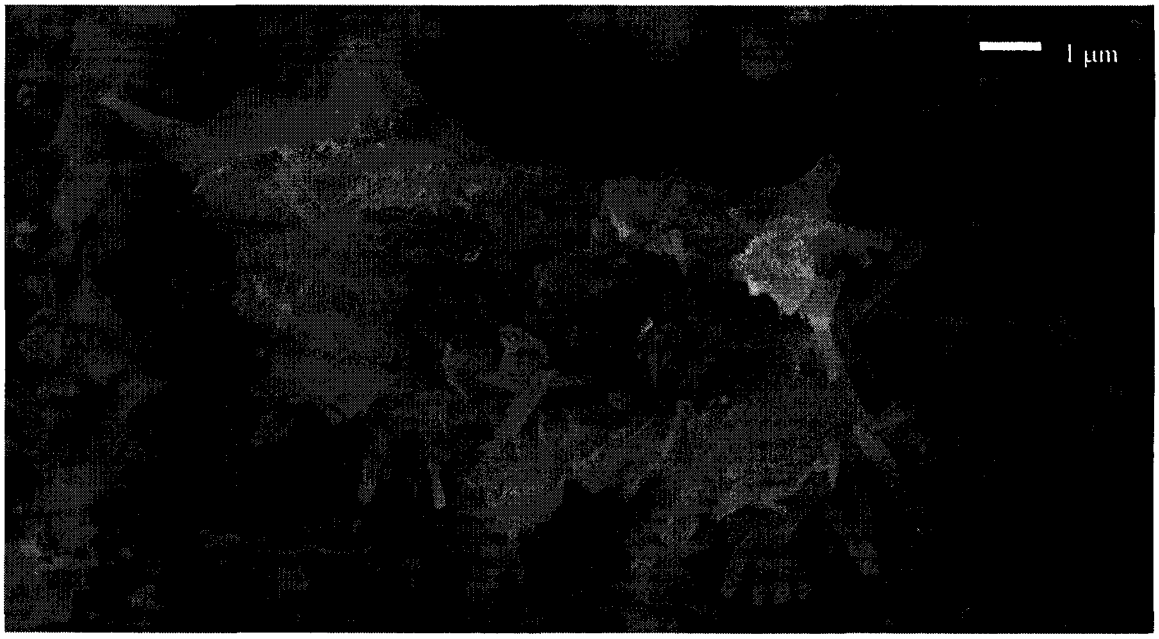


Figure 50. SEM Picture of Generic Crustal Particle (High Level, AB)

- Crustal particle which is non-spherical, crystalline, and primarily comprised of Ca with varying amounts of other crustal elements.

Table 42. EDX Elemental Scan of Generic Crustal Particle (High Level, AB)

Library Standards: /imix/spectra/system standards (LDL 0.1%)

Accelerating Voltage	20 keV
Takeoff Angle	56.8 degrees

Elements	wt%
S	9.0
Si	11.5
Mg	0.7
Ca	64.5
K	0.6
Mn	0.2
Fe	0.7
Cu	0.4
Al	4.4
Cd	0.5
Cl	7.2

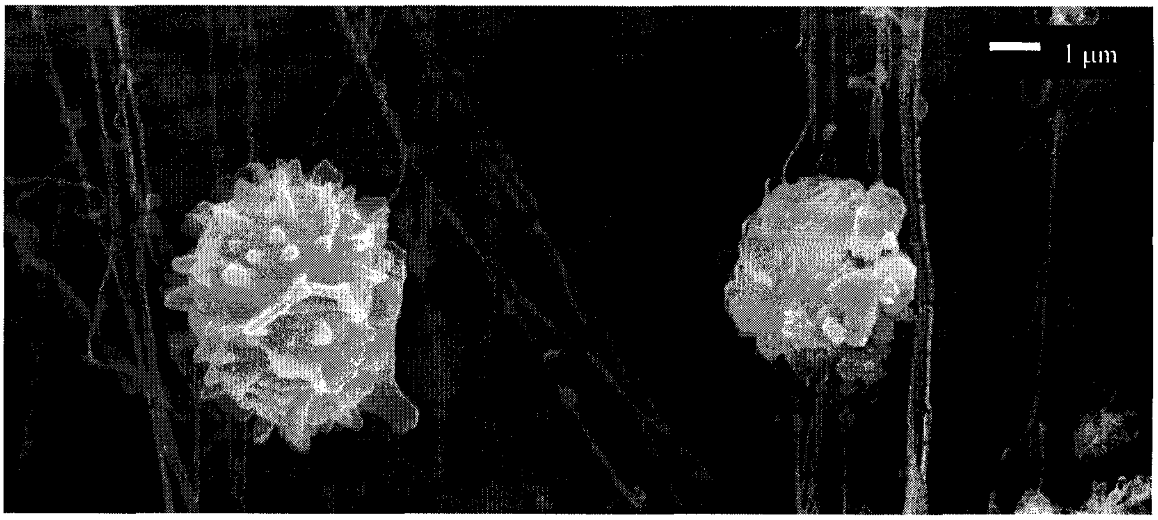


Figure 51. SEM Picture of Organic Particle (left side) and Crustal Clay Particle (right side) (High Level, AB)

- Crustal clay particle which is non-spherical, platy, and primarily comprised of Si and Ca with a spherical organic particle.

Table 43. EDX Elemental Scan of the Crustal Clay Particle (High Level, AB)

Library Standards: /imix/spectra/system standards (LDL 0.1%)
Accelerating Voltage 20 keV
Takeoff Angle 56.8 degrees

Elements	wt%
Si	52.2
Ca	14.2
Fe	8.0
Al	19.3
K	1.6
Na	1.5
Mg	2.4
Cl	0.8

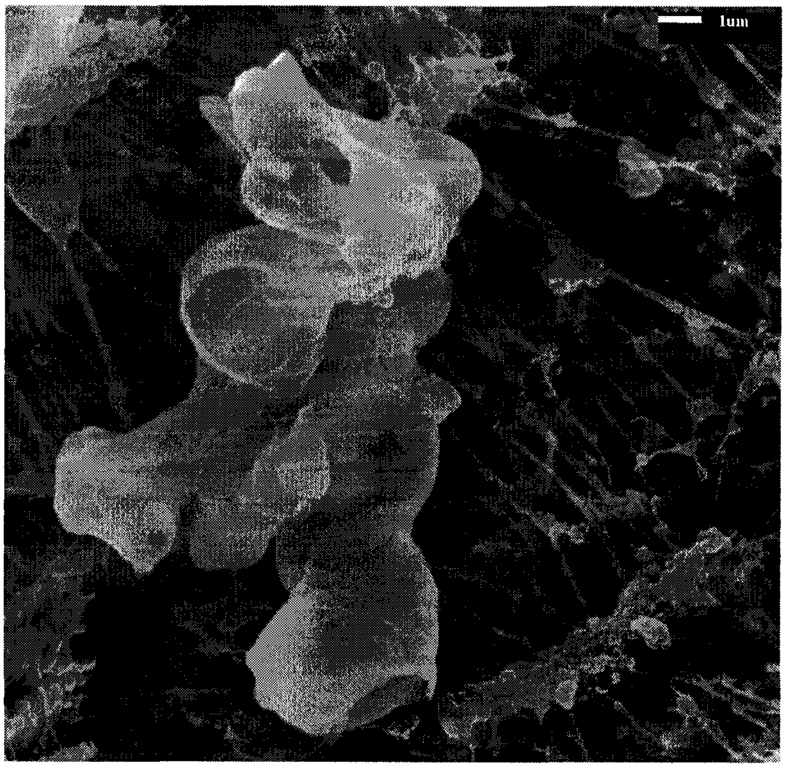


Figure 52. SEM Picture of Salt Particle (High Level, AB)

- Salt particle which is non-specific in shape, and primarily comprised of Na and Cl with minor amounts of other crustal elements.

Table 44. EDX Elemental Scan of Salt Particle (High Level, AB)

Library Standards: /imix/spectra/system standards (LDL 0.1%)

Accelerating Voltage	20 keV
Takeoff Angle	56.8 degrees

Elements	wt%
S	0.6
Si	1.9
Na	41.0
Mg	0.6
Ca	9.0
K	4.9
Ti	0.2
Mn	0.4
Fe	0.5
Ni	0.2
Al	0.6
Cl	40.0

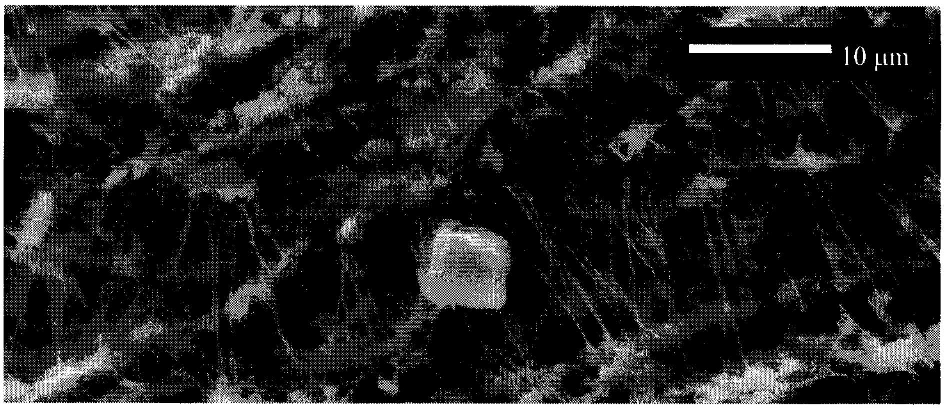


Figure 53. SEM Picture of Salt Particle in Winter (High Level, AB)

- Salt particle mixed with silica, primarily comprised of Na and Cl with varying amounts of other crustal elements.

Table 45. EDX Elemental Scan of Salt Particle in Winter (High Level, AB)

Library Standards: /imix/spectra/system standards (LDL 0.1%)

Accelerating Voltage	20 keV
Takeoff Angle	56.8 degrees

Elements	wt%
Na	29.8
Cl	70.3

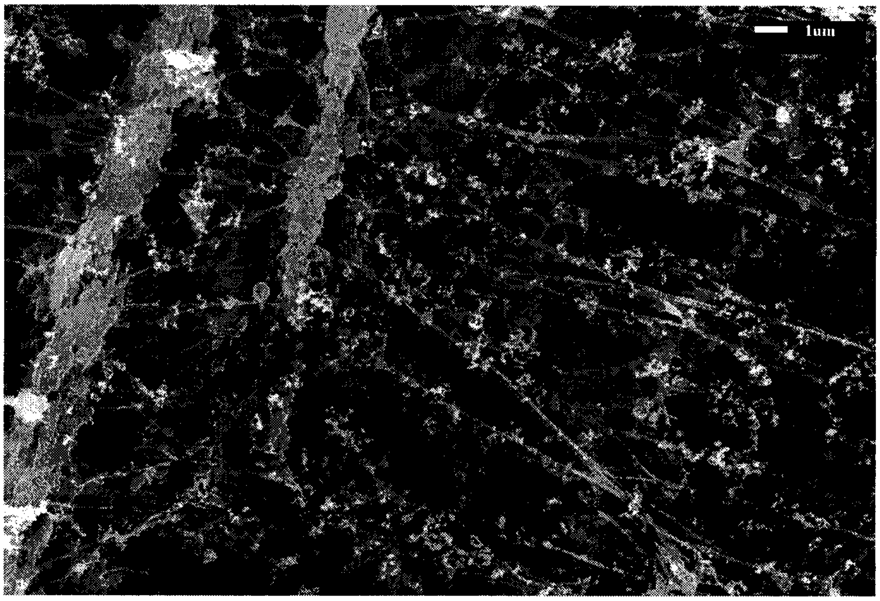


Figure 54. SEM Picture of Combustion Particles in Spring (High Level, AB)

- Combustion particles are small loose porous structures which are difficult to scan with EDX due to their weak structure and small size and shape.

Figure 55. SEM Close-up of Combustion Particles in Spring (High Level, AB)

- Oil particles are small and smooth in appearance, and cover the surface of a filter (these particles were difficult to scan with EDX as they were extremely small and tended to deform when examined).

Table 46. EDX Elemental Scan of Combustion Particles in Spring (High Level, AB)

Library Standards: /imix/spectra/system standards (LDL 0.1%)

Accelerating Voltage	20 keV
Takeoff Angle	56.8 degrees

Elements	wt%
Na	70.4
K	1.3
Ca	3.5
Ti	4.3
Cu	7.3
Zn	13.2

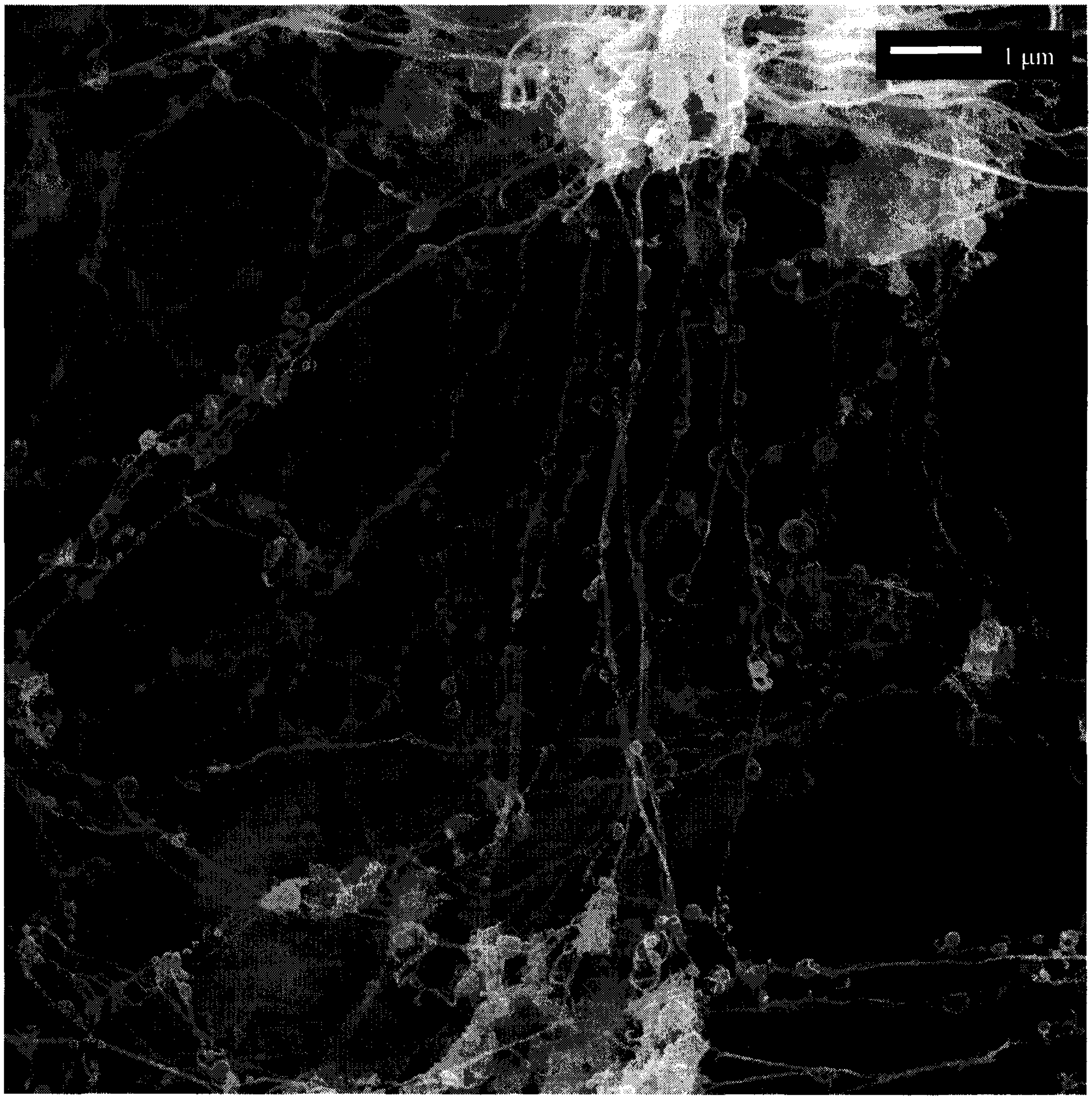


Figure 56. SEM Overview Picture of Oil Particles (High Level, AB)

- Oil particles are small and smooth in appearance, and can cover areas of a filter.

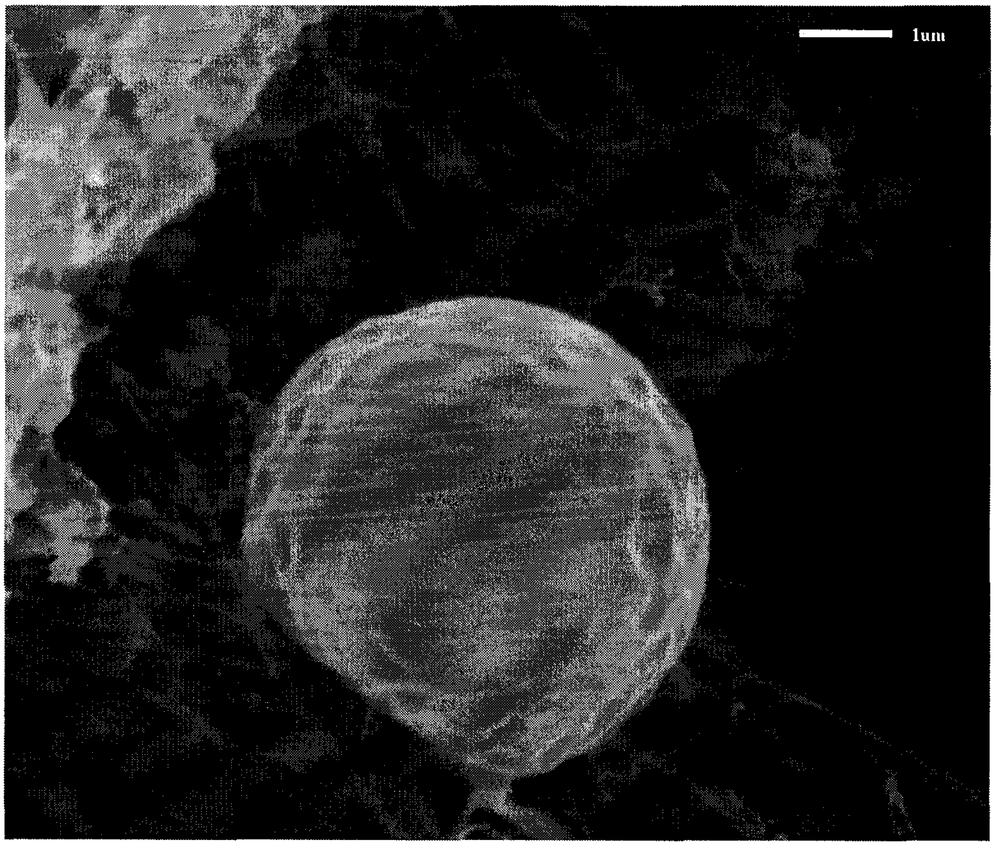


Figure 57. SEM Close-up Picture of Combustion Particle in August (High Level, AB)

- From repetitive tests on oil particles, the following close-up scan was performed.

Table 47. EDX Elemental Scan of Combustion Particle in August (High Level, AB)

Library Standards: /imix/spectra/system standards (LDL 0.1%)
Accelerating Voltage 20 keV
Takeoff Angle 56.8 degrees

Elements	wt%
Al	16.8
K	8.9
Na	10.0
Mg	15.3
Cl	1.7
Mn	0.8
V	2.1
Rb	32.0
Ce	12.4

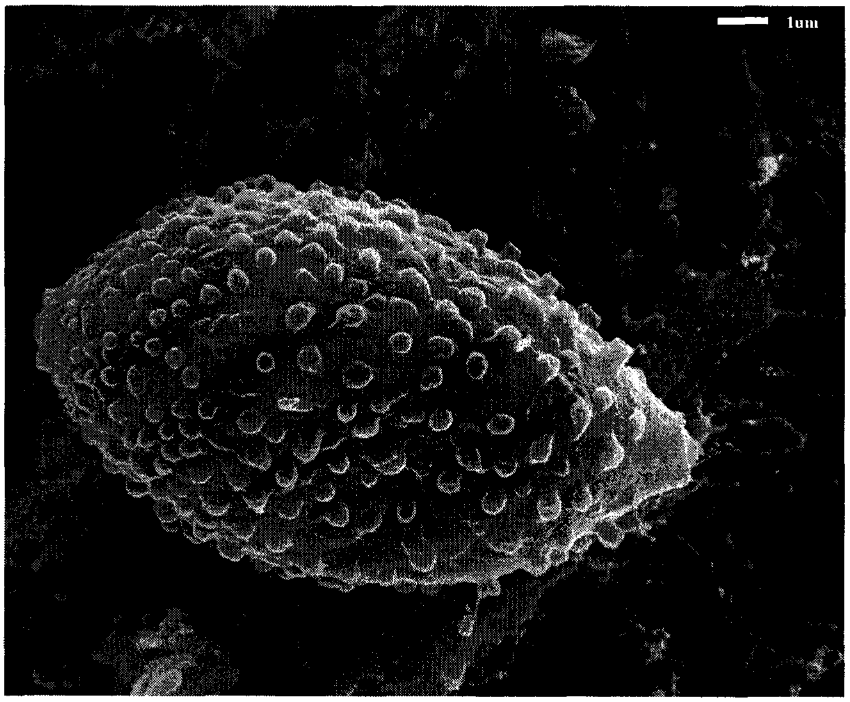


Figure 58. SEM Picture of Organic Particle in Spring (High Level, AB)

- Organic particles are identifiable from their distinct shape and form. Elementally the EDX is unable to quantify the composition of organic particles.

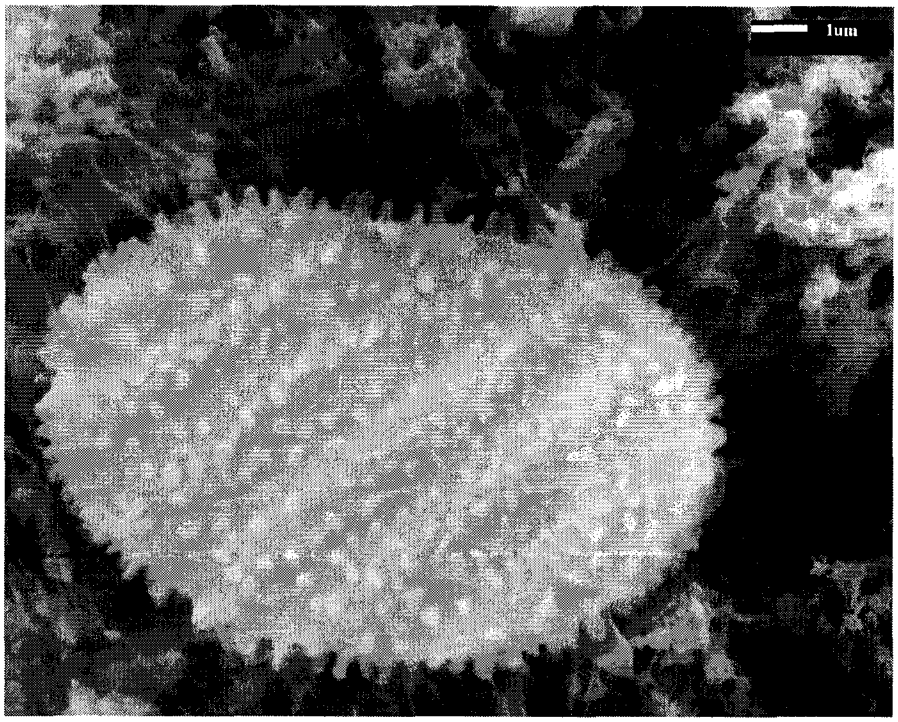


Figure 59. SEM Picture Organic Particle in Summer (High Level, AB)

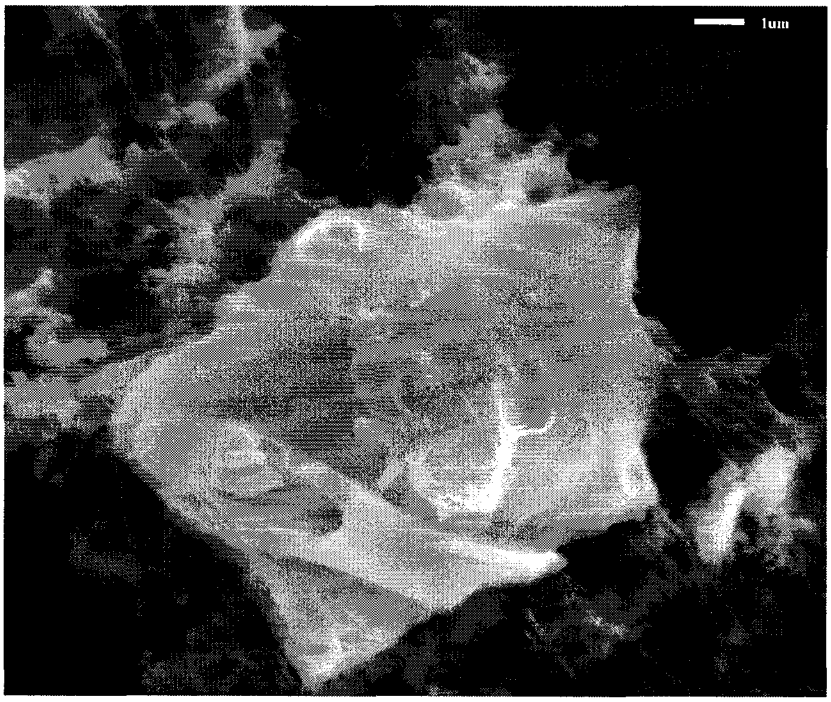


Figure 60. SEM Picture of Plastic Particle (High Level, AB)

- Part of the classification was "other" particles (e.g. glue or resin particles that appeared similar to silica crustal particles). The difference was that these particles gave a similar elemental signature as the filter background (high in F).

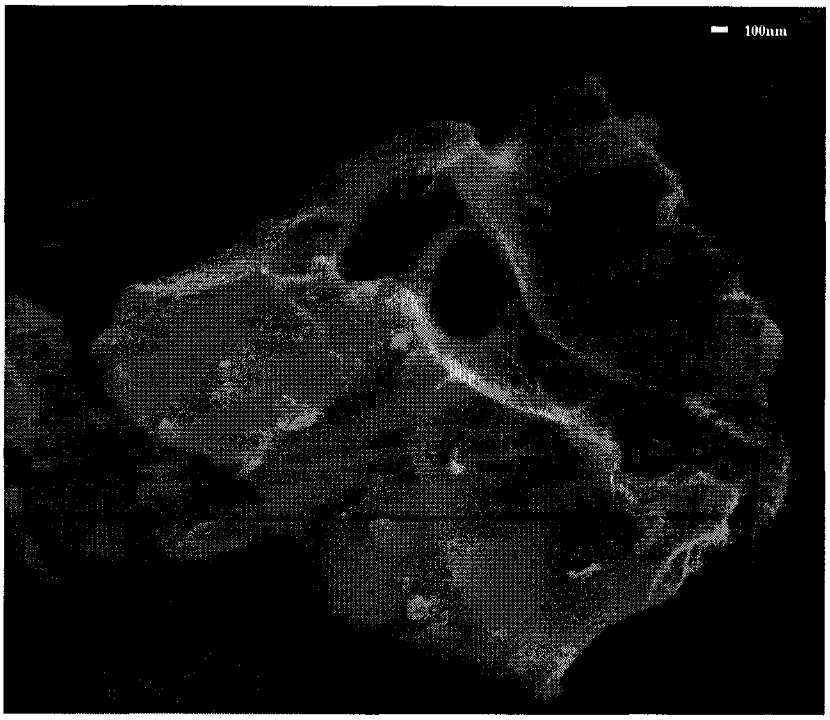


Figure 61. SEM Picture of a Second Plastic Particle (High Level, AB)

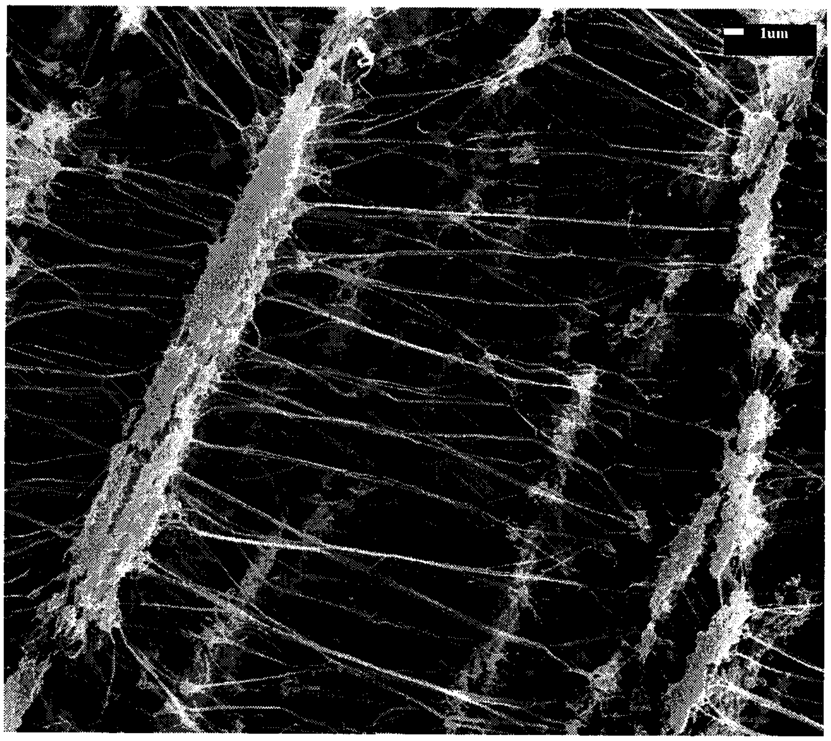


Figure 62. SEM Picture of Blank Filter

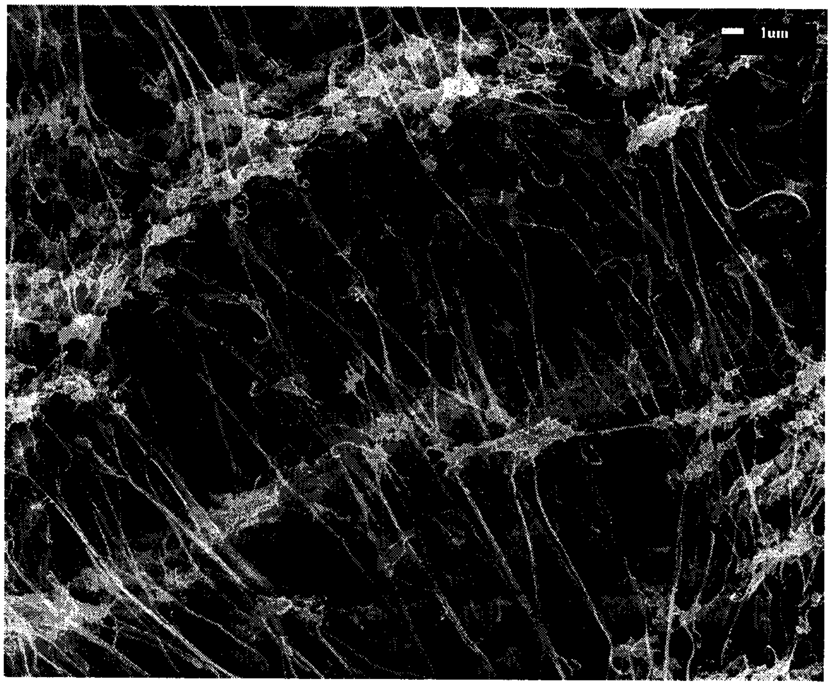


Figure 63. SEM Picture of Second Blank Filter

Table 48. Summary of Particle classifications from 33, 24-hour PM_{10} Filter Samples from High Level, AB - 403 particles analyzed

Particle	Descriptive Properties	Winter n=7	Spring n=6	Summer n=8	Fall n=12
Crustal	Silica	41	27	37	53
	Clay	14	20	29	57
	Salt	17	2	-	-
Industrial exhaust	Flyash	-	-	-	-
	Sintered	-	-	-	-
Exhaust	Soot	4	12	11	14
	Oil droplets	3 (a)	9 (b)	6 (c)	12 (a)
Biological	Pollen, spores	-	5 (c)	6 (b)	11 (c)
	Fibrous	-	-	-	-
Other		2	2	3	6
TOTAL		81	77	92	153

Note: (a) – only these particles were analyzed by EDX >50% surface area covered
(b) – only these particles were analyzed by EDX >25% surface area covered
(c) – only these particles were analyzed by EDX <25% surface area covered

The most abundant particles observed by SEM on filters, but not counted, were those from combustion sources in the form of small (fine) oil particles. These oil droplets tended to cover majority of the surface filter area (>50%) in the winter and fall sampling (as seen in Figure 56) in comparison to the appearance of blank filters (Figure 62 and 63). The most prevalent combustion particles (oil droplets and soot particles) were found in the spring, summer and fall (5%, 4%, and 6% respectively) with only 2% found in winter samples.

The second most abundant particles observed by SEM on filters, but not counted, were biological particles (excluding the fact that there were no biological particles present in winter). Biological particles present in summer samples were noted to cover more than 25% of the filter (e.g. plant fragments, spores, and insect fragments). Whereas, these biological particles covered less than 25% of the filter surface for spring and fall samples. The higher biological loading during warmer periods was primarily a result of intense agricultural activity in which the northern climate allows for longer periods of sunlight and increased growing periods. In contrast there is virtually no plant and insect activity in winter months, with snow cover hindering re-suspension.

The most abundant individual particles that were observed by SEM, analyzed by EDX, and counted were crustal particles (as noted in Table 48). These included crustal silica (identifiable by sharp glassy appearance) and crustal clay (identifiable by platy agglomerated structure).

The common crustal materials of clay and silica particles were found to be in much more abundance during the spring, summer and fall sampling periods. Crustal particles accounted for ~69% of the particles observed by SEM, analyzed by EDX, and counted for all four periods. This finding was expected due to the dominance of sources of open crustal material surrounding the community of High Level (fields, road dust, and gravel dust).

In the winter months snow hinders re-suspended crustal material aside from road-derived sources such as silica and salt from road sanding. Salt particles present in winter samples at ~5%. This finding was expected due to silica (sand) and salt applied on local roads in the community.

Filter samples in High Level, AB did not indicate examples of industrial exhaust particles such as flyash and sintered particles from the 403 particles examined. However, there were a number of particles classified as "other" (13) during sampling. This category was <5% of the total particles observed by SEM, analyzed by EDX, and counted. The primary types of these particles were plastic and rust fragments.

9.1.3 Receptor Model – Source Apportionment Model

A principle component analysis (PCA) was performed using the elemental % abundance data determined by EDX analysis. The laboratory study (Chapter 7) and field study (Chapter 8) were unable to provide confirmation of the ability of low volume sampling/SEM-EDX for quantification of selected trace metals (i.e. As, Cr, Co, Cu, Pb, V, Ni, and Cd).

However, Ren et al. (2003) reported that SEM-EDX is capable of quantifying trace amounts of Cr, Cu, and Ni at lower levels than what was observed in particles loaded on filters from the field study in Chapter 8. In addition, average % abundances of other trace elements of interest in ambient PM_{10} (As, Co, Pb, V, and Cd) were of similar magnitudes to that measured for Cr, Cu, and Ni in particles loaded on filters from the field study. Thus PCA was undertaken to demonstrate the capability of using data from low volume sampling/SEM-EDX to identify generic sources of particulate matter in the community.

With a limited number of filter samples collected from each site (total of 33 filter samples), it was necessary combine elemental data from the two sites for PCA after Chu et al. (2003). Chu et al. (2003) combined elemental data from 42 filter samples collected at 14 individual sites to identify general sources of particulate matter based on 19 elemental tracers. Although sample size was limited, prior classification of important particulate types (summarized in Table 48) would enable factor interpretation.

A total of twenty-six elements were analyzed with the SEM-EDX (Si, Ca, Fe, Al, K, Ti, Na, Mg, Cl, Mn, P, S, Cu, Br, I, Zn, V, Cr, Rb, Ce, Ni, Sc, Se, Sr, Pb and Te) on every each filter. These elements were chosen based on their source profiles and suspected abundances (Chapter 5). The PCA was prepared according to the following steps (Appendix C):

- Mass concentrations ($\mu g/m^3$) were multiplied by the average weight % of 10 randomly selected particles analyzed at the SEM-EDX for all 33 filter samples collected. This results in the mass concentrations of individual elements (ng/m^3).
- 24-hour average PAH concentration data were initially included as a factor to help identify potential sources.
- Resulting elements and PAH mass concentrations were transformed into a dimensionless standardized form (as per Equation 7).
- The z-score matrix was used for PCA utilizing SYSTAT® 10.2 (Systat Software, Inc., 2002). The PCA was performed with a Varimax rotation to simplify the interpretation of the principle components (Henry and Hidy, 1979).

The procedure used in the PCA utilized a process of eliminating elements that did not meet the following criteria (after Harrison et al., 1997; and Hidy, 1988):

- Elements that are near the detection limit or have low abundances are removed to avoid false indications of sources or source relationships.
- Elements that are not clearly distinct to one principle factor (source) are removed to avoid false source relationships.
- Elements that are not significantly related to one principle factor are removed to allow for very distinct relationships.

The procedure used to determine these factors are discussed below.

The PCA was originally performed using 12 parameters (11 elements and total PAHs) from the original 26 elements and total PAHs identified. In consideration of the criterion used by Harrison et al. (1997) and Hidy (1988), those parameters with >15% non-detectable quantities were excluded from the PCA after USEPA Guidance for Data Quality Assurance (EPA, 2000b). The percent non-detectable quantities for each parameter included in the initial PCA are shown in Table 49. This initial PCA resulted in four factors with eigenvalues greater than one, which combined to account for 77% of total variance (Table 50).

In consideration of the second criterion used by Harrison et al. (1997) and Hidy (1988), the PCA was repeated after removing those elements that were not clearly distinct (positively correlated) to one principle factor. This included the element Rb and the total PAH parameter. In the case of Rb, it was not positively correlated with any principle factor. In the case of total PAHs, this parameter was mildly correlated with principle factors 1 and 3. Both of these parameters gave conflicting indications of unclear associations with the four factors and were removed.

The second PCA with the parameters Rb and total PAHs removed resulted in three factors with eigenvalues greater than one that combined to account for 72% of the total variance (Table 51). The results of the PCA up to this point indicated the possible identity of the first two factors:

- Principle factor 1 was strongly correlated with the elements Si, Ca, Fe, Al, and Mg (re-suspended crustal elements).

Table 49. Input Parameters for PCA

Elements and PAH	% Abundance (n=33)	% of Non-detects (n=33)
Si	39.9	0%
Ca	16.1	0%
Fe	10.2	0%
Al	11.3	0%
K	3.9	0%
Mg	2.3	0%
Ti	1.1	3%
Na	3.2	3%
Mn	0.3	3%
Cl	4.6	9%
Rb	1.8	12%
PAH	4.1 ng/m^3	15%
Cu	0.5	70%
V	<0.1	70%
S	0.3	73%
Br	0.1	85%
I	<0.1	85%
Pb	<0.1	85%
P	<0.1	88%
Ni	<0.1	88%
Sr	0.2	88%
Cr	<0.1	91%
Zn	<0.1	94%
Ce	<0.1	94%
Sc	<0.1	94%
Se	<0.1	94%
Te	<0.1	94%

NOTE: Shaded elements excluded from initial PCA.

- Principle factor 2 was strongly correlated with the elements Na and Cl (re-suspended salt materials).

The results of the PCA were compared to Table 7 and to the morphological results discussed previously in this field study. The result of the PCA are presented again in Table 52 with only those factor loadings that indicated an element strongly associated with a particular source shown (i.e. greater than 0.4).

Table 50. PCA Results – First Analysis

Factors	1	2	3	4
Si	0.8	-0.2	-0.3	0.3
Ca	0.8	0.2	0.1	-0.1
Fe	0.6	0.1	-0.6	-0.1
Al	0.9	-0.1	-0.3	0.1
K	0.0	0.1	-0.4	0.6
Ti	0.0	0.8	-0.1	0.0
Na	0.1	0.9	0.1	0.0
Mg	0.9	0.0	0.1	0.2
Cl	0.1	0.9	0.2	0.1
Mn	0.1	0.0	0.2	0.8
Rb	0.1	-0.2	-0.9	0.1
PAH	0.4	-0.6	0.4	0.2
Eigenvalue	3.6	2.9	1.6	1.2
Variance explained by rotated components	3.3	2.9	1.8	1.3
Percent of total variance explained	27.3	23.9	15.0	11.1

Table 51. PCA Results – Second Analysis

Factors	1	2	3
Si	0.8	-0.2	0.3
Ca	0.7	0.3	-0.1
Fe	0.8	0.1	-0.1
Al	0.9	-0.1	0.1
K	0.1	0.1	0.6
Ti	0.1	0.8	0.0
Na	0.0	0.9	0.0
Mg	0.8	0.0	0.3
Cl	0.0	1.0	0.1
Mn	0.1	0.0	0.9
Eigenvalue	3.4	2.6	1.2
Variance explained by rotated components	3.2	2.6	1.4
Percent of total variance explained	32.1	25.7	13.7

Table 52. PCA Summary Results

Probable Sources	1	2	3
Si	**0.8**		
Ca	**0.7**		
Fe	**0.8**		
Al	**0.9**		
K			**0.6**
Ti		**0.8**	
Na		**0.9**	
Mg	**0.8**		
Cl		**1.0**	
Mn			**0.9**
Eigenvalue	3.4	2.6	1.2
Variance explained by rotated components	3.2	2.6	1.4
Percent of total variance explained	32.1	25.7	13.7

The first principle component contributed 32% of the total variance of the data set. This component was identified as re-suspended crustal materials (e.g. road dust, weathered material, agricultural sources – Table 7), due to the strong correlation with the lithophilic elements silica, calcium, iron, aluminum, and magnesium. Within the community of High Level, these sources could include re-suspension of PM_{10} from agricultural activities, open field, and open roadways.

The second principle component contributed to 26% of the total variance of the data set. This principle component was easily identified as salt aerosols based on strong correlations with sodium and chloride (Table 7). This source was likely the result of re-suspension of salt materials associated with road de-icing activities during winter periods.

The third principle component contributed to 14% of the total variance of the data set. This principle component was strongly associated with potassium and manganese and was inferred to be associated with biomass combustion sources (Table 7). Specific sources of biomass combustion were likely the result of wood burning occurring within the community. In addition morphological and elemental scans of oil particles (e.g. Table 47) indicated the main presence potassium and trace manganese.

Results from the PCA provided indications of several regional sources of ambient PM_{10} in the community of High Level (re-suspended crustal material, re-suspension of salt materials associated with road de-icing, and combustion). These suggested sources accounted for 72% of the total variance from the original data set. The largest contribution was from open crustal sources (32%), the next largest contribution was from re-suspension of salt materials associated with road de-icing activities (26%), and the final source of combustion particles accounted for 14%. A total of 28% of the PM_{10} collected at the two receptor sites originated from unknown sources that could not be identified from the PCA (Figure 64). Morphological observation of PM_{10} filter samples clearly indicated the frequent occurrence of organic particles during spring, summer, and fall – which can also be considered an important source contributing to the composition of ambient PM_{10} in the community.

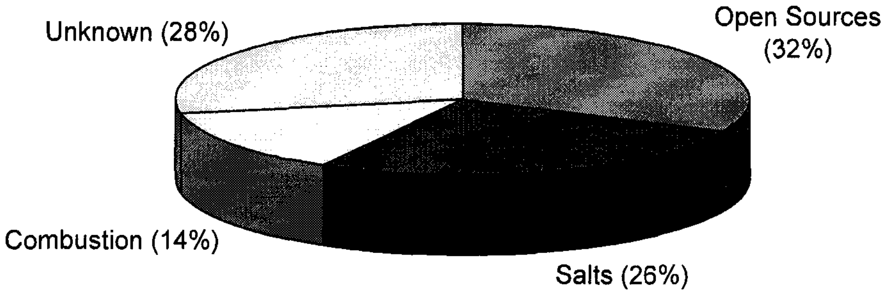


Figure 64. Generic Sources of PM_{10} from Samples Collected in High Level, AB

9.1.4 Maximum Concentrations vs. Wind Direction

In order to provide an independent assessment of inferred regional PM_{10} sources in High Level resulting from the principle component analysis, maximum elemental concentrations associated with wind direction were evaluated. Based on the sampling sites used in the community (Figure 8), re-suspended crustal material (e.g. associated with road dust, weathered material, agricultural sources) was obvious and could originate from all directions. These sources were not of interest in this particular evaluation.

Interest was in attempting to confirm the importance of the latter two suggested factors (re-suspension of salt materials associated with road de-icing, and combustion). A major provincial highway (#35) existed to the east of the sampling sites (Figure 8). In addition, most of the commercial and industrial activities in the community are situated to the south and east of these sampling sites. These activities were initially suspected as providing important contributions to these latter factors and were further evaluated by examining maximum concentrations of individual elements associated with these factors and corresponding wind directions.

Wind direction is one of the most important factors affecting a source-to-site relationship for re-suspended or emitted particulate matter. Meteorological data and calculated elemental concentrations collected at the two sampling sites were combined to derive "maximum elemental concentration wind roses" for selected elements associated with re-suspension of salt materials from road de-icing and combustion. These elements included Na, Cl, and Ti associated with re-suspension of salt materials from road de-icing and K and Mn associated with biomass combustion. The mass concentrations were calculated by the following:

- The mass concentrations for each element were determined by using the TEOM PM_{10} mass concentrations ($\mu g/m^3$) recorded at each corresponding period (24-hours) when a MiniVol sample was collected, to ensure consistency in mass concentrations.
- The mass concentrations ($\mu g/m^3$) were multiplied by the average weight % of 10 randomly selected particles analyzed at the SEM-EDX for all 33 samples collected. Mass concentrations of individual elements were then reported in ng/m^3 (Appendix J).
- In addition, the Wind Direction was averaged over the 24-hours to obtain an average wind direction that could be used to determine the maximum mass concentration occurrences of the selected elements.

Maximum mass concentrations were defined as those concentrations greater than the average plus one standard deviation. For example, the average mass concentration for sodium based on 33 24-hour average samples was calculated as 255 ng/m^3. Adding one standard deviation of 392 ng/m^3 to this quantity resulted in a value of 647 ng/m^3 (~650 ng/m^3) as the maximum mass concentration (Table 53). Therefore 24-hour average mass concentrations of sodium >650 ng/m^3 were accounted for in the maximum mass concentration roses.

The first set maximum mass concentration roses were prepared for the elements associated with re-suspension of salt materials (Na, Cl, and Ti). The maximum mass concentration rose for sodium is shown in Figure 65. Figure 65 shows that 60% of the maximum sodium occurrences were the ESE and 40% from the ENE during the entire study. Figures 66 and 67 show the maximum mass concentration roses for chloride and titanium, respectively.

Table 53. Maximum Mass Concentrations for Selected Elements

Elements	Average Mass Concentration (ng/m^3)	Standard Deviation of Mass Concentrations (ng/m^3)	Maximum Mass Concentration (ng/m^3)
Na	255	392	647 (~650)
Cl	389	761	1,150
Ti	60	75	135
K	239	250	489 (~500)
Mn	22	48	70

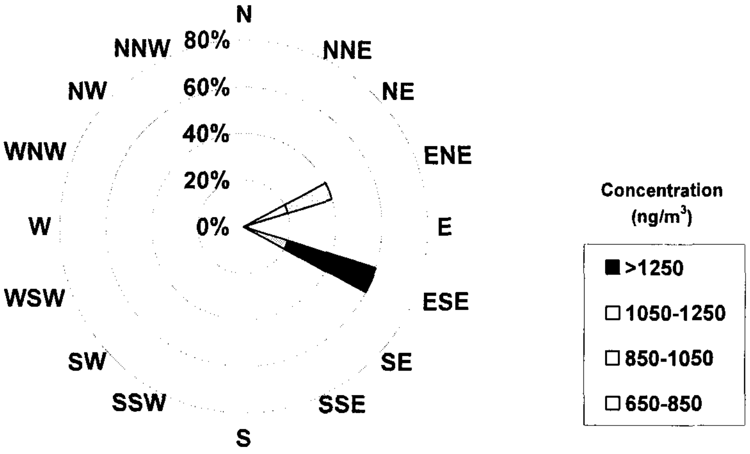


Figure 65. Maximum Mass Concentration Roses for Sodium for the Entire Sampling Period

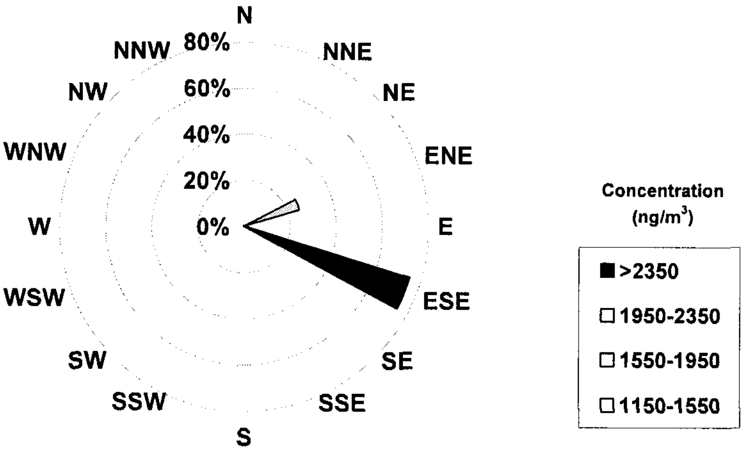


Figure 66. Maximum Mass Concentration Roses for Chloride for the Entire Sampling Period

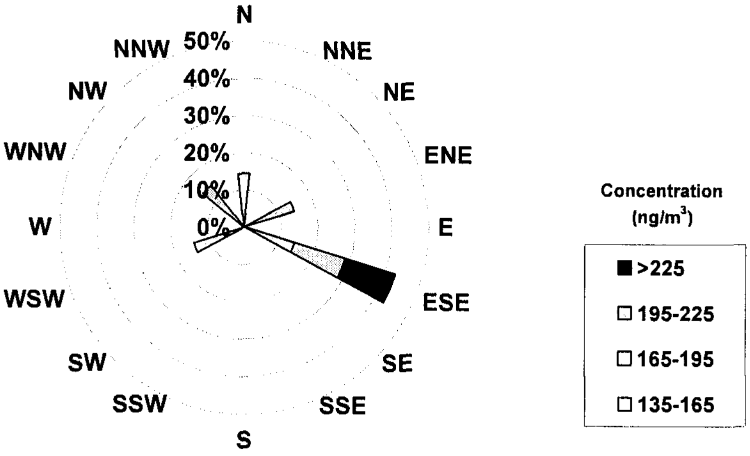


Figure 67. Maximum Mass Concentration Roses for Titanium for the Entire Sampling Period

Results of the maximum mass concentration rose for chloride (Figure 66) indicated 75% of the maximums occurring from the ESE and 25% from the ENE. Whereas for titanium, 43% of the maximum occurrences were from the ESE with <15% occurrences from each of the four directions; ENE, N, NW and WSW (Figure 67). Figures 66 and 67 similarly indicate maximum elemental concentrations occurring with winds from the ESE. Results shown in Figures 65 to 67 were consistent with location of the provincial highway (#35) and commercial and industrial activities in the community (situated to the south and east of the sampling sites). In the case of sodium and chloride – no maximum mass concentration roses were observed with winds from the north, west, and south. This further supported findings of the principle component analysis as the second factor being associated with re-suspension of salt materials and the fact that these activities would be considered important to the south and east of the sampling sites.

The second set of maximum mass concentration roses were prepared for the elements associated with combustion (potassium and manganese). Results of the potassium maximum concentration occurrences indicated 50% of the maximums occurring from the ESE, 25% from the E and 25% from the NW (Figure 68). Results of the manganese maximum concentration occurrences indicated 67% of the maximum occurrences from the ESE, and 33% occurred from the E (Figure 69).

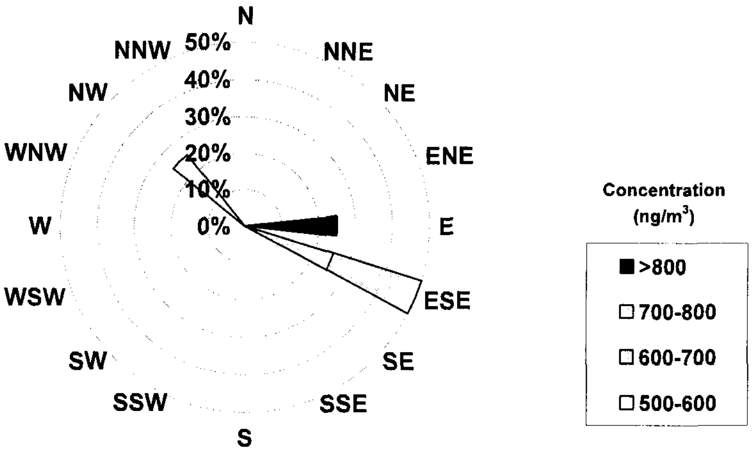


Figure 68. Maximum Mass Concentration Roses for Potassium for the Entire Sampling Period

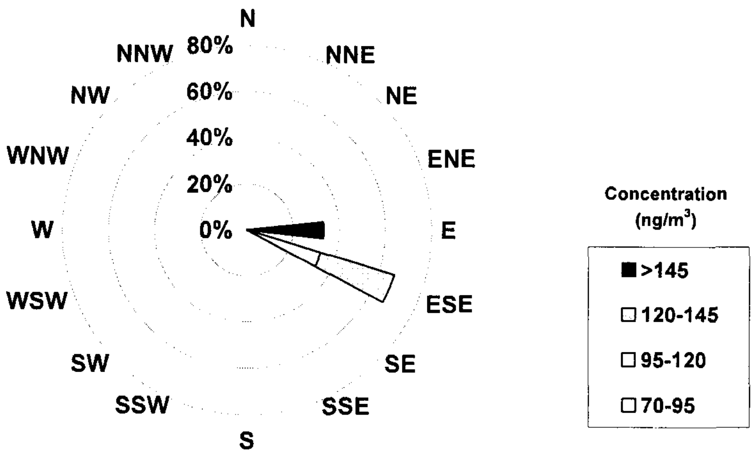


Figure 69. Maximum Mass Concentration Roses for Manganese for the Entire Sampling Period

Results shown in Figures 68 and 69 were again consistent with location of the provincial highway (#35) and commercial and industrial activities in the community (situated to the south and east of the sampling sites). This is indicative of dominant combustion sources originating to the south and east of the sampling sites. Although not shown, these inferred combustion sources were most predominate during summer and fall. This is logical as residential wood burning (a combustion source) could originate from all directions during winter.

9.2 Findings

Based on the analysis from the field study, the following findings are presented:

1. Comparison of 24-hour average PM_{10} concentrations measured with two low volume MiniVols (n=33) and a continuous TEOM demonstrated close similarity ($r^2 = 0.87$), with paired t-test results indicating no differences between each measurement method during the field sampling program ($P \leq 0.05$).
2. Similar to that observed in Chapter 8, individual particle analysis (SEM-EDX)

allowed important qualitative information about particle morphology (form and shape) to be obtained. Combined with elemental information (% abundance), particle morphology provided useful information for the initial indication of particulate matter sources. Morphological observations clearly showed the presence of numerous organic materials (e.g. fungal spores and pollen fragments) in ambient air during warm periods (spring, summer, and fall) and combustion particles (e.g. soot and fine oil droplets) that might otherwise be unaccounted for in a bulk analysis procedure.

3. Use of % abundance data from low volume sampling/SEM-EDX for principle component analysis yielded the following regional sources of PM_{10} in the community of High Level, Alberta: re-suspended crustal material (32%), re-suspension of salt materials associated with road de-icing (26%), and combustion sources (14%), with 28% unaccounted for. Frequent occurrences of organic particles during spring, summer, and fall indicate that these particles are an important contribution to the composition of ambient PM_{10} in the community.
4. Maximum mass concentration roses for selected elements concurred with findings of the principle component analysis for re-suspension of salt materials associated with road de-icing and combustion sources. Maximum mass concentration roses for sodium and chloride were consistent with winds originating from location of the provincial highway (#35) and commercial and industrial activities in the community (situated to the south and east of the sampling sites). Maximum mass concentration roses for potassium and manganese were similarly consistent with winds originating from location of the provincial highway (#35) and commercial and industrial activities in the community (situated to the south and east of the sampling sites).

10. SUMMARY and CONCLUSIONS

10.1 The Problem Statement Revisited

Conventional studies for particulate matter source apportionment typically use fixed FRM samplers followed by bulk analytical techniques. Because of limitations posed by common bulk analytical techniques identified by Koutrakis (1998), a need exists to examine alternative sampling and analytical techniques.

In recent years portable, low volume particulate matter samplers have been used for gravimetric studies, e.g. the Minivol portable air sampler (Airmetrics, Eugene, OR). Low volume samplers are becoming more accessible due to technological miniaturization. These samplers have an advantage of being able to be deployed in non-traditional locations (e.g. without access to power).

However given the low particle masses collected by these samplers, a more suitable analytical technique is required for source apportionment applications. Research was conducted using a low volume sampler coupled with an individual particle analysis technique (SEM-EDX) to determine if this combination of methods could be used to identify probable sources of ambient particulate matter.

10.2 Important Factors in Source Identification

Individual particle analysis is a promising technique that can help identify potential sources and relationships between particles captured by samplers. Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX) analysis is an ideal tool for identification of PM_{10} and $PM_{2.5}$ through visualization of the particle's morphology and elemental signature. This type of information can then be used to aid in identification of particulate matter origins.

Airborne particles originate from a vast mixture of both natural and anthropogenic (human-caused) sources. Potential advantages of individual particle analysis, specifically SEM-EDX, include characterization of particle morphology (size, shape, and texture). For example, for better understanding of particle size and shape, measurements can be made directly from the particle (Figures 70 and 71). These particle measurements may aid in the understanding of individual particle properties in relation to potential sources.

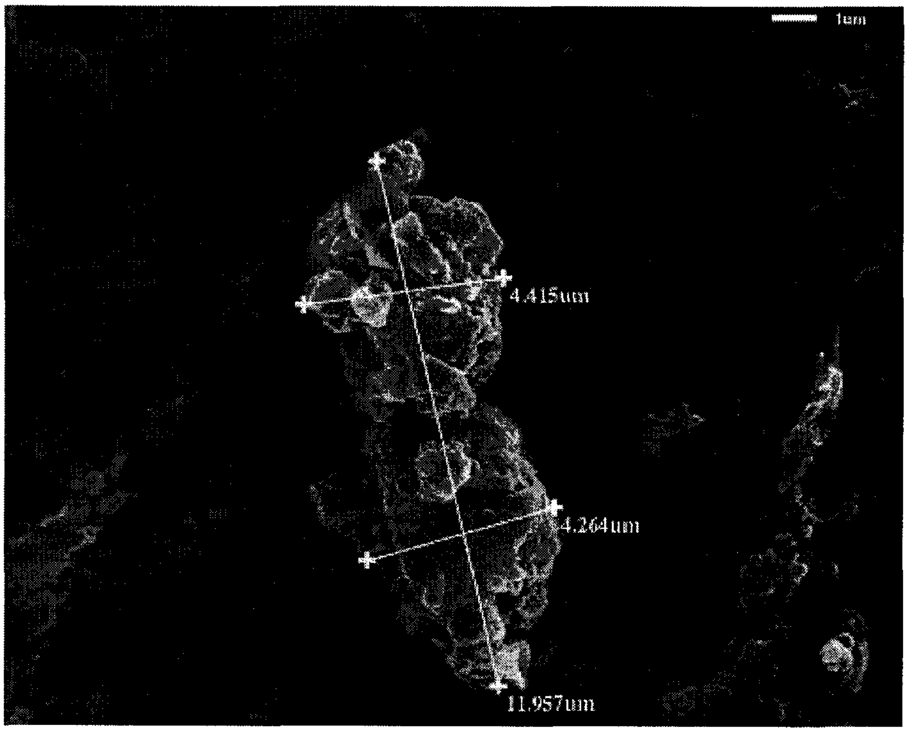


Figure 70. SEM used for Particle Size Identification

A second important advantage of individual particle analysis includes identification of the type and quantities of elements through Energy Dispersive X-Ray (EDX) analysis. An example of SEM-EDX analysis on a crustal clay particle is presented in Figure 72 (SEM picture) and Figure 73 (EDX scan of particle). These figures demonstrate the ability to classify individual particles based on morphology (non-

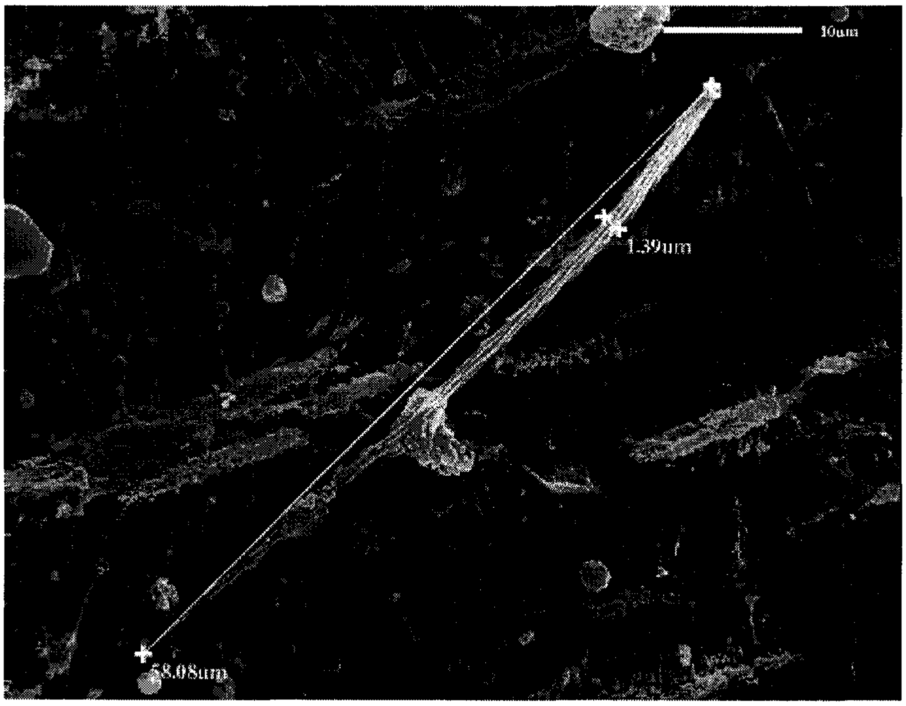


Figure 71. SEM used for Particle Identification and Size Identification

specific irregular flake like shape) as well as identifying the elemental abundances from this particle (primarily Si and Ca). This form of individual particle analysis is not easily performed with a filter collected from a FRM sampler (Figure 74), which shows an example of particles covering the surface area of the filter. Whereas a filter collected with a low volume sampler (Figure 75), shows a spatial covering of particles, which can make individual particle analysis more practical.

Being able to determine particle size properties (morphology) and individual particle elemental composition provides valuable information on potential sources of collected particulate matter. In addition, having the ability to use low volume samplers for an ambient sampling program (both collection and analysis) enables a cost-effective air quality management program in urban or remote sites (Zou and Hooper, 1997).

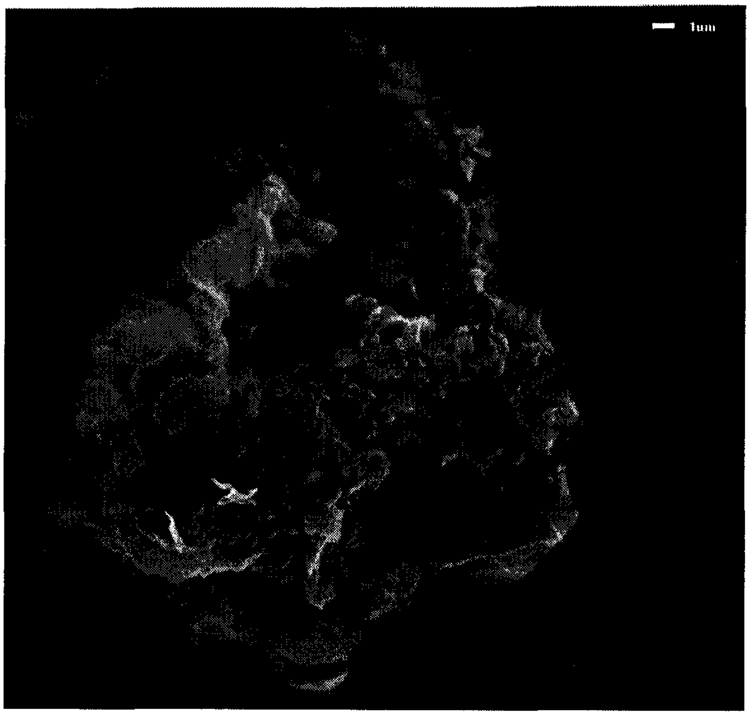
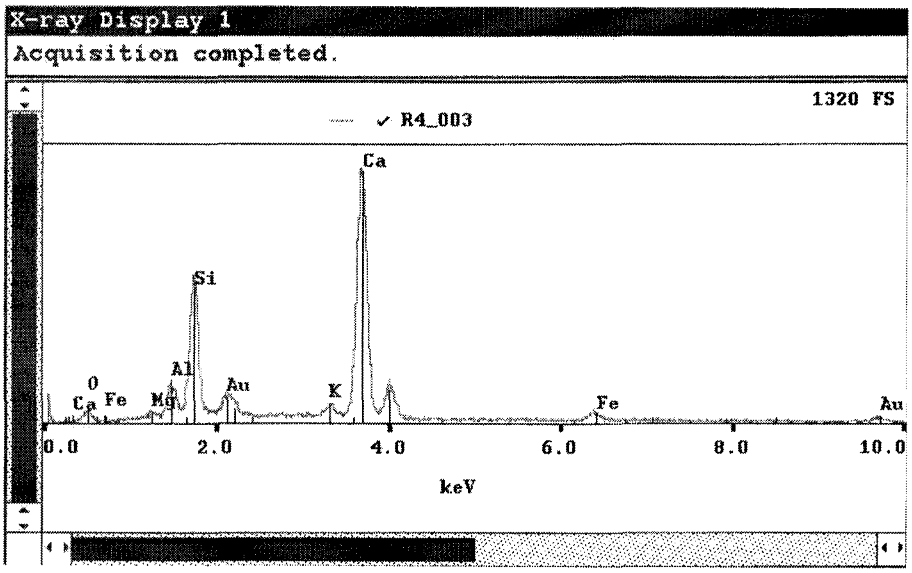


Figure 72. SEM-EDX used for Particle Identification and Elemental Fingerprinting (Photo of a crustal clay particle at 2700x)


X-ray Display 1

Acquisition completed.

Figure 73. EDX Scan used for Elemental Fingerprinting (from crustal clay particle)

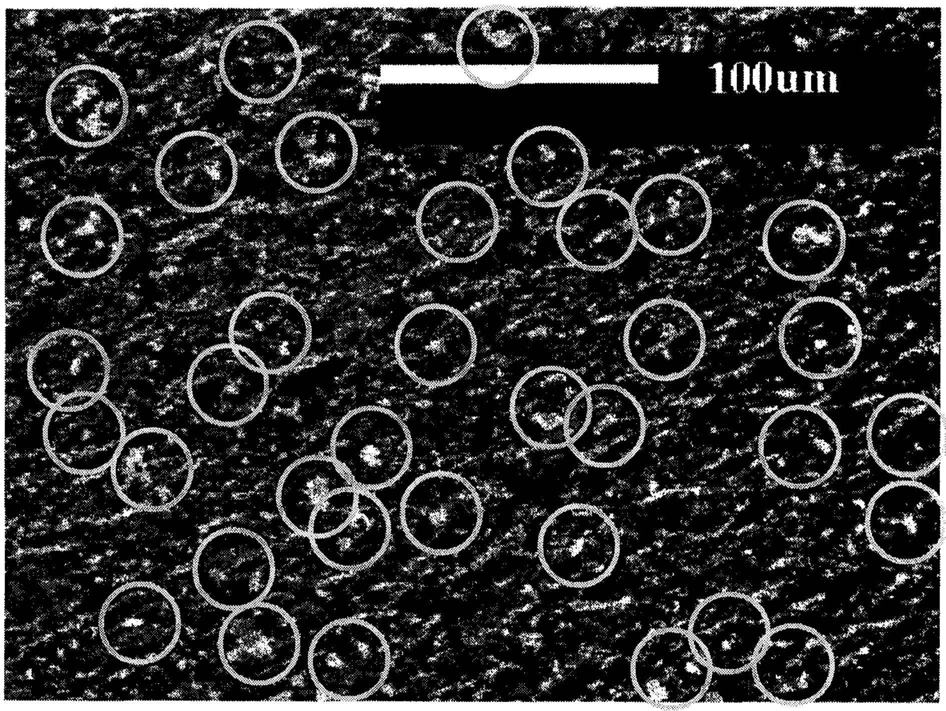


Figure 74. SEM Picture (100x) of a FRM Sampler Filter - Several Individual Particles Highlighted

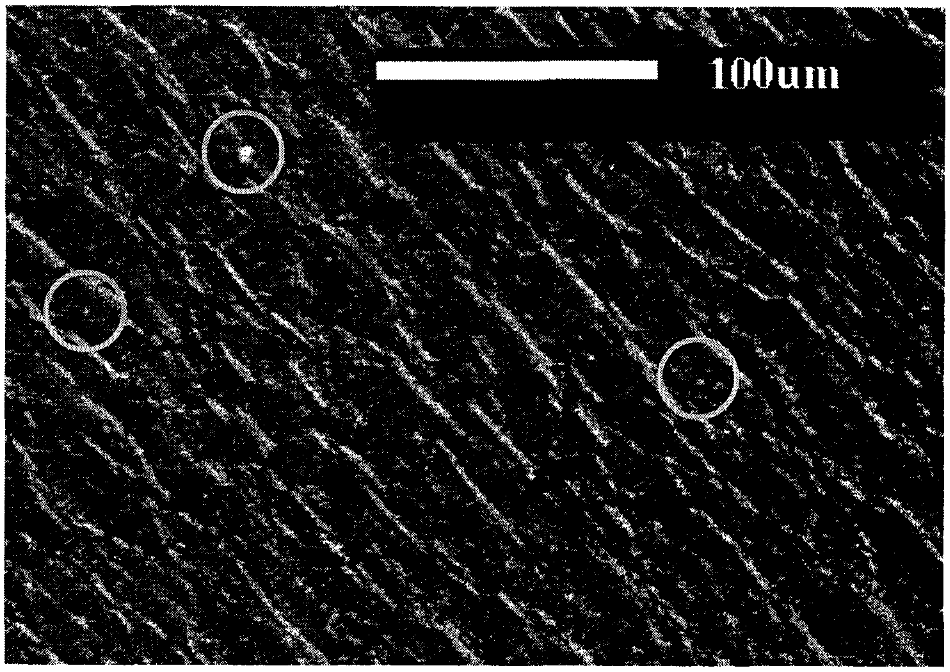


Figure 75. SEM Picture (100x) of a Low Volume Loaded Filter – Individual Particles are Highlighted

10.3 Conclusions

Low volume samplers have been used in limited capacity due to uncertainties in their capabilities and concerns over analytical detection limits. Research was carried out to determine if low volume sampling coupled with individual particle analysis could be used to identify and classify particulate matter in relation of their probable sources using morphological and elemental information. The main conclusions from this study are:

1. Individual particle analysis (SEM-EDX) was able to provide information about particle morphology (form, shape, and texture) and elemental properties (type and % abundance). This information can then be used to provide a preliminary indication of probable sources of ambient particulate matter. This information would not be possible using bulk analytical techniques that only provide information on elemental properties. Because this categorization can be based solely on identification of individual particles by SEM-EDX, it would not be necessary to analyze a large number of filters to indicate probable sources of ambient particulate matter. Ideally, one representative filter sample could be able to provide a preliminary indication of probable sources provided that enough individual particles are considered in the analysis.

2. Low volume sampling using a MiniVol portable air sampler in laboratory experiments and field collection experiments demonstrated close agreement between a Grimm dust analyzer (laboratory) and Tapered Elemental Oscillating Microbalance (TEOM) (field) sampled over 24-hour periods. Laboratory results (n=10)

demonstrated close agreement between MiniVols and the Grimm ($r^2 = 0.95$ to 0.99), with paired t-test results indicating no statistical difference in the collection ability of each sampling method ($P \leq 0.05$). Field results (n=33) similarly demonstrated close agreement between MiniVols and the TEOM ($r^2 = 0.87$), with paired t-test results indicating no statistical difference in the collection ability of each sampling method ($P \leq 0.05$).

3. Another feature in demonstrating that low volume sampling/individual particle analysis (SEM-EDX) is a viable alternative for airborne particulate matter source apportionment is establishing the minimum number of particles collected on a filter to be subjected to individual particle analysis. Paired t-tests of laboratory results demonstrated that SEM-EDX analysis of a minimum of 10 randomly-selected particles within a filter area measured similar elemental quantities of up to 40 randomly-selected particles within the filter area for NIST–1648 Standard Reference Material collected by low volume samplers ($P \leq 0.05$). Based on these findings it was recommended that no less than 10 randomly-selected particles should be analyzed within a 13 mm-diameter filter surface area for low volume sampling and individual particle analysis applications. This was further confirmed by the results of the field study indicating that by averaging 10 randomly-selected ambient particles gave similar results ($P \leq 0.05$) to ICP-MS results.

4. Teflon filters were found to be an excellent medium for collecting and analyzing individual particles by SEM-EDX. These filters provided minimal background

material that interfered with predominate elements found from generic ambient sources. Teflon filters that are numerically stamp coded are best for tracking and handling prior to analysis.

5. Another important feature in demonstrating low volume sampling and individual particle analysis as a viable alternative for airborne particulate matter source apportionment is its ability to quantify the abundance of elements present in particles collected. NIST 1648 Urban Particulate Matter Standard Reference Material was used in sealed chamber experiments to measure average elemental quantities (% abundance) by collecting samples of the material on low volume samplers. Paired t-test results of this laboratory study demonstrated that SEM-EDX analysis of 10 randomly selected particles on a filter sample could detect similar elemental quantities as measured from ICP-MS ($P \leq 0.05$) and compared to the corresponding SRM certificated quantities ($P \leq 0.05$). These findings support that individual particle analysis method can provide representative quantitative data on elements (e.g. type and % abundance) when combined with low volume sampling of airborne particulate matter.

6. Morphological observation of field-derived filter samples made with scanning electron microscopy allowed for identification of organic particles (e.g. fungal spores and pollen fragments) and oil particles (droplets). Distinct size and shape characteristics of these particles, and in the case of fine oil droplets – the frequency of occurrence of these particles, allowed for an indication of quantities present on a filter

surface in comparison to other particles. In terms of count, there were times when these particles dominated particle types observed on a filter surface. In these instances, these particles may have the ability to bias source apportionment applications based on measurement of elemental quantities using bulk analysis techniques alone.

7. A field study comparing 24-hour low volume sampling/SEM-EDX with low volume sampling/ICP-MS (n=10) was able to demonstrate similar measurement of selected elements, including silica, calcium, iron, aluminum, magnesium, potassium, sodium, zinc, titanium, and manganese ($P \leq 0.05$). Due to insufficient material collected for analysis with ICP-MS there was an inability to demonstrate comparable findings with the results determined by SEM-EDX for the trace elements arsenic, chromium, cadmium, lead, copper, nickel, vanadium and cobalt ($P \leq 0.05$) with low volume sampling/ICP-MS (n=10). A Further investigation indicated that there was not enough particle mass collected on the Minivol filters to reliably quantify the eight trace elements of interest using ICP-MS. Thus ICP-MS was not providing a true representation of elemental quantities in ambient PM_{10} in the field study. Further comparative analysis of these trace elements under defined (e.g. laboratory or field controlled) conditions are recommended to demonstrate that low volume sampling/SEM-EDX can provide comparable measurements of trace elemental quantities.

8. A second field sampling program was conducted by collecting a minimum number of 24-hour average PM_{10} samples (n=33) at two sites over four seasons using low volume samplers and individual particle analysis in High Level, Alberta. A receptor modeling technique using principle component analysis (PCA) was performed using elemental abundances reported from the individual particle analysis. Utilizing a detailed summary of source fingerprints summarized from the literature, the PCA provided sufficient information for identifying three probable generic sources of particulate matter in the community. These included re-suspended crustal material (32%), re-suspension of salt materials associated with road de-icing (26%), and combustion sources (14%). Approximately 28% of the probable origins of ambient PM_{10} could not be accounted for. Maximum mass concentration roses for selected elements concurred with findings of the PCA for re-suspension of salt materials associated with road de-icing and combustion sources.

10.4 Potential Applications and Engineering Significance

There has been a higher level of demand from the public to determine what is in the air they breathe. The ability to deploy small and remote air samplers to aid in identifying and classifying individual particle's origin at sampling locations would be a great tool for air quality scientists and engineers. The application of both the low volume samplers and individual particle analysis has the ability to be used in both indoor and outdoor studies. This tool would be practical for answering questions of particulate matter sources in problem environments for industry, government agencies, and the public. The main engineering applications from this study include:

- Individual particle analysis techniques developed can be utilized in air sampling projects and ambient dust collection projects conducted by industry and government agencies in all different regions.
- Low volume samplers are more cost effective allowing industry and governments to collect credible scientific data through individual particle analysis.
- Individual particle analysis of single samples may be used to identify probable sources based on particle classification of the sample collected.

11. RECOMMENDATIONS

In terms of future research, the following recommendations are made:

1. This study identified comparable measurement capabilities of SEM-EDX for major elements compared to ICP-MS. To further evaluate SEM-EDX capabilities of trace elements in comparison with ICP-MS, further evaluations are recommended. A chamber study is recommendation to be performed with SRM NIST 1633b - Coal Flyash which contains high amounts of important trace elements. Mass injections can be collected with low volume samplers for collection of duplicate samples for analysis of ICP-MS and SEM-EDX.

2. To further evaluate trace elemental capabilities of the SEM-EDX it is recommended that a duplicate field test be performed with low volume samplers collocated with duplicate FRM samplers. This would enable evaluation of trace elements collected on both low and FRM samplers in conjunction with individual particle analysis and ICP-MS. It is also recommended to increase sampling periods to ensure adequate material is collected by the low volume samplers for comparable analysis with ICP-MS.

3. This study focused on low volume integrated samplers; newer low volume "real-time" particulate analyzers are now available in portable housings through technological improvements. By coupling the real-time trending capabilities with

individual particle analysis may strengthen the potential source to receptor modeling capabilities. Further research work could be directed at particle identification utilizing filters collected from these low volume analyzers.

4. To aid in the automation of particle classification or speciation, it is recommended to utilize techniques of real-time low volume sampling coupled with new technology of computer controlled scanning electron microscopy. These time-of-flight techniques may enable fast collection and identification of samples as well as aiding fast particle identification based on specific time-released sources (e.g. traffic rush-hour periods or facility loading periods).

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Appendix A 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}	25 $\mu g/m^3$ averaged over 24 hours (*reference level*)
	$PM_{2.5}$	15 $\mu g/m^3$ averaged over 24 hours (*reference level*)
	$PM_{2.5}$	30 $\mu g/m^3$ averaged over 24 hours (Canada Wide Standard)[a]
	TSP	120 $\mu g/m^3$ as a 24-hour average concentration (max acceptable)
		120 $\mu g/m^3$ as a 24-hour 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-hour average concentration
		70 $\mu g/m^3$ as an annual geometric mean
BC	TSP	150 $\mu g/m^3$ as a 24-hour average concentration (desirable)
		200 $\mu g/m^3$ as a 24-hour 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-hour average concentration
		60 $\mu g/m^3$ as an annual geometric mean
QB	TSP	150 $\mu g/m^3$ as a 24-hour average concentration
		70 $\mu g/m^3$ as an annual geometric mean
United States Environmental Protection Agency (EPA, 1997c; State of California, 2000)	PM_{10}	150 $\mu g/m^3$ as a 24-hour average concentration [b]
		50 $\mu g/m^3$ as an annual mean concentration [c]
	$PM_{2.5}$	65 $\mu g/m^3$ as a 24-hour average concentration [d]
		15 $\mu g/m^3$ as an annual mean concentration [c]
CA (Californa Air Resource Board)	PM_{10}	50 $\mu g/m^3$ as a 24-hour average concentration
		30 $\mu g/m^3$ as an annual geometric mean concentration
	$PM_{2.5}$	*As per Federal Regulations*
European Union (European Union, 1997)	PM_{10}	50 $\mu g/m^3$ as a 24-hour limit value not to be exceeded more than 25 times per year (January 1st 2005)
		30 $\mu g/m^3$ as an annual limit value (January 1st 2005)
		50 $\mu g/m^3$ as a 24-hour limit value not to be exceeded more than 7 times per year (January 1st 2010)
		20 $\mu g/m^3$ as an annual limit value (January 1st 2010)
England (UK Department of the Environment, 2000)	PM_{10}	50 $\mu g/m^3$ as a 24-hour mean concentration, not to be exceeded more than 35 times a year (*December 31st 2004*)
		40 $\mu g/m^3$ as an annual mean (*December 31st 2004*)
Australia (NEPC, 1998)	PM_{10}	50 $\mu g/m^3$ as a 24-hour average concentration
World Health Organization (Pryor and Barthelmine, 1996)	PM_{10}	70 $\mu g/m^3$ as a 24-hour 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-hour 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-hour $PM_{2.5}$ concentrations

Appendix B MiniVol and TEOM Calibration Information

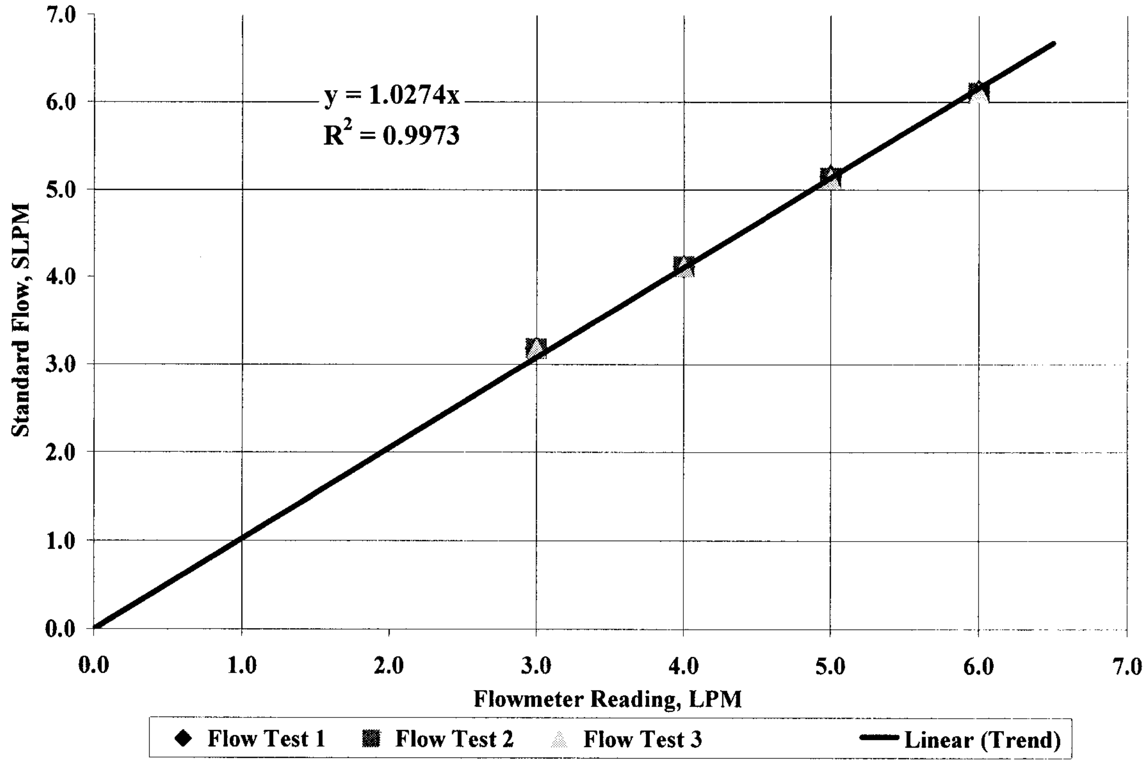

Figure B1. MiniVol 2325 Calibration Curve

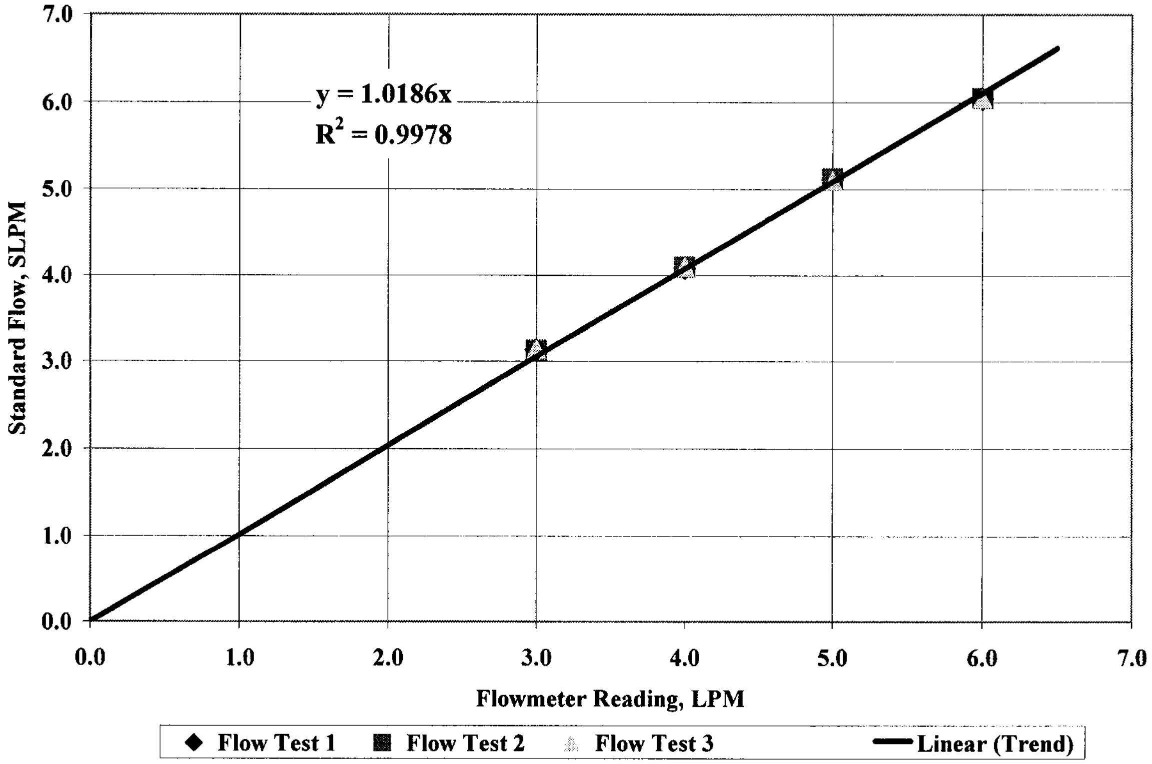

Figure B2. MiniVol 2324 Calibration Curve

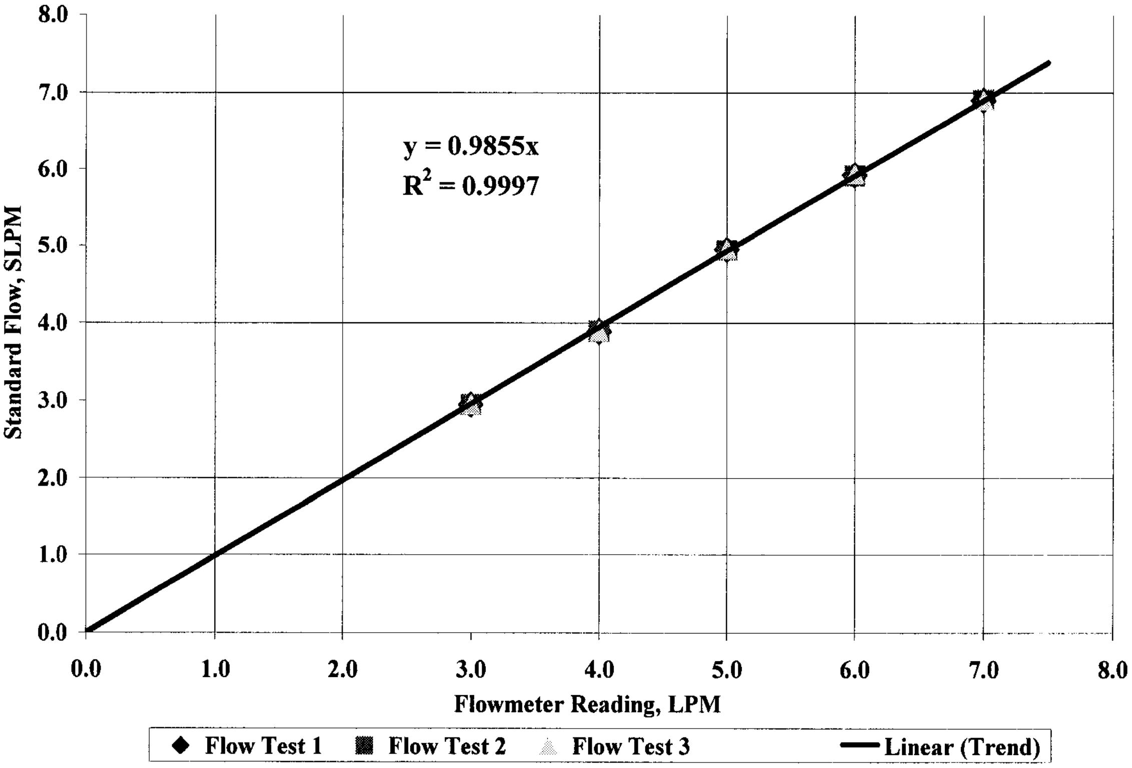

Figure B3. MiniVol 2201 Calibration Curve

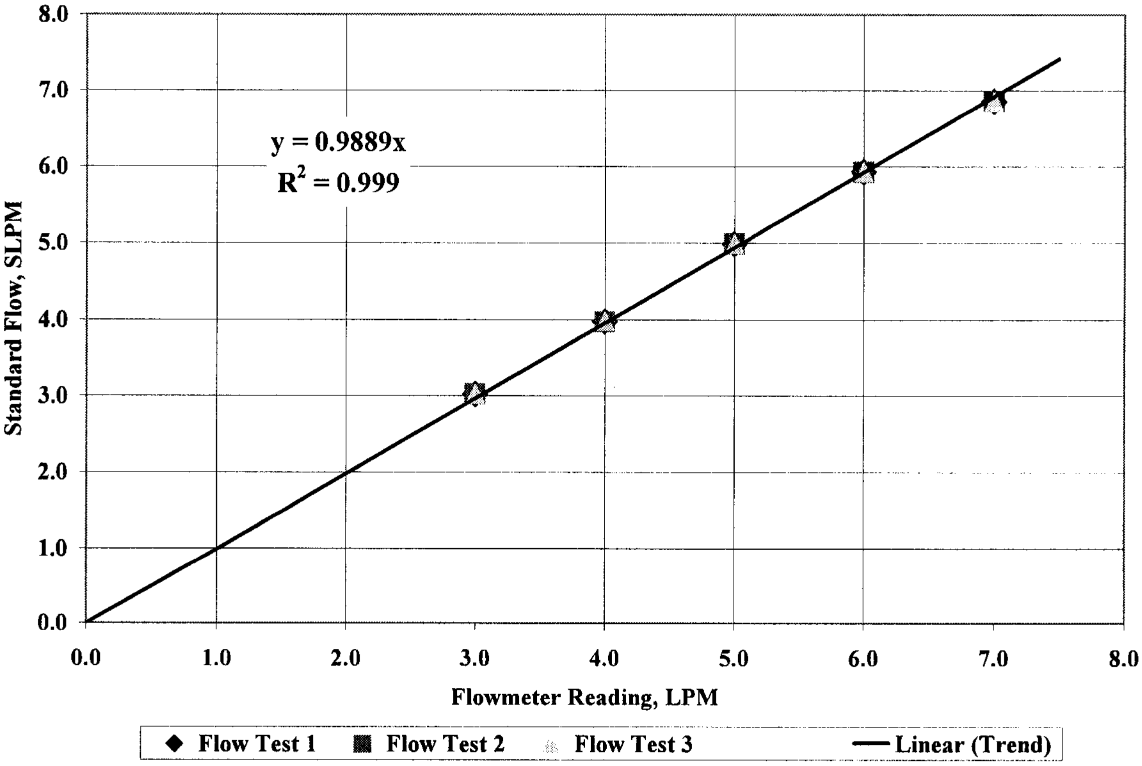

Figure B4. MiniVol 2127 Calibration Curve

Table B1. TEOM Operation Information

Operator must press <Data Stop> on the keypad before editing is allowed for all screens except "SET ANALOG O/P" screen. After changes are made the operator must press <Run> from the keypad to start sampling.

Parameter	Factory Values	TEOM Set Up
SET TEMPS/FLOWS SCREEN		Press <Step Screen> 2 times from main screen
T-Case	50.00 °C Set Point	Set to 40°C for PM_{10}
T-Air	50.00 °C Set Point	Set to 40°C for PM_{10}
T-Cap	50.00 °C Set Point	Set to 40°C for PM_{10}
T-Encl	50.00 °C Set Point	Set to 40°C for PM_{10}
F-Main	3.00 l/min.	See note
F-Aux	13.67 l/min.	See note
T-A/S (Average/Standard Temp)	99 for Average Temp	Ensue this is set at 99
P-A/S (Average/Standard Press.)	9 for Ave Press	Ensue this is set at 9
Fadj Main	1.000 (factor) Main Flow Adj.	No change
Fadj Aux	1.000 (factor) Aux Flow Adj.	No change

Note:

Flow was checked at Alberta Environment using a BIOS DryCal® Primary Flow Meter (BIOS International, SMG/interlink, Texas, USA)
Main flow was checked and read 2.95 SLPM (± 0.2 SPLM) therefore acceptable
Auxilary flow was checked and read 13.55 SLPM (± 1.0 SPLM) therefore acceptable
Total flow was checked and read 16.50 SLPM
Leak Check on the main line indicated 0.02 SLPM (<0.15 SLPM) therefore acceptable
Leak Check on the aux line indicated 0.02 SLPM (<0.15 SLPM) therefore acceptable
Temperature check was within 1 degree therefore acceptable
Pressure check was within 1.5% of atm therefore acceptable

Table B2. TEOM Setup Information

SET HARDWARE SCREEN		Press <Step Screen> 3 times from main screen
Cal Constant>	****.***	This number **must** match the label located inside the sensor unit (tapered element block).
Ser. Num		Should match the number on the sensor and control unit
Wait time	1800 sec. (temp/flow stability)	Standard time.
MR/MC Ave	300 sec. (averaging time)	
TM Ave	300 sec. (averaging time)	
Const A	3.000 (U.S. EPA setting: 3.000)	Leave as 3.000
Const B	1.030 (U.S. EPA setting: 1.030)	Leave as 1.030

Table B3. TEOM Time Information

SET TIME SCREEN		**Press <Time/Date> on keypad.**
Second, Minute, Hour	Current M.S.T.	Mountain Standard Time
Day, Month, Year	Current M.S.T.	Mountain Standard Time

Table B4. TEOM Output Information

SET ANALOG O/P SCREEN	Press <A/O> on keypad
Var 1	Enter code <008> for **Mass Concentration** in $\mu g/m^3$
Var 2	Enter code <057> for **30-minute average Mass Concentration** in $\mu g/m^3$
Var 3	Enter code <058> for **1-hr average Mass Concentration** in $\mu g/m^3$
Var 4	Enter code <060> **for 24-hr average Mass Concentration** in $\mu g/m^3$
Var 5	Enter code <009> **for total mass collected** in μg
Var 6	Enter code <130> for **Ambient Temp** in degrees Celcius
Var 7	Enter code <131> for **Ambient Pressure** in atm
Var 8	Enter code <041> for **System Status**

Appendix C Laboratory and Field Protocols

Sampling protocols are developed for weighing, handling, transporting, and examination of low volume sampling filters. As for the TEOM, PAS 2000, Campbell Scientific meteorological station, and Grimm, the equipment is set up, calibrated and run according to their operation manual specifications. To ensure sampling and laboratory procedures were adhered to, sampling protocols were developed prior to each phase of research commencing. There are very limited numbers of people that can handle the equipment and samples with the primary researcher always present; therefore protocols will be strictly followed.

A step-by-step protocol for both phases of sampling was developed, with adherence to environmental sampling standards (EPA, 1994a; EPA, 1996a; ASTM 1998) and laboratory procedures (Alberta Environmental Centre, 1993; JEOL Ltd., 1997; EPA, 1999b)

Weighing Protocol (Pre and Post)

- Filters are only picked up by Teflon tipped forceps.
- Forceps are cleaned using methanol before and after handling the filter (note – allowing enough time for methanol to dry before handling the filter).
- Scale is checked through an internal calibration prior to use and after weighing every 10 filters.
- For every 10 filters weighed, randomly choose one filters to be re-weighed for verification.

Pre-weighing

- New filters are stored in their sealed box, in the weighing room.
- Filter packages are only opened in a laminar-flow hood
- Filters are inspected for flaws such as rips or tears and if found, filter is dispose of.
- New filters are placed in petri slides (supplied with the filters).
- Filters in the petri slides are moved into the weighing room for stabilization.
- The filters in the petri slides remain in the room for 48 hours.
- Filters are individually weighed a minimum of three times each.

  - Sample numbers are recorded on the petri slides to identify filters in the field.
  - Two blanks are also pre-weighed and brought into the field.

Post-weighing

  - Filters returned from the field, have the paraffin wrap removed the slides placed into the weighing room.
  - Slides remain in the room for 48 hours.
  - Filters are individually weighed a minimum of three times each.

Field Handling Protocol

- All filter exchanges are made in shelter (vehicle, or inside a shed).
  - Filter number verified on the petri slide.
  - Confirm number from sample sheet the sample number to be used.
- Remove filter assembly from the Minivol and open the filter holder.
  - Inspect the filter and holder for damage.
- Place / remove the appropriate filter number from the petri slide with cleaned forceps, and place / remove from the Minivol filter holder.
  - Ensure the filter is appropriately seated in the filter holder.
- In the field log book mark all appropriate information:
  - Date, time, Location, Minivol #, sample test (PM_{10} or $PM_{2.5}$), Battery #, Filter #, Start / End time, Start / End elapsed time, and Start / End flow rate.
  - Minivol flow rate is determined by the calibration calculation utilizing the ambient temperature and pressure.

Transporting Protocol

- After the appropriate filter has been taken out of the Minivol filter holder and placed back into the appropriate petri slide, the slide is wrapped with a thin paraffin wax.

- The slide is then packed into a tackle box in a flat position, and packed in place with foam to keep movement to an absolute minimum during transport.
- The tackle box is transported in a manner such that it will not tip or become logged on its side during the time of travel.

MiniVol Protocol

- MiniVol flows are re-tested to ensure adequate flows prior to extended sampling operations.
- For cleaning the impaction plates on the MiniVol sampling heads, the heads are removed, inspected, cleaned and re-greased:
    - Once a week during field sampling.
    - After each mass injection for the laboratory sampling.

SEM–EDX Analysis Protocol

- Filter preparation only performed in a laminar-flow hood to prevent passive deposition on the filter.
- The 47 mm Teflon filter are mounted on a 13 mm stub with carbon tape, with the plastic ring removed. This left approximately 20 mm of the center filter surface to represent the entire filter.
- The filters are to be pre-coated with gold for better transmission and imagery.
- When analyzing a filter, particles are to be chosen at random for quantification analysis.
- Individual Particle analysis was performed following:
    - Each filter was examined in two parts, a broad overview followed by individual particle analysis
    - For the individual particles the filter was examined in a sweeping pattern starting from the top of the filter, moving left to right

  - As the filter was being moved, a random area would be chosen, and slowly surface would be brought into full magnification. If there were particles present, one would be chosen and then focus would be moved to a new area.
  - A minimum of 10 particles were analyzed by EDX, with more examined for morphology (as time permits). This was due to particles such as organics and combustion particles that are not able to be scanned EDX.
  - The morphology of particles were noted based on their size, shape and elemental signature. These were then classified into specific groups identified in Chapter two).
- Field blanks and batch blanks were treated the same as a field or laboratory sample to ensure consistency in analysis. However due to lack of particles on blank samples a minimum of 10 particles was not typically not possible.
- Elemental weight % was determined by averaging the 10 random particles analyzed on each filter. This enabled consistency between samples collected both in the laboratory and field samples. This also enabled several filters to be analyzed in a timely and consistent manner.
- % Abundance was calculated by:
  - $\%\,\text{Abundance SEM-EDX} = \dfrac{\text{Individual elemental weight }\%}{\sum \text{Total elemental weight }\%}$
- An assumption made for SEM-EDX analysis was that the particles collected on the filter were uniformly distributed across the collection area.
- Mass concentrations ($\mu g/m^3$) are multiplied by the average weight % of 10 randomly selected particles (SEM-EDX) and converted to (ng/m^3) by multiplying by 1000. This results in the mass concentrations of individual elements (ng/m^3).

ICP-MS Analysis Protocol – Laboratory Phase

- Filter preparation only performed in a laminar-flow hood to prevent passive deposition on the filter.

- The plastic ring around the 47 mm Teflon filter is cut off prior to the acid digestion.
- The remaining filter was prepared according to SW-846 Method 3050b – Acid Digestion for ICP-MS analysis (EPA, 1996b).
- % Abundance was calculated by:
    - $\%\,\text{Abundance ICP-MS} = \dfrac{\text{Individual elemental concentration } (\mu\text{g/m}^3)}{\sum \text{Total elemental concentrations } (\mu\text{g/m}^3)}$

ICP-MS Analysis Protocol – Field Phase

- Filters were pre and post weighed at the Alberta Research Council (ARC), therefore the filter was only collected from the ARC deployed for the 24-hr test, and returned to the ARC for analysis. The procedure for analysis is in Appendix E.

Laboratory Chamber Handling and Injection Protocol

- Filter preparation only performed in a laminar-flow hood to prevent passive deposition on the filter.
- The corner weights from the top of the chamber are removed to allow for the lid to be removed.
- Using a sampling head removal tool, the two MiniVol heads are removed and taken out of the chamber.
- The heads are cleaned and filter exchanged according to the MiniVol protocols.
- The tank is cleaned between injections with a squeegee vacuum system. The chamber was then left for a minimum of one hour to settle.
- The MiniVol heads are then put back into the chamber (with a new filter), and tank top re-sealed.
- The water trap is filled to appropriate level.
- The Grimm dust sampler is then turned on and monitored for one hour and if particle count is between one and zero, then injection of dust can be done.

Appendix D XRF Analysis Results

The samples prepared for the XRF were placed on a concrete "puck" to avoid flexing or bending of the filter. The results of the test indicated that the concrete background was more prevalent than the sample material collected. In addition there was very little difference between a collected field sample and the blank used for comparison.

Table D1. XRF Analysis

Channel	Slope Intercept	First Calculated	Last Calculated	24-hr Field Sample 4-Feb-00 14:19:33 15-Jan-01 13:27:55	Blank Sample 4-Feb-00 14:19:33 15-Jan-01 13:27:55
Al	1.07	4-Feb-00	15-Jan-01	1.16	1.24
	0.00	14:19:33	13:27:55		
Ca	0.95	4-Feb-00	15-Jan-01	718.31	684.64
	0.00	14:19:33	13:27:55		
Fe	0.98	4-Feb-00	15-Jan-01	18.64	18.23
	0.00	14:19:33	13:27:55		
K	0.99	4-Feb-00	15-Jan-01	8.74	8.63
	0.00	14:19:33	13:27:55		
Mg	1.06	4-Feb-00	15-Jan-01	1.48	1.57
	0.00	14:19:33	13:27:55		
Mn	0.84	4-Feb-00	15-Jan-01	1.57	1.32
	0.00	14:19:33	13:27:55		
Na	1.62	4-Feb-00	15-Jan-01	0.29	0.47
	0.00	14:19:33	13:27:55		
P	0.94	4-Feb-00	15-Jan-01	0.31	0.29
	0.00	14:19:33	13:27:55		
S	0.96	4-Feb-00	15-Jan-01	2.36	2.26
	0.00	14:19:33	13:27:55		
Si	0.90	4-Feb-00	15-Jan-01	5.77	5.21
	0.00	14:19:33	13:27:55		
Ti	0.98	4-Feb-00	15-Jan-01	1.93	1.90
	0.00	14:19:33	13:27:55		

Appendix E University of Alberta ICP-MS Methods and Detection Limits

Method Used for Analysis:

SW-846 3050B – Acid Digestion of Sediments, Sludges, and Solids (EPA, 1996b)

Table E1. University of Alberta – Department of Chemistry ICP-MS Instrumental Detection Limits

Element	Instrumental Detection Limits (μg/filter)
Aluminum	4.5
Antimony	3.2
Arsenic	5.3
Barium	0.2
Beryllium	0.03
Boron	0.5
Cadmium	0.4
Calcium	1
Chromium	0.7
Cobalt	0.7
Copper	0.6
Iron	0.7
Lead	4.2
Magnesium	3
Manganese	0.2
Molybdenum	0.8
Nickel	1.5
Selenium	7.5
Silicon	5.8
Silver	0.7
Sodium	2.9
Thallium	4
Vanadium	0.8
Zinc	0.2

Appendix F Alberta Research Council ICP-MS Methods and Detection Limits

ELEMENTAL ANALYSIS METHODOLOGY OF TEFLON OR ZEFLUOR FILTER-COLLECTED AIRBORNE PARTICULATE MATTER WITH INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

Scope and Application

1. Method development for the digestion of the airborne particulate matter samples collected on air filters with subsequent ICP-MS determination of the chemical element content.

2. Quantitative analysis of the toxic trace metals in airborne particulate matter retained on the filters of ambient air pollution monitors and/or personal exposure monitors is rather challenging to analytical chemists. First, the amount of the inhalable particulate retained on the Teflon filter is relatively small. The loading of a typical Teflon filter is in the range of 0.04-1.0 mg. Collected over 24 hours with an air flow rate of 10 L/min for the typical amounts of coarse (PM_{10}) and fine ($PM_{2.5}$) particulate matter retained on the Teflon filter of an air sampler. Therefore, when an analytical instrument with an aqueous sample introduction system is employed, the analytical method has to be highly sensitive. Secondly, for human exposure assessment purposes, it is the total metal content of the inhalable particulate matter, as opposed to total recoverable metals or extractable metals, that is of interest. This means that the particulate matter retained must be completely digested. Thirdly, clean-laboratory procedures in a clean-laboratory environment have to be employed to guarantee the analysis at ultra-trace levels.

3. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) has become one of the most attractive detection systems for trace element analysis because of its excellent detection limits, wide linear dynamic range, multi-element capability, and the ability to measure isotope ratios. ICP-MS offers very low detection limits in a range of 1 to 100 pg/mL for most elements. The only analytical method that has sufficiently low detection limits to permit routine multi-elemental (up to 65

elements) analysis of small (0.1-1 mg) aerosol samples is ICP-MS (Jalkanen and Häsänen, 1996).

4. The contained particulate matter on Teflon filter is digested using a mixture of concentrated nitric acid and hydrofluoric acid in closed test tubes at constant temperature. The whole sample preparation procedure will have to be performed in a clean-laboratory environment. A suitable clean-laboratory digestion procedure which will result in low digestion blanks, total dissolution of the particulate matter, a reduced final volume of the dissolution solution, a suitable matrix in the final aqueous solution for the ICP-MS determination. The digestion procedure should not result in any loss of the target metal.

5. The goal of this method is to perform air particulate matter sample decomposition with HNO_3-HF. The preparation type is defined as Air Particulate Total Recoverable (A). This method is applicable to most airborne particulate matter including PM_{10}, $PM_{2.5}$ and Total Suspended Particulates (TSP) to determine the following 65 elements:

Aluminum (Al)
Antimony (Sb)
Arsenic (As)
Barium (Ba)
Bismuth (Bi)
Beryllium (Be)
Boron (B)
Bromine (Br)
Cadmium (Cd)
Calcium (Ca)
Cerium (Ce)
Cesium (Cs)
Chloride (Cl)
Chromium (Cr)
Cobalt (Co)
Copper (Cu)
Dysprosium (Dy)
Erbium (Er)
Europium (Eu)
Gadolinium (Gd)
Gallium (Ga)
Germanium (Ge)
Gold (Au)
Holmium (Ho)
Indium (In)
Iodine (I)
Iron (Fe)
Lanthanum (La)
Lead (Pb)
Lithium (Li)
Magnesium (Mg)
Manganese (Mn)
Mercury (Hg)
Molybdenum (Mo)
Neodymium (Nd)
Nickel (Ni)
Niobium (Nb)
Palladium (Pd)
Platinum (Pt)
Praseodymium (Pr)
Phosphorus (P)
Potassium (K)
Rubidium (Rb)
Samarium (Sm)
Scandium (Sc)
Selenium (Se)
Silicon (Si)
Silver (Ag)
Sodium (Na)
Strontium (Sr)
Sulfur (S)
Tantalum (Ta)
Tellurium (Te)
Terbium (Tb)
Thallium (Tl)
Thorium (Th)

Tin (Sn)
Titanium (Ti)
Tungsten (W)
Uranium (U)
Vanadium (V)
Yttrium (Y)
Ytterbium (Yb)
Zinc (Zn)
Zirconium (Zr)

Estimated instrument detection limits (IDL) and method detection limits (MDL) for these elements are compared and listed in Table 1.

Mass Measurement

The PM mass is measured by gravimetric analysis. The net PM mass on a filter is determined by weighing the filter before and after sampling with a micro balance in a temperature and relative humidity controlled environment. Prior to the gravimetric measurement, the Teflon filters are conditioned for 24 hours at a constant relative humidity of 40±1% and at a constant temperature of 22±3 °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.

Analysis of Elements/Metals

The PM samples are prepared and digested in a clean-laboratory environment. The digestion is carried out using a mixture of nitric acid and hydrofluoric acid in closed vessels at a constant temperature (60 °C hot water bath for 5-7 days). The digested solutions are then diluted using distilled deionized water (DDW) and analyzed by an inductively coupled plasma-mass spectrometer (ICP-MS) for about 80 isotopes and up to 65 elements.

The ICP-MS system used is the Perkin-Elmer Elan DRC-II, equipped with the GemTip cross-flow nebulizer, Ryton spray chamber, plasma torch with an alumina injector and a Cetac ADX-500 autosampler. In the ICP-MS analysis, the external standard calibration curves are plotted linearly through zero for each analyte. All results were reagent blank subtracted. Results for the filter samples were also corrected for laboratory filter blank levels. The interferences of calcium oxides and hydroxides on the measurements of ^{57}Fe, ^{59}Co and ^{60}Ni isotopes were corrected (Wu, et al. 1996). Analytical results for the 36 elements listed will be reported.

QA/QC

The following quality control protocols will be implemented for each batch of field sample analysis by ICP-MS:

1. The quality of the DDW used for preparing standards and diluting samples should be pre-checked by ICP-MS full mass region scanning.

2. Matrix matched NIST standard reference materials (SRMs) such as Coal Fly Ash (1633b) and Urban Particulate Matter (1648) should be included using the same reagent quantities as used in sample preparation, placed in test tube of the same type, and processed with every 20 samples.

3. Filter blank samples including laboratory blank and field blank should be prepared using the same reagent quantities as used in sample preparation, placed in test tube of the same type, and processed with every 20 samples. The results from laboratory and field filter blanks may be further used for sample blank subtraction propose.

4. Duplicate samples, brought through the entire sample preparation and analytical procedure, should be processed on a routine basis. A duplicate filter sample should be obtained in sampling and processed with every 20 samples.

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Table F1. Comparison of Instrumental Detection Limits and Method Detection Limits of ICP-MS for Elemental Analysis of Particulate Matters on Air Filters

Elements	m/z	Units	TestID	IDL	MDL*
Ag	107	ng/Filter	107A0	0.02	0.4
Al	27	ng/Filter	027A0	3	50
As	75	ng/Filter	075A0	0.2	0.4
Au	197	ng/Filter	197A0	0.3	0.3
B	10	ng/Filter	010A0	8	15
Ba	137	ng/Filter	137A0	0.2	1
Be	9	ng/Filter	009A0	0.05	0.1
Bi	209	ng/Filter	209A0	0.02	0.05
Br	79	ng/Filter	079A0	10	50
Ca	43	µg/Filter	043A0	0.15	1
Cd	114	ng/Filter	114A1	0.1	1
Ce	140	ng/Filter	140A0	0.05	1
Cl	35	µg/Filter	035A0	1	3
Co	59	ng/Filter	059A1	0.1	1
Cr	52	ng/Filter	053A0	1	5
Cs	133	ng/Filter	133A0	0.005	0.01
Cu	65	ng/Filter	065A0	0.8	8
Dy	163	ng/Filter	163A0	0.005	0.05
Er	166	ng/Filter	166A1	0.003	0.01
Eu	153	ng/Filter	153A1	0.005	0.01
Fe	57	ng/Filter	057A1	50	200
Ga	71	ng/Filter	071A0	0.1	0.2
Gd	158	ng/Filter	158A1	0.02	0.04
Ge	74	ng/Filter	074A0	0.04	0.1
Hg	202	ng/Filter	202A0	0.5	3
Ho	165	ng/Filter	165A0	0.016	0.03
I	127	ng/Filter	127A0	1.2	3
In	115	ng/Filter	115A0	0.016	0.03
K	39	ng/Filter	039A0	50	100
La	139	ng/Filter	007A0	0.02	0.1
Li	7	ng/Filter	007A0	0.1	1
Mg	25	µg/Filter	025A0	0.003	0.03
Mn	55	ng/Filter	055A0	0.1	10
Mo	98	ng/Filter	098A0	0.1	1
Na	23	ng/Filter	023A0	10	100
Nb	93	ng/Filter	093A0	0.15	0.2
Nd	146	ng/Filter	146A0	0.06	0.2
Ni	60	ng/Filter	060A1	0.5	5
P	31	ng/Filter	031A0	60	100
Pb	208	ng/Filter	208A1	0.2	4

Pd	108	ng/Filter	108A0	0.1	0.5
Pr	141	ng/Filter	141A0	0.02	0.1
Pt	195	ng/Filter	195A0	0.03	0.1
Rb	85	ng/Filter	085A0	0.08	0.2
S	34	µg/Filter	034A0	4	8
Sb	121	ng/Filter	121A0	0.04	0.2
Sc	45	ng/Filter	045A1	1	5
Se	77	ng/Filter	077A0	2.5	5
Si	29	µg/Filter	029A0	2	2
Sm	152	ng/Filter	152A1	0.02	0.1
Sn	118	ng/Filter	118A0	1	5
Sr	86	ng/Filter	086A0	4	8
Ta	181	ng/Filter	181A0	0.1	0.1
Tb	159	ng/Filter	159A0	0.002	0.005
Te	128	ng/Filter	128A0	0.2	1
Th	232	ng/Filter	232A0	0.04	0.08
Ti	47	ng/Filter	047A0	5	10
Tl	203	ng/Filter	205A0	0.003	0.01
U	238	ng/Filter	238A0	0.005	0.01
V	51	ng/Filter	051A0	0.08	0.2
W	184	ng/Filter	184A0	0.1	2
Y	89	ng/Filter	089A0	0.02	0.1
Yb	174	ng/Filter	174A0	0.005	0.01
Zn	66	ng/Filter	066A0	1	10
Zr	90	ng/Filter	090A0	0.2	1

* - derived from within-run standard deviations of duplicate digestion/analysis of field blank samples and digestion filter blanks

Appendix G National Institute of Standards and Technology – Standard Reference Material® 1648 – Urban Particulate Matter

St
National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1648

Urban Particulate Matter

This Standard Reference Material (SRM) is intended primarily for use as a control material and in the evaluation of methods used in the analysis of atmospheric particulate matter and materials with a similar matrix. It consists of 2 g of natural atmospheric particulate matter collected in an urban location. While not represented to be typical of the area in which it was collected, its use should typify the analytical problems of atmospheric samples obtained from industrialized urban areas.

The certified values expressed in mass fraction, for the constituent elements are shown in Table 1. Noncertified values expressed in mass fraction, are given for information only in Table 2. The analytical methods used in the characterization of this SRM are shown in Table 3. The certified values are based on measurements of 6 to 30 samples by each of the analytical methods indicated.

NOTICE AND WARNING TO USERS

Expiration of Certification: The certification of SRM 1648 is valid, within the measurement uncertainty (ies) specified, until **31 December 2008**, provided the SRM is handled in accordance with instructions given in this certificate (see Instructions for Use). This certification is nullified if the SRM is damaged, contaminated, or modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Return of the attached registration card will facilitate notification.

Instructions for Use: This material may contain a number of chemicals of unknown toxicities. Therefore, the utmost caution and care must be exercised in its use. A minimum of 100 mg of the dried material (See Instructions for Drying) should be used for any analytical determination to be related to the certified values of this certificate. When not in use, this material should be kept in its original bottle and stored at temperatures between 10 °C to 30 °C. It should not be exposed to intense sources of radiation, including ultraviolet lamps or sunlight. Ideally, the bottle should be kept in a desiccator in the recommended temperature range.

Instructions for Drying: The certified concentrations are reported on a "dry-weight" basis. This material should be dried at 105 °C for 8 h before use because concentrations determined on undried samples must therefore be adjusted for the moisture content.

The technical and support aspects involved in the original preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by T.E. Gills. Measurement activities for revision of this certificate were coordinated through the Standard Reference Materials Program by B.S. MacDonald.

Gaithersburg, MD 20899
Certificate Issue Date: 28 April 1998

Thomas E. Gills, Chief
Standard Reference Materials Program

11/16/78 (original certificate date); 5/11/82 (additional certification update); 8/30/91 (editorial)
*This revision reports a change in the certified value of vanadium, the addition of the manganese certified value, the subsequent removal of the manganese information value, and change in expiration date.

Statistical analysis of the revised certification data for manganese and vanadium was performed by K.R. Eberhardt of the NIST Statistical Engineering Division.

Homogeneity Assessment: Randomly selected bottles were used for the analytical measurements. Each analyst examined at least 6 bottles. No correlation was found between measured values and the bottling sequence. Also, the results of measurements of samples from different bottles were not significantly different from the measurements of replicate samples from single bottles. Accordingly, all bottles of this SRM have been assigned the same certified values of constituent elements.

Source and Preparation of Material: This SRM was prepared from urban particulate matter collected in the St. Louis, MO area in a baghouse specially designed for this purpose. The material was collected over a period in excess of 12 months and, therefore, is a time-integrated sample. The material was removed from the filter bags, combined in a single lot, screened through a fine mesh sieve to remove extraneous materials and thoroughly blended in a v-blender. The material was then packaged into sequentially numbered bottles.

Table 1. Certified Values of Constituent Elements

Major Constituents		Minor Constituents	
Element	Content[a] Mass Fraction, in %	Element	Content[a] Mass Fraction, in %
Aluminum[b]	3.42 ± 0.11	Lead	0.655 ± 0.008
Iron	3.91 ± 0.10	Sodium[b]	0.425 ± 0.002
Potassium[b]	1.05 ± 0.01	Zinc	0.476 ± 0.014

Trace Constituents

Element	Content[a] mg/kg	Element	Content[a] mg/kg
Arsenic	115 ± 10	Nickel	82 ± 3
Cadmium	75 ± 7	Selenium[b]	27 ± 1
Chromium	403 ± 12	Uranium	5.5 ± 0.1
Copper	609 ± 27	Vanadium[c]	127 ± 7
Manganese[c]	786 ± 17		

[a] The uncertainties of the certified values, except those noted, include errors associated with both measurement and material variability. They represent the 95 % tolerance limits for individual subsamples, i.e., 95 % of the subsamples from a single unit of this SRM would be expected to have a composition within the indicated range of values 95 % of the time.

[b] The indicated constituent was certified as a part of the NIST update certification program, in August 1991. The value for each indicated constituent is the "best value" based on all measurement methods used and the associated uncertainty is expressed as the standard error considering variability within and between analytical methods.

[c] The uncertainty in the certified value is calculated as $U = ku_c + B$ where u_c is the combined standard uncertainty calculated according to the ISO Guide [1] and k is a coverage factor. The additional quantity, B, is an allowance for the differences between methods of analysis and is taken to be equal to the difference between the most discrepant method value and the certified value. The expanded uncertainty (U) given is intended to approximate the 95 % level of confidence.

Table 2. Noncertified Values for Constituent Elements

Major Constituents		Minor Constituents	
Element	Content Mass Fraction, in %	Element	Content Mass Fraction, in %
Sulfur	5.0	Chlorine	0.45
Magnesium	0.8	Titanium	0.40

Trace Constituents

Element	Content mg/kg	Element	Content mg/kg
Antimony	45	Iodine	20
Barium	737	Lanthanum	42
Bromine	500	Rubidium	52
Cerium	55	Samarium	4.4
Cesium	3	Scandium	7
Cobalt	18	Silver	6
Europium	0.8	Thorium	7.4
Hafnium	4.4	Tungsten	4.8
Indium	1.0		

Table 3. Methods of Analysis

Element	Methods	Element	Methods
Aluminum	DCPAES, NAA	Lead	AAS, IDMS, POL
Antimony	NAA	Magnesium	NAA
Arsenic	NAA, SPECTR	Manganese	AAS, NAA, DCPAES
Barium	NAA	Nickel	AAS, IDMS, POL
Bromine	NAA	Potassium	AAS
Cadmium	AAS, IDMS, NAA, POL	Rubidium	NAA
Cerium	NAA	Samarium	NAA
Cesium	NAA	Scandium	NAA
Chlorine	NAA	Selenium	AAS, NAA, FES
Chromium	IDMS, NAA	Sodium	AAS, NAA, FES
Cobalt	NAA	Silver	NAA
Copper	AAS, IDMS, SPECTR	Sulfur	IC
Europium	NAA	Thorium	NAA
Hanfium	NAA	Titanium	NAA
Indium	NAA	Tungsten	NAA
Iodine	NAA, PAA	Uranium	IDMS
Iron	AAS, IDMS, NAA, SPECTR	Vanadium	NAA
Lanthanum	NAA	Zinc	AAS, IDMS, NAA, POL

Methods

AAS	Atomic Absorption Spectrometry	FES	Flame Emission Spectrometry
DCPAES	DC Plasma Atomic Emission Spectrometry	NAA	Neutron Activation Analysis
IC	Ion Chromatography	PAA	Photon Activation Analysis
IDMS	Isotope Dilution Thermal Ionization Spectrometry	POL	Polarography
		SPECTR	Spectrophotometry

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SUPPLEMENTAL INFORMATION

The values listed below are based on measurements made in a single laboratory and are given for information only. While there is no reason to suspect systematic bias in these values, no attempt was made to evaluate the bias attributable to either the method or the laboratory. The method used for each set of measurements and the standard deviation of the means are also listed.

Constituent	Mass Fraction, in %	One Standard Deviation
Nitrogen (NO_3)	1.07	0.03
Nitrogen (NH_4)	2.01	0.04
Sulfate	15.42	0.07
Silicon Dioxide (SiO_2)	26.8	0.2
Freon Soluble	1.19	0.24

Methods Used

Nitrate (NO_3) - Extraction with water and measurement by ASTM Method D992.
Ammonia (NH_4)- NaOH addition followed by steam distillation and titration.
Sulfate - Extraction with water and measurement by ASTM D516.
Silicon Dioxide (SiO_2)- Solution and measurement by ASTM Method E350.
Freon Soluble - Extraction with Freon 113, using the Method described in "Standard Methods in Examination of Water and Waste Water," 14th Ed., p. 518, American Public Health Association, Washington DC.

REFERENCES

[1] *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st Ed., ISO, Geneva, Switzerland, (1993): see also Taylor, B.N. and Kuyatt, C.E., "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results," NIST Technical Note 1297, U.S. Government Printing Office, Washington, DC (1994).

[2] Kucera, J. and Soukal, L., Low Uncertainty Determination of Manganese and Vanadium in Environmental and Biological Reference Materials by Instrumental Neutron Activation Analysis, Berm-7, (Apr. 97).

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Appendix H Multi-Particle Statistical Comparison Tests

Table H1. Multi-particle Incremental Average of Individual Particle Results (based on wt%) – Test One, Filter 19

	Avg of 5	Avg of 10	Avg of 15	Avg of 20	Avg of 25	Avg of 30	Avg of 35	Avg of 40
Al	9.2% |0.43| < 2.02, do not reject	8.3% |0.22| < 2.01, do not reject	8.5% |0.34| < 2.01, do not reject	7.3% |-0.25| < 2.00, do not reject	7.4% |-0.20| < 2.00, do not reject	7.2% |-0.33| < 1.99, do not reject	8.2% |0.28| < 1.99, do not reject	7.7%
Fe	12.4% |1.65| < 2.02, do not reject	9.2% |0.71| < 2.01, do not reject	8.6% |0.50| < 2.01, do not reject	7.4% |-0.20| < 2.00, do not reject	7.4% |-0.21| < 2.00, do not reject	7.2% |-0.37| < 1.99, do not reject	7.8% |0.07| < 1.99, do not reject	7.7%
K	4.2% |0.09| < 2.02, do not reject	3.2% |-0.57| < 2.01, do not reject	5.0% |0.64| < 2.01, do not reject	4.3% |0.20| < 2.00, do not reject	4.0% |-0.06| < 2.00, do not reject	3.9% |-0.13| < 1.99, do not reject	4.0% |-0.06| < 1.99, do not reject	4.0%
Na	1.3% |0.45| < 2.02, do not reject	0.7% |-0.44| < 2.01, do not reject	0.7% |-0.34| < 2.01, do not reject	0.6% |-0.66| < 2.00, do not reject	0.8% |-0.34| < 2.00, do not reject	0.9% |-0.05| < 1.99, do not reject	0.8% |-0.23| < 1.99, do not reject	0.9%
Zn	2.0% |-0.53| < 2.02, do not reject	2.3% |-0.52| < 2.01, do not reject	2.9% |-0.23| < 2.01, do not reject	2.3% |-0.74| < 2.00, do not reject	2.8% |-0.33| < 2.00, do not reject	3.2% |-0.04| < 1.99, do not reject	3.5% |0.22| < 1.99, do not reject	3.2%
S	3.3% |-1.50| < 2.02, do not reject	13.7% |-0.08| < 2.01, do not reject	14.4% |-0.03| < 2.01, do not reject	14.4% |0.03| < 2.00, do not reject	14.0% |-0.05| < 2.00, do not reject	15.5% |0.32| < 1.99, do not reject	14.0% |-0.05| < 1.99, do not reject	14.2%
Mg	1.4% |-0.21| < 2.02, do not reject	1.6% |-0.13| < 2.01, do not reject	2.1% |0.50| < 2.01, do not reject	1.6% |-0.04| < 2.00, do not reject	1.8% |0.20| < 2.00, do not reject	1.8% |0.19| < 1.99, do not reject	1.6% |-0.05| < 1.99, do not reject	1.7%
Ti	2.4% |0.70| < 2.02, do not reject	2.1% |0.62| < 2.01, do not reject	1.6% |0.16| < 2.01, do not reject	1.4% |-0.22| < 2.00, do not reject	1.4% |-0.18| < 2.00, do not reject	1.8% |0.45| < 1.99, do not reject	1.7% |0.22| < 1.99, do not reject	1.5%
Si	33.2% |0.28| < 2.02, do not reject	29.5% |-0.14| < 2.01, do not reject	29.1% |-0.23| < 2.01, do not reject	33.8% |0.53| < 2.00, do not reject	33.1% |0.45| < 2.00, do not reject	30.4% |-0.01| < 1.99, do not reject	30.6% |0.02| < 1.99, do not reject	30.5%
Ca	25.5% |0.23| < 2.02, do not reject	24.9% |0.22| < 2.01, do not reject	22.1% |-0.34| < 2.01, do not reject	22.7% |-0.23| < 2.00, do not reject	22.8% |-0.21| < 2.00, do not reject	23.7% |-0.01| < 1.99, do not reject	22.8% |-0.23| < 1.99, do not reject	23.7%
Cl	2.2% |1.16| < 2.02, do not reject	1.7% |0.85| < 2.01, do not reject	1.5% |0.63| < 2.01, do not reject	1.2% |0.11| < 2.00, do not reject	1.5% |0.74| < 2.00, do not reject	1.4% |0.69| < 1.99, do not reject	1.3% |0.36| < 1.99, do not reject	1.1%
Mn	0.4% |-0.47| < 2.02, do not reject	0.3% |-0.79| < 2.01, do not reject	1.1% |0.97| < 2.01, do not reject	0.8% |0.41| < 2.00, do not reject	0.8% |0.19| < 2.00, do not reject	0.7% |-0.08| < 1.99, do not reject	0.6% |-0.26| < 1.99, do not reject	0.7%

Table H2. Multi-particle Incremental Average of Individual Particle Results (based on wt%) – Test 2, Filter 14

	Avg of 5	Avg of 10	Avg of 15	Avg of 20	Avg of 25	Avg of 30	Avg of 35	Avg of 40
Al	7.2% |-0.27| < 2.02, do not reject	8.5% |0.24| < 2.01, do not reject	8.8% |0.44| < 2.01, do not reject	8.3% |0.21| < 2.00, do not reject	7.2% |-0.45| < 2.00, do not reject	7.4% |-0.36| < 1.99, do not reject	8.0% |0.02| < 1.99, do not reject	7.9%
Fe	7.8% |-0.21| < 2.02, do not reject	7.8% |-0.23| < 2.01, do not reject	6.9% |-1.03| < 2.01, do not reject	7.1% |-1.01| < 2.00, do not reject	7.0% |-1.18| < 2.00, do not reject	7.3% |-0.89| < 1.99, do not reject	8.0% |-0.23| < 1.99, do not reject	8.2%
K	4.3% |-0.32| < 2.02, do not reject	3.8% |-0.76| < 2.01, do not reject	3.8% |-0.92| < 2.01, do not reject	4.9% |-0.01| < 2.00, do not reject	4.5% |-0.39| < 2.00, do not reject	5.0% |0.12| < 1.99, do not reject	4.6% |-0.26| < 1.99, do not reject	4.9%
Na	2.1% |0.77| < 2.02, do not reject	1.8% |0.47| < 2.01, do not reject	1.5% |0.10| < 2.01, do not reject	2.0% |0.93| < 2.00, do not reject	1.7% |0.46| < 2.00, do not reject	1.6% |0.16| < 1.99, do not reject	1.5% |0.06| < 1.99, do not reject	1.5%
Zn	2.0% |-0.54| < 2.02, do not reject	2.1% |-0.60| < 2.01, do not reject	2.8% |0.21| < 2.01, do not reject	3.2% |0.84| < 2.00, do not reject	3.2% |0.87| < 2.00, do not reject	3.0% |0.65| < 1.99, do not reject	2.7% |0.18| < 1.99, do not reject	2.6%
S	11.6% |-0.41| < 2.02, do not reject	12.7% |-0.28| < 2.01, do not reject	13.3% |-0.16| < 2.01, do not reject	14.3% |0.12| < 2.00, do not reject	14.4% |0.14| < 2.00, do not reject	14.0% |0.03| < 1.99, do not reject	14.4% |0.17| < 1.99, do not reject	13.9%
Mg	1.7% |-0.32| < 2.02, do not reject	1.2% |-1.19| < 2.01, do not reject	1.1% |-1.63| < 2.01, do not reject	1.4% |-1.17| < 2.00, do not reject	1.7% |-0.55| < 2.00, do not reject	1.8% |-0.23| < 1.99, do not reject	1.9% |-0.06| < 1.99, do not reject	1.9%
Ti	2.2% |0.34| < 2.02, do not reject	2.2% |0.44| < 2.01, do not reject	2.2% |0.41| < 2.01, do not reject	2.3% |0.67| < 2.00, do not reject	2.2% |0.55| < 2.00, do not reject	2.2% |0.53| < 1.99, do not reject	2.0% |0.06| < 1.99, do not reject	1.9%
Si	42.7% |1.00| < 2.02, do not reject	37.2% |0.31| < 2.01, do not reject	38.5% |0.62| < 2.01, do not reject	34.3% |-0.29| < 2.00, do not reject	36.0% |0.12| < 2.00, do not reject	36.0% |0.12| < 1.99, do not reject	35.3% |-0.06| < 1.99, do not reject	35.5%
Ca	14.4% |-0.47| < 2.02, do not reject	17.9% |0.03| < 2.01, do not reject	16.5% |-0.25| < 2.01, do not reject	18.2% |0.11| < 2.00, do not reject	17.9% |0.06| < 2.00, do not reject	17.8% |0.01| < 1.99, do not reject	17.7% |0.00| < 1.99, do not reject	17.7%
Cl	1.2% |0.03| < 2.02, do not reject	2.0% |1.34| < 2.01, do not reject	1.7% |1.10| < 2.01, do not reject	1.3% |0.40| < 2.00, do not reject	1.3% |0.46| < 2.00, do not reject	1.1% |0.01| < 1.99, do not reject	1.1% |0.00| < 1.99, do not reject	1.1%
Mn	0.5% |-0.32| < 2.02, do not reject	0.3% |-1.24| < 2.01, do not reject	0.5% |-0.21| < 2.01, do not reject	0.6% |0.26| < 2.00, do not reject	0.7% |0.34| < 2.00, do not reject	0.7% |0.43| < 1.99, do not reject	0.6% |0.08| < 1.99, do not reject	0.6%

Appendix I High Level Field Sampling Charts

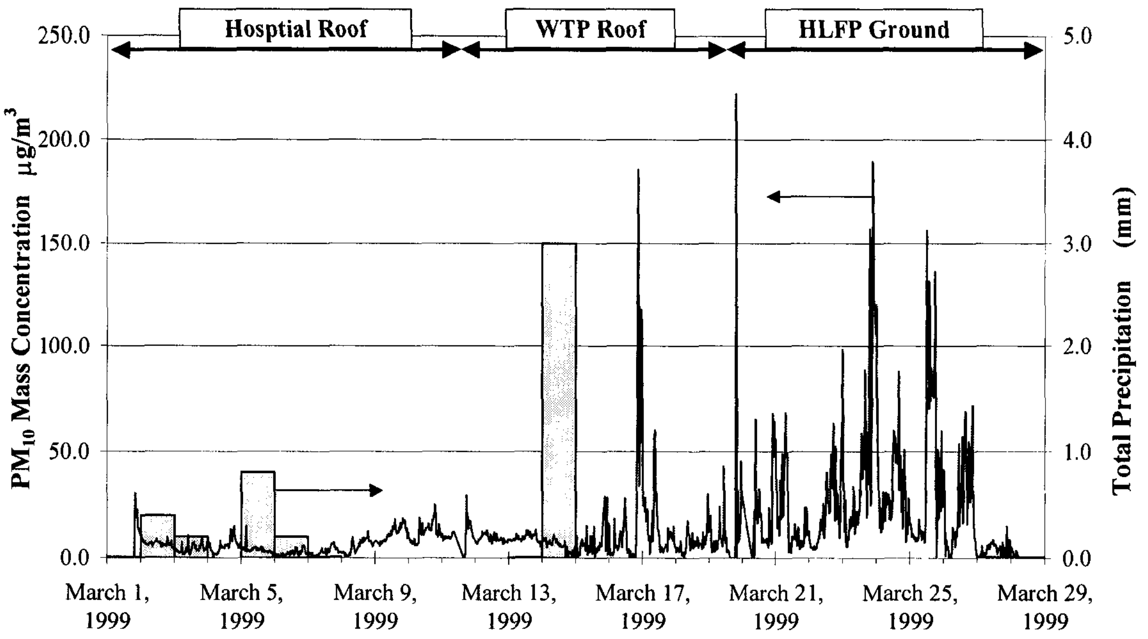


Figure I1. PM_{10} TEOM Winter Sampling Summary – March 1 to March 28, 1999

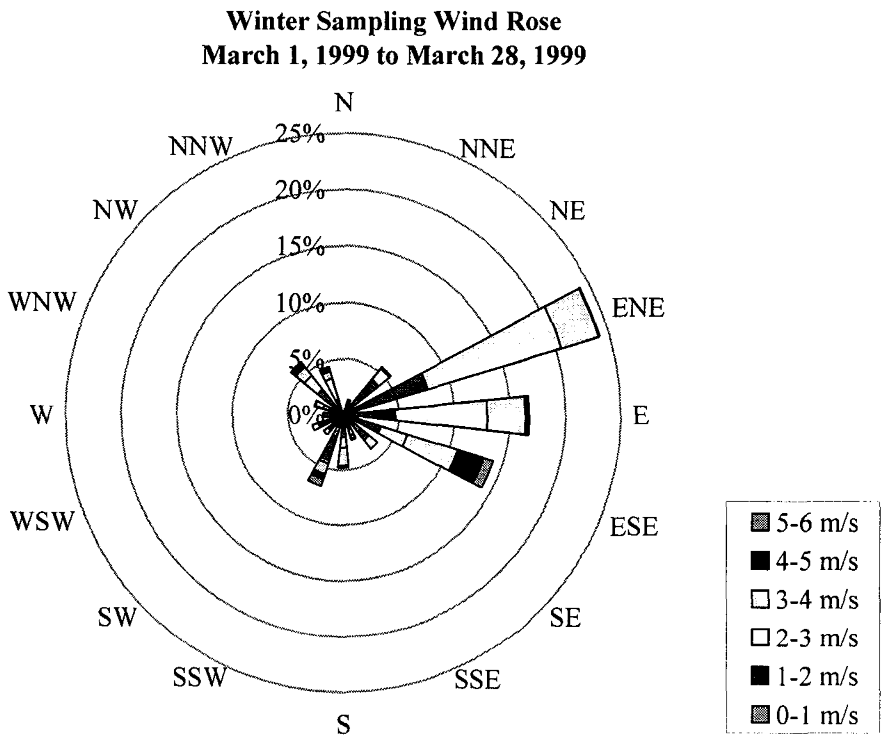


Figure I2. Winter Sampling Wind Rose – March 1 to March 28, 1999

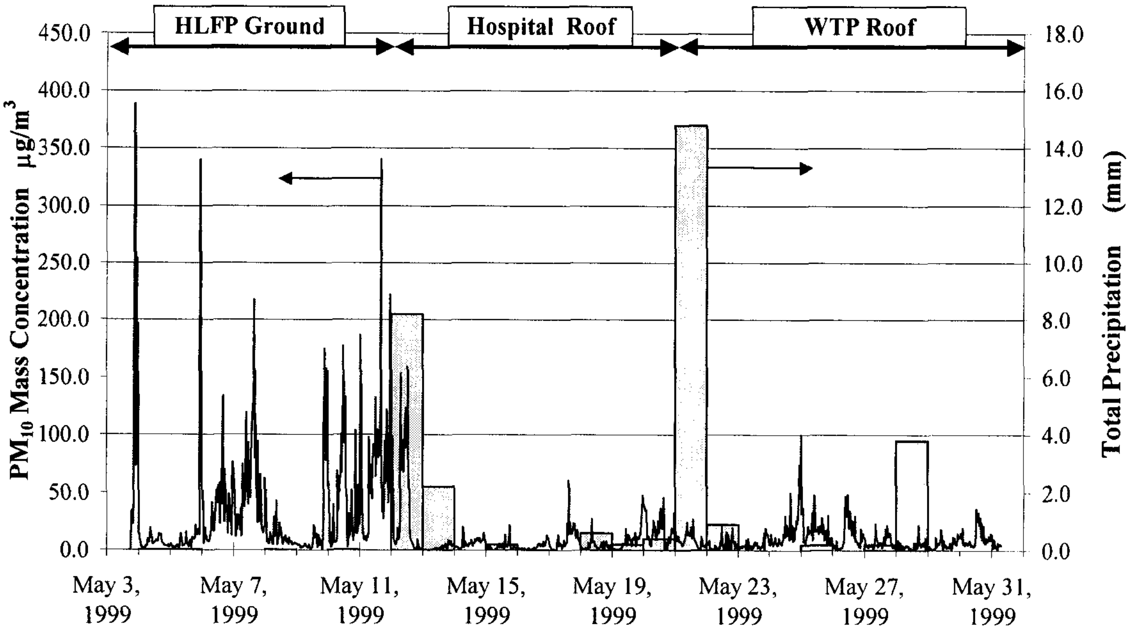


Figure I3. PM$_{10}$ TEOM Spring Sampling Summary – May 3 to May 31, 1999

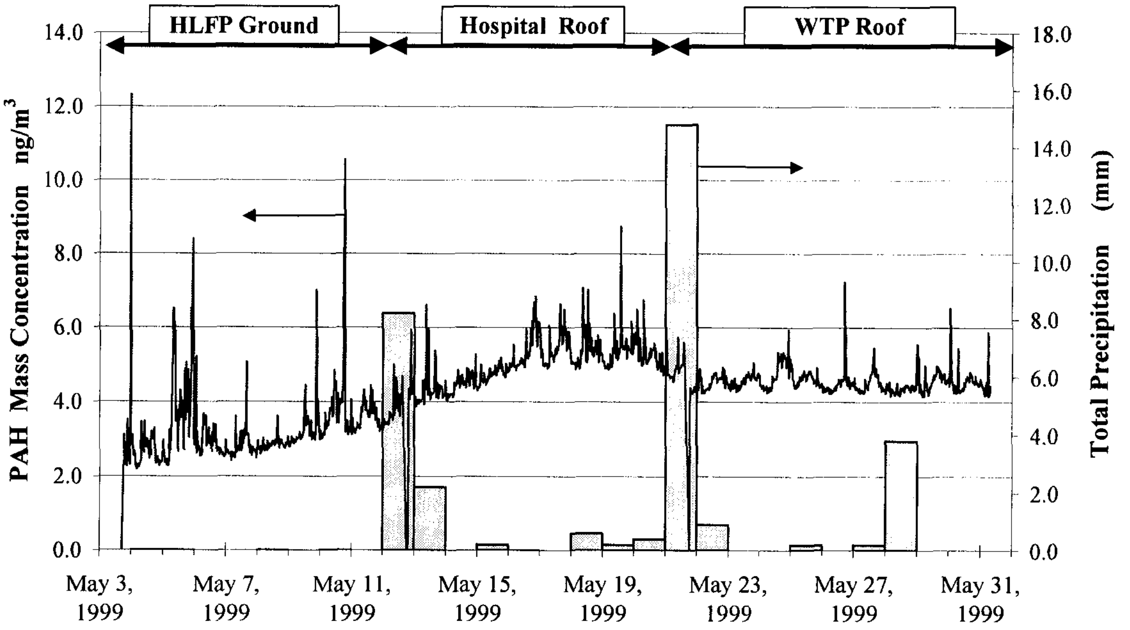


Figure I4. PAH Spring Sampling from May 3 to May 31, 1999

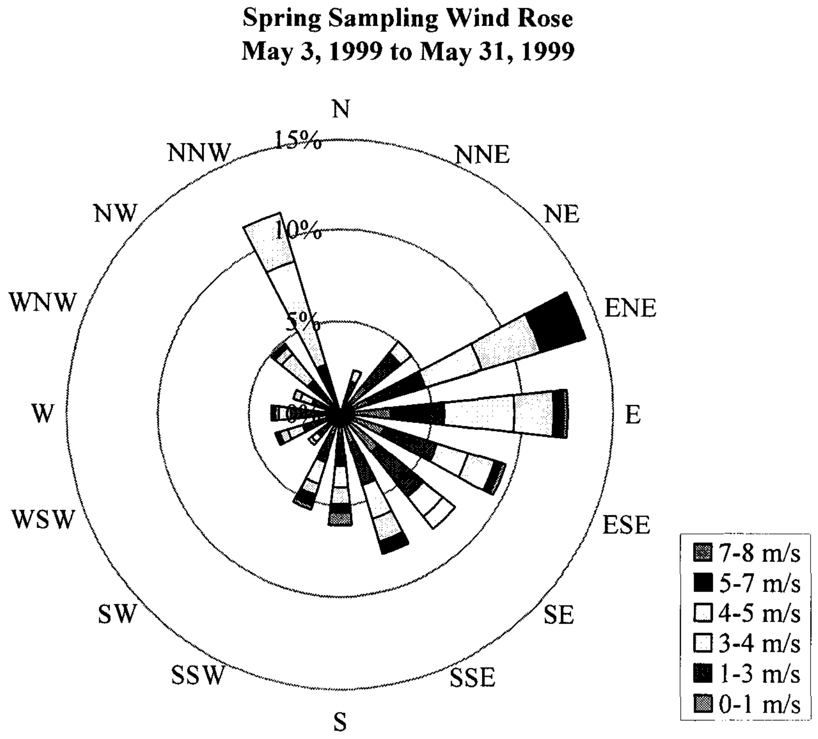


Figure I5. Spring Sampling Wind Rose – May 3 to May 31, 1999

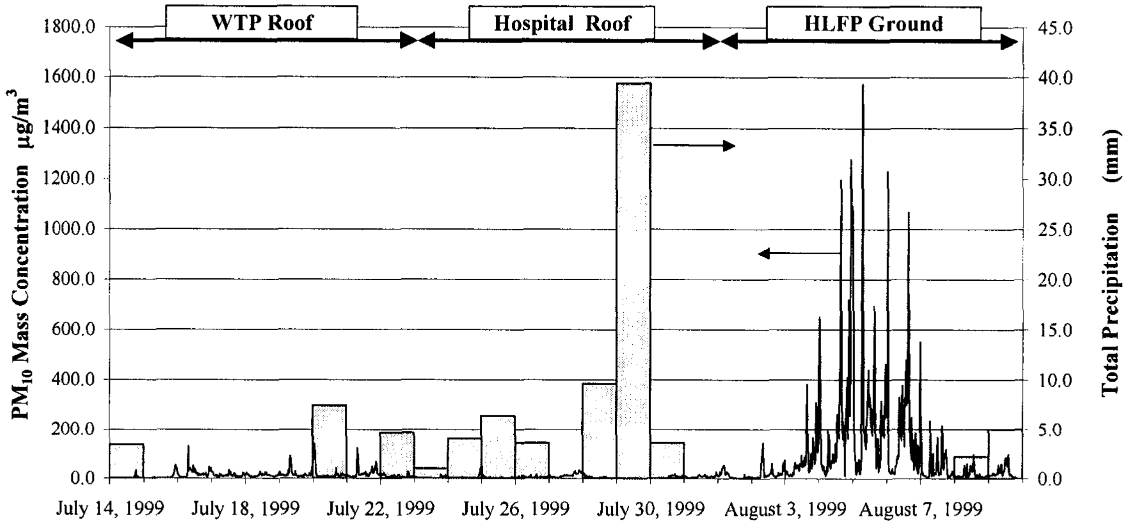


Figure I6. PM$_{10}$ TEOM Summer Sampling Summary – July 14 to August 9, 1999

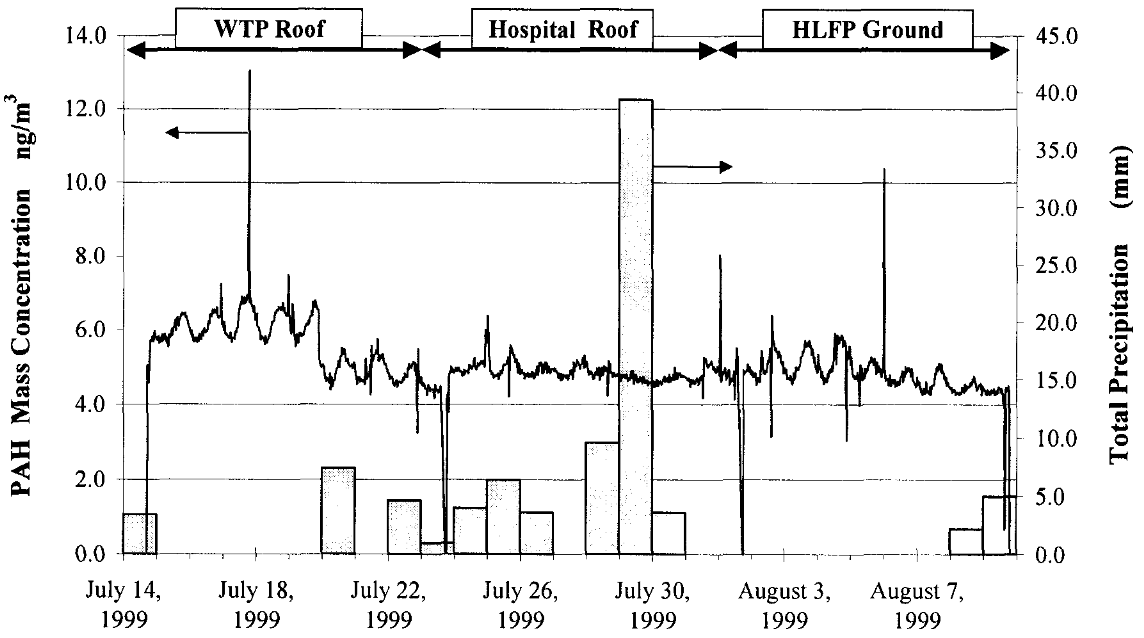


Figure I7. PAH Summer Sampling from July 14 to August 9, 1999

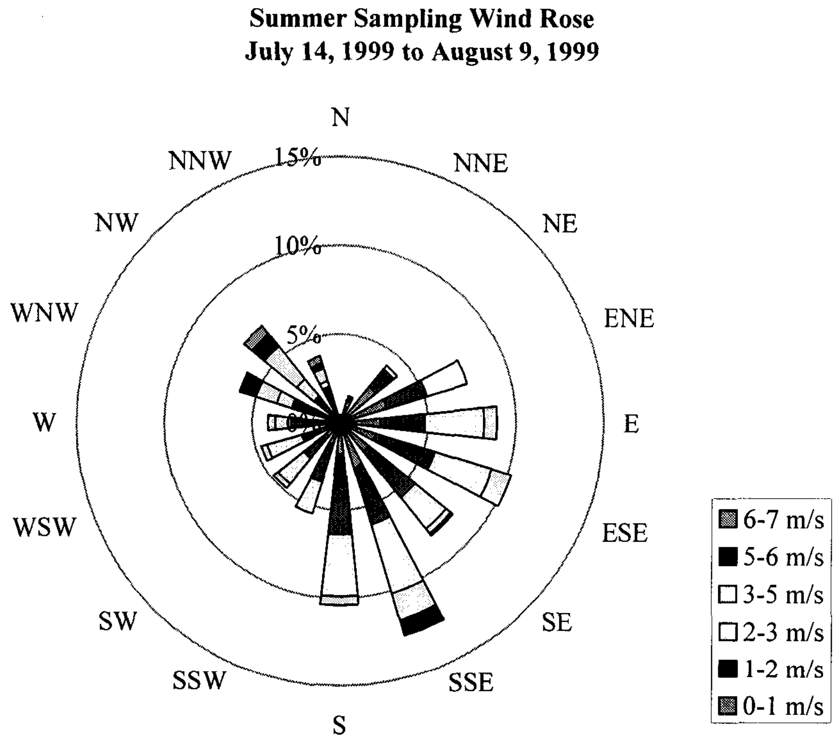


Figure I8. Summer Sampling Wind Rose – July 14 to Aug 9, 1999

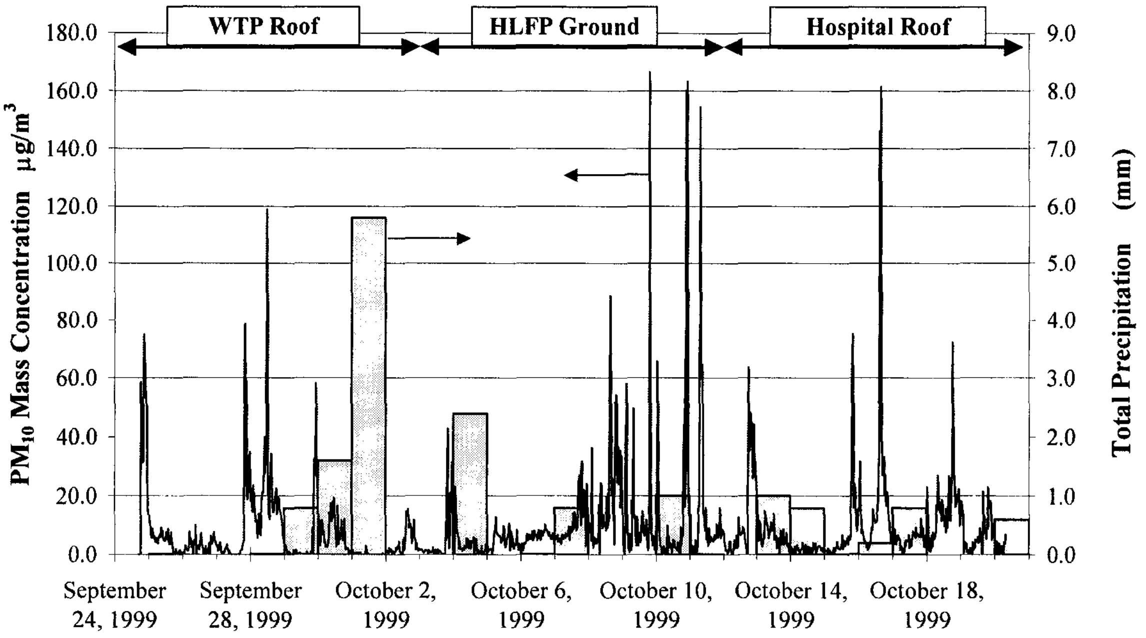


Figure I9. PM$_{10}$ TEOM Fall Sampling Summary – September 24 to October 20, 1999

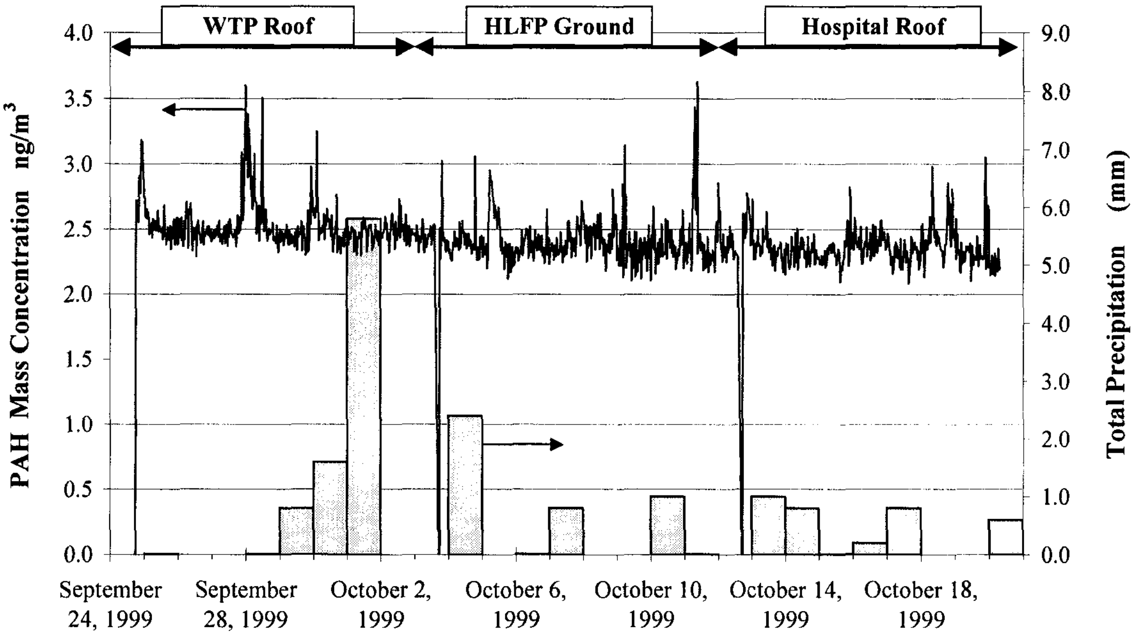
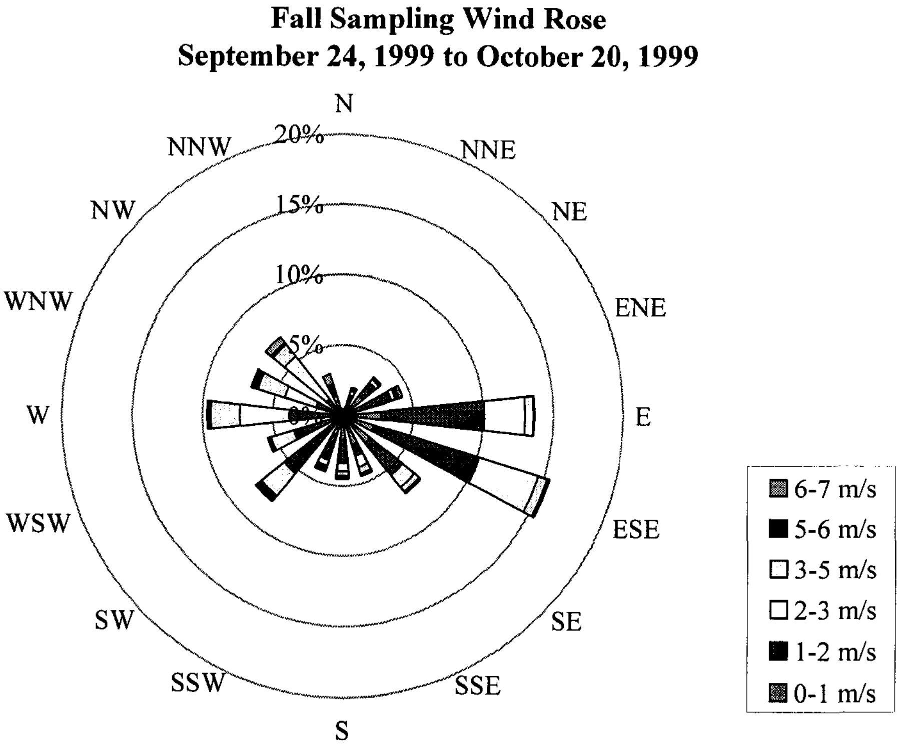


Figure I10. PAH Fall Sampling from September 24 to October 20, 1999



Fall Sampling Wind Rose
September 24, 1999 to October 20, 1999

Figure I11. Fall Sampling Wind Rose – Sept 24, 1999 to Oct 20, 1999

Appendix J Mass Concentrations of Elements from High Level Field Sampling

Table J1. Selected Elemental Mass Concentrations from Samples collected in High Level, AB (based on 33 field samples)

Wind Direction	Si	Ca	Fe	Al	K	Ti	Na	Mg	Cl	Mn
degrees	Mass concentration in ng/m^3 (based on %abundance x TEOM mass concentration)									
108	2230	1129	784	679	285	178	1377	203	2411	13
62	1464	1512	325	643	170	176	979	195	1977	19
105	1568	1992	1001	676	350	228	1121	126	2407	23
108	1905	1691	739	730	286	211	1259	194	2464	20
43	1217	1042	313	281	22	7	461	4	671	3
60	1962	1399	815	731	78	15	710	17	791	4
75	1018	978	347	279	30	7	214	11	444	2
326	2361	797	231	937	116	24	83	20	34	9
342	1171	217	130	224	28	8	49	24	27	0
335	1985	1611	276	724	73	51	49	95	65	2
152	2132	1195	372	476	376	16	99	73	101	47
107	3388	1925	494	780	716	24	153	156	130	101
113	3349	1890	536	759	650	24	153	135	143	87
321	433	278	164	92	21	4	5	73	5	1
326	344	339	151	134	20	5	12	63	6	1
139	5695	3031	986	1401	268	32	87	883	44	12
136	4189	3726	1431	1865	266	31	106	743	43	5
83	4455	411	483	1145	225	31	224	711	733	260
255	3961	115	947	1545	177	38	48	73	2	10
240	3338	2017	895	836	60	19	69	78	39	1
83	6595	120	500	1088	377	0	10	9	0	6
252	905	322	358	261	33	187	5	53	18	8
235	848	121	123	130	464	24	0	19	213	8
357	3217	120	522	938	168	182	3	130	1	6
3	2869	529	650	416	72	11	32	55	10	15
309	851	80	1005	291	504	215	71	35	2	4
289	1770	147	313	339	60	1	47	39	9	14
241	3682	95	447	1124	81	23	53	80	0	1
233	1827	2343	494	704	254	13	6	117	2	9
121	4786	1019	3580	1741	264	55	125	230	1	10
113	5046	2281	2140	1894	145	87	41	741	3	14
338	2728	544	764	469	1195	42	127	100	41	12
346	2523	1552	220	951	64	17	636	205	3	6