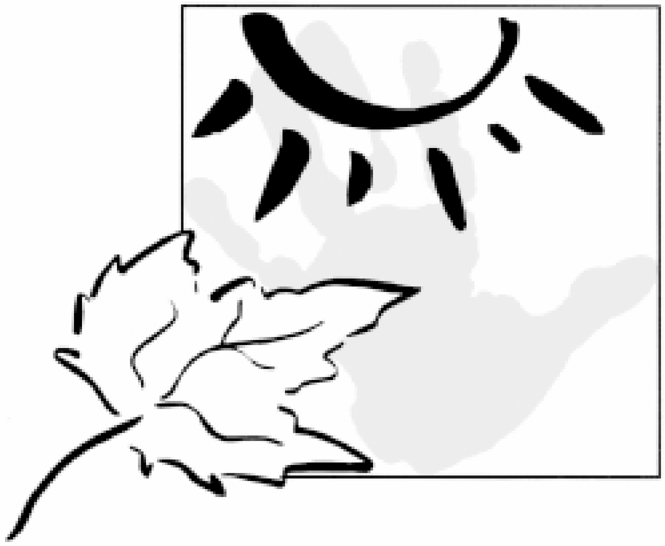
NATIONAL AMBIENT AIR QUALITY OBJECTIVES FOR PARTICULATE MATTER



PART 1: SCIENCE ASSESSMENT DOCUMENT

A report by the
CEPA/FPAC Working Group
on Air Quality Objectives
and Guidelines

This report is published under Section 8 of the Canadian Environmental Protection Act (CEPA).

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PREFACE

The Canadian Environmental Protection Act (*CEPA*), passed into law in 1988, replaces and builds upon the Clean Air Act and the Environmental Contaminants Act. The opening statement of the Act declares that "the protection of the environment is essential to the well-being of Canada". *CEPA* allows the federal government to assess substances and control their impact through national environmental quality objectives, guidelines, codes of practice, and/or regulations.

Provincial governments have the primary responsibility in many areas of air pollution control, with federal actions integrated with those of the provinces. The *CEPA* Federal/Provincial Working Group on Air Quality Objectives and Guidelines, consisting of representatives of federal, provincial and territorial departments of environment and health, reviews and recommends ambient air quality objectives.

Canada's *National Ambient Air Quality Objectives(s)* prescribe targets for air quality, measured at the relevant receptor (persons, plants, animals, materials). *National Ambient Air Quality Objectives are national goals*[1] *for outdoor air quality that protect public health, the environment, or aesthetic properties of the environment.* The development of NAAQOs involves first a scientific review of the physical and chemical properties of a substance, its sources, environmental, animal and human health effects, and environmental and human exposure assessment, and secondly, integration of this information within a framework of risk assessment. The Science Assessment Document contains this critical scientific evaluation, and lays the scientific groundwork for establishing the air quality objectives. Reference Levels, levels above which there are demonstrated effects on human health and/or the environment, are identified. A document outlining the process followed in reviewing and interpreting the scientific information is published separately[1]. This document contains the scientific evaluation of Particulate Matter.

National Ambient Air Quality Objectives are for focussing air quality management strategies and plans. The derivation of these targets may consider some element of benefit/risk analysis, reflecting a philosophy of environmental health protection and long term risk reduction while recognizing technological and economic limits. The broad range of potential responses by the population, the ecosystems, and organisms in the environment are considered. Given the range of these sensitivities however, the resulting objectives may not protect all.

The process[2] of establishing National Ambient Air Quality Objectives is a dynamic and continuous one. The air quality objectives are established to provide the current state of knowledge about an air quality parameter, a uniform scale for assessing the quality of air in all parts of Canada, and guidance to governments for making risk management decisions such as planning control strategies and setting local standards.

It is recognized that not all locations in Canada will meet these air quality objectives immediately, or at all times, and that priority given to meet these values may be based on factors such as available control technology, costs, benefits, and the degree to which the recommended objectives are exceeded. The expectation is that strategies will be implemented to facilitate the reduction of ambient air concentrations to a level at or below the air quality objective(s) as soon as practicable. The principles of continuous improvement and nondegradation of environmental quality are advocated.

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[1] A Protocol for the Development of National Ambient Air Quality Objectives Part 1: Science Assessment Document and Derivation of the Reference Levels, WGAQOG, 1996.

[2] A draft document, Protocol for the Development of National Ambient Air Quality Objectives. Part 2, outlines the process for developing air quality objectives.

NOTE:

In January 1998, Canadian Environment Ministers (with the exception of Quebec) signed the Canada-Wide Accord on Environmental Harmonization and its sub-agreement on Canada-Wide Standards (CWSs). The CWS process provides new tools for the management of environmental issues of national interest. Recognizing that both NAAQOs and CWSs have a role to play in the management of air quality, federal, provincial, and territorial health and environment departments have integrated the NAAQO and CWS processes. Air pollutants that have been identified by governments as needing to be managed will be targeted for either CWS or NAAQO development, not both.

In January 1998, Environment Ministers identified particulate matter as a priority for Canada-Wide Standards. As a result, federal, provincial, and territorial health and environment departments agreed that NAAQOs for particulate matter will no longer be developed. Rather, this Science Assessment Document will form the Risk Assessment report for the development of CWSs for particulate matter.

Availability of this Particulate Matter Science Assessment Document has been announced in the *Canada Gazette* Part I. This report is published under Section 8 of the *Canadian Environmental Protection Act* (CEPA).

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS

ACRONYMS

AHH	Aryl hydrocarbon hydroxylase
AISI	American Iron and Steel Institute
BAL	Bronchoalveolar lavage
BALT	Bronchus-associated lymphatic tissue
BaP	Benzo[a]pyrene
BS	British Smoke Shade or Black Smoke
CAAMP	Canadian Acid Aerosol Measurement Program
CARE	Centre for Atmospheric Research Experiments
CCN	Cloud condensation nuclei
CEPA	Canadian Environmental Protection Act
CHIEF	Clearing House for Inventory and Emission Factors
CI	Confidence interval
CMB	Chemical mass balance
CMD	Count median diameter
CoH	Coefficient of Haze
COPD	Chronic obstructive pulmonary disease
DRUM	Davis Rotating-drum Universal-size-cut Monitoring
EC	Elemental carbon
EPA	Environmental Protection Agency
EPS	Environmental Protection Service
ERDA	Energy Research Development Authority
ESP	Electrostatic precipitator
ETS	Environmental tobacco smoke
FAC	Fractional aerosol coefficient
FAM	Fixed ambient monitor
$FEF_{25–75}$	Mean forced expiratory flow during the middle half of forced vital capacity
FEV_1	Forced expiratory volume in one second
FP	Fine particles
FPAC	Federal–Provincial Advisory Committee
FRG	(former) Federal Republic of Germany
FVC	Forced vital capacity
GVRD	Greater Vancouver Regional District
HIS	Health Interview Survey
IADN	International Acid Deposition Network
IASI	Indoor Air Sampling Impactor
ICD	International Classification of Disease
Ig	Immunoglobulin
IL	Interleukin
IMPROVE	Interagency Monitoring of Protected Visual Environments
IP	Inhalable particulates
ISWS	Illinois State Water Survey
LD_{50}	Lethal dose for 50% of the test population
LFV	Lower Fraser Valley
LOEL	Lowest-observed-effect level
MAMU	Mobile Air Monitoring Unit
MDL	Minimum detectable limit
$MEF_{25\%}$	Maximum flow at 25% of vital capacity

MMAD	Mass median aerodynamic diameter
MMD	Mass median diameter
MMEF	Maximum mid-expiratory flow
MMT	Methylcyclopentadienyl manganese tricarbonyl
MOUDI	Micro Orifice Uniform Deposit Impactor
MTD	Maximum tolerated dose
NAAQO	National Ambient Air Quality Objective(s)
NAAQS	National Ambient Air Quality Standard
NAPS	National Air Pollution Surveillance
NRCC	National Research Council of Canada
NSSC	Neutral sulphite semi-chemical
NTP	National Toxicology Program
OC	Organic carbon
OECD	Organisation for Economic Co-operation and Development
PAH	Polycyclic aromatic hydrocarbon
PAN	Peroxyacetyl nitrate
PCA	Principal component analysis
PEC	Particulate elemental carbon
PEF	Peak expiratory flow
PEM	Personal exposure monitor
PM	Particulate matter
$PM_{2.5}$	Particulate matter 2.5 µm or less in diameter
PM_{10}	Particulate matter 10 µm or less in diameter
PMN	Polymorphonuclear leukocytes
POM	Polycyclic organic material
PREVENT	Pacific Northwest Regional Visibility Experiment Using Natural Tracers
P-TEAM	Particle Total Exposure Assessment Methodology
REVEAL	Regional Visibility Experimental Assessment in the Lower Fraser Valley
RR	Relative risk
RSP	Respirable suspended particulate
RWC	Residential wood combustion
SAM	Stationary ambient monitor
SCAQS	Southern California Air Quality Study
SIM	Stationary indoor monitor
SIP	State Implementation Plan
SMSA	Standard Metropolitan Statistical Area
SSI	Size selective inlet
TEOM	Tapered Element Oscillation Microbalance
THEES	Total Human Environmental Exposure Study
TNF	Tumour necrosis factor
TP	Thoracic particles
TSP	Total suspended particulate
UQM	Upper quartile mean
VAQS	Valley Air Quality Study
VKmT	Vehicle–kilometres travelled
VOC	Volatile organic compound
V/Q	Ventilation–perfusion ratio
VRP	Visibility Reducing Particles
WHO	World Health Organization

CHEMICAL COMPOUNDS

CO	Carbon monoxide
Fe_3O_4	Black iron oxide
Ga_2O_3	Gallium oxide
H^+	Hydrogen ion
H_2SO_4	Sulphuric acid
HCl	Hydrochloric acid
HNO_3	Nitric acid
K_2CO_3	Potassium carbonate
N_2O_5	Dinitrogen pentoxide
NaCl	Sodium chloride
NH_3	Ammonia
NH_4Cl	Ammonium chloride
NH_4HSO_4	Ammonium bisulphate
NH_4NO_3	Ammonium nitrate
$(NH_4)_2SO_4$	Ammonium sulphate
NO	Nitric oxide
NO_2	Nitrogen dioxide
NO_3^-	Nitrate
NO_x	Nitrogen oxides
O_3	Ozone
OH•	Hydroxyl radical
SO_2	Sulphur dioxide
SO_4^{2-}	Sulphate
SO_x	Sulphur oxides

UNITS

cfm	cubic feet per minute
cm	centimetre
cm^2	square centimetre
cm^3	cubic centimetre
d	day
g	gram
Gg	gigagram
h	hour
km	kilometre
kt	kilotonne
L	litre
µg	microgram
µm	micrometre
m^2	square metre
m^3	cubic metre
mg	milligram
min	minute
mL	millilitre
mm	millimetre
Mt	megatonne
nm	nanometre
s	second
wk	week
yr	year

1 INTRODUCTION

The *Canadian Environmental Protection Act (CEPA)* Federal/Provincial Working Group on Air Quality Objectives and Guidelines (WG) is directed by the *CEPA* Federal-Provincial Advisory Committee (FPAC) to develop National Ambient Air Quality Objectives (NAAQOs) for airborne pollutants and to undertake their periodic reassessment. NAAQOs are established to provide a measure of protection to public health and the environment from adverse effects due to airborne pollutants.

Air Quality Objective (AQO) development begins with a scientific review that is embodied within this document, the Science Assessment Document. The evaluation of available scientific data is followed by the identification of Reference Levels through appropriate analyses as outlined in “A Protocol for the Development of National Ambient Air Quality Objectives: Part One: Science Assessment Document and Derivation of the Reference Level(s)” (CEPA/FPAC WGAQOG, 1997).The Reference Level is a level above which there are demonstrated effects on a receptor (human or environmental). More than one form of Reference Level can be identified (e.g., 24 h, SUM60) for one or more receptors. The availability of control technology, the potential economic impacts associated with reducing ambient air pollutant concentrations, public/stakeholder consultation on AQO options, and other considerations, are introduced during the derivation of the Air Quality Objective. Several options are considered, including concentrations higher, lower or equivalent to the Reference Level, depending on ambient background concentrations, uncertainties in the underlying scientific data, and the additional factors listed above.

Canadian air quality objectives for total suspended particulate matter (TSP) were first developed in the 1970s and were revised in the 1980s. At that time, three ranges of air quality objectives were formulated – “desirable”, “acceptable” and “tolerable”. The TSP objectives are based upon earlier scientific research, before the late 1960s, when many air pollution episodes resulted in severe health effects – leading to several thousand premature deaths over a period of a few days, in cities such as London, England. Governments of the day took steps to reduce pollution levels, consisting primarily of combustion-related particulate matter (PM) usually combined with sulphur dioxide, and episodes of severe air pollution similar to the London fog episodes have now become rare.

The TSP air quality objectives, like those developed in the US, Britain and Europe, were based upon the assumption that low ambient concentrations of PM measured in North America and Western European cities were not associated with any adverse effects on health or the environment. Beginning about 1990, an avalanche of scientific studies carried out in the US, Canada, Britain and Europe cast serious doubt on this assumption. The studies demonstrated adverse effects on cardiorespiratory health, including both increased hospitalizations and increased premature mortality, associated with ambient PM levels that were often far below the current TSP objectives. These findings prompted reexamination of the objectives, not only in Canada, but also in the US, Britain, the European Community, and the World Health Organization.

This Science Assessment Document represents the Canadian reexamination of particulate matter air pollution and its relationship to increases in health and environmental effects. Rather than discard the TSP objectives, which the Working Group acknowledges are outdated both temporally and scientifically, new air quality objectives for particulate matter equal to or less than 10 microns in diameter (PM_{10}) and its fine subfraction ($PM_{2.5}$) are being developed. The evaluation focusses on the smaller particles, as compared to total suspended particles that range in size from 0.005 µm up to 100 µm, because the recent evidence shows that particle size is important. Size influences the site of deposition in the human respiratory tract and the consequent degree of toxicity that may be experienced. Particle size also reflects the origin and formation of airborne particles; larger sized particles are often of crustal origin and smaller particles come from combustion processes.

In addition, it is the fine fraction that contributes to reduced visibility in the atmosphere.

Included in this document is a description of PM: physical and chemical characteristics, monitoring methods, sources and behaviour in the environment, background and ambient concentrations, exposure of Canadians, and an evaluation of the available toxicological information and data. This is followed by the risk characterization for human and environmental receptors and the development of Reference Levels based on the scientific information.

2 PHYSICAL AND CHEMICAL CHARACTERISTICS OF PM

"Particulate matter" or "PM" refers to all airborne solid and liquid particles – except pure water – that are microscopic in size. Particle diameters may range from approximately 0.005 µm to 100 µm, although the suspended portion generally consists of particles less than 40 µm. Particulate matter is unique among atmospheric constituents in that it is not defined based on its chemical composition. It may include a broad range of chemical species, such as elemental and organic carbon compounds; oxides of silicon, aluminum and iron; trace metals; sulphates; nitrates and ammonium.

Several terms have been used to describe types of particulate matter. Table 2.1 defines some of the more common terms. The fraction of particulate matter that is currently included under federal air quality objectives in Canada is total suspended particulate matter (Canada Gazette, 1989), which by general agreement, refers to particles with diameters less than 100 µm and which ". . . excludes substances with a known specific toxic effect (arsenic, asbestos, benzo-a-pyrene, beryllium, sulphuric acid mist, etc.) and refers only to those which are chemically relatively inert" (SAQO, 1976).

The current discussion will focus on PM_{10} and its fine subfraction, $PM_{2.5}$. The term "PM_{10}" refers to particles that are 10 µm or less in diameter. Particles of this size range are also called "thoracic particles," reflecting the fact that they can be inhaled into the tracheobronchial and alveolar (thoracic) regions of the respiratory system. They are also sometimes referred to as "inhalable particles", although this term is generally applied to particles smaller than 15 µm in diameter. PM_{10} is generally subdivided into a fine fraction ($\leq$2.5 µm) or less in diameter ($PM_{2.5}$) and a coarse fraction (>2.5 µm) in diameter, reflecting its typically *bimodal* distribution. Sometimes, the fine fraction refers to particles less than 2.0 µm in diameter; for this report, "fine" will refer to 2.5 µm or less. These particles are sometimes referred to as "respirable particles".

Particles are further classified as "primary" or "secondary" in nature. Primary particles are those emitted directly into the atmosphere, whereas secondary particles are formed through physical or chemical transformations that take place in the atmosphere. Primary PM_{10} may result from natural or human (anthropogenic) activities. Natural sources include windblown dust, sea spray and wildfires. Anthropogenic sources include fuel combustion, industrial processes and transportation. High-temperature combustion sources contribute to the fine fraction of PM_{10}, whereas particles produced by grinding activities or wind erosion are predominantly found in the coarse fraction. Secondary particles are predominantly found in the fine fraction, and can also be of either natural or anthropogenic origin. They typically result from reactions involving such precursor gases as sulphur dioxide (SO_2), nitrogen oxides (NO_x), ammonia (NH_3) and various organic gases, yielding particle sulphate, nitrate and condensed organic compounds.

The behaviour of particulate matter in the atmosphere and its potential to affect human health and atmospheric visibility are dependent on its' physical and chemical characteristics. These characteristics, in turn, are dependent on the source type and on formation processes that particles undergo at the source or in the atmosphere. In the following sections, the major physical and chemical characteristics of PM will be described. Further discussion of the characteristics associated with particulate emissions from specific sources can be found in Chapter 4. For a more detailed treatment of particulate matter, the reader is referred to the US Environmental Protection Agency (EPA) criteria document for particulate matter (US EPA, 1982a; 1996). For comparison purposes, the reader is also referred to the National Research Council of Canada (NRCC) document (NRCC, 1982) for a Canadian perspective.

2.1 PARTICLE SIZE

Particle size is considered the most important parameter in characterizing the physical behaviour of particulate matter, as it affects removal processes, atmospheric residence times and the contribution of light scattering to visibility degradation. Particle size is typically defined in terms of its diameter. Although

Table 2.1 Terminology Relating to Atmospheric Particles (after Seinfeld, 1986)

Terminology	Definition[1]
Aerosols, aerocolloids, aerodisperse systems	Tiny particles dispersed in gases.
Dusts	Suspensions of solid particles produced by mechanical disintegration of material such as crushing, grinding, and blasting. $D_p > 1.0$ µm.
Fog	A loose term applied to visible aerosols in which the dispersed phase is liquid. Usually, a dispersion of water or ice.
Fume	The solid particles generated by condensation from the vapour state, generally after volatilization from melted substances, and often accompanied by a chemical reaction such as *oxidation*. Often the material involved is noxious. $D_p < 1$ µm.
Hazes	An aerosol that impedes vision and may consist of a combination of water droplets, pollutants, and dust. $D_p < 1$ µm.
Mists	Liquid, usually water as particles suspended in the atmosphere at or near the surface of the earth; small water droplets floating or falling, approaching the form of rain, and sometimes distinguished from fog as being more transparent or as having particles perceptibly moving downward. $D_p > 1$ µm.
Particle	An aerosol particle may consist of a single continuous unit of solid or liquid containing many molecules held together by intermolecular forces and primarily larger than molecular dimensions (>0.001 µm). A particle may also be considered to consist of two or more such unit structures held together by interparticle adhesive forces such that it behaves as a single unit in suspension or upon deposit.
Smog	A term derived from smoke and fog, applied to extensive contamination by aerosols. Now sometimes used loosely for any contamination of the air.
Smoke	Small gas-borne particles resulting from incomplete combustion, consisting predominantly of carbon and other combustible material, and present in sufficient quantity to be observable independently of the presence of other solids. $D_p \geq 0.01$ µm.
Soot	Agglomerations of particles of carbon impregnated with “tar,” formed in the incomplete combustion of carbonaceous material.

[1] In the list of definitions, D_p refers to the equivalent diameter of a spherical particle of unit density that has the same settling velocity as the collected particle.

liquid aerosol particles are nearly always spherical, and solid particles are often irregularly shaped, equivalent diameters are used to correct for these deviations from sphericity.

The *aerodynamic diameter* is the most commonly used expression for particle size. Based on Stokes’ law, which describes the forces acting on a falling sphere in a stagnant medium, it defines the equivalent diameter of a spherical particle that has the same settling velocity as the collected particles. If the density of the collected particles is known, the equivalent diameter D_p is referred to as the Stokes’ diameter. If it is not known, a particle density of 1 g/cm^3 is assumed, and the equivalent diameter is referred to as the equivalent aerodynamic diameter. Stokes’ Law is applicable to particles with diameters between 1 and 100 µm. Below 1 µm, the assumption that the airstream in contact with the particle has the same velocity as the particle is no longer valid, and the Cunningham correction factor must be applied to account for particle slip between air molecules. This factor is estimated to vary with the nature of the particle surface, with reported values of 0.7 for rough spheres, 0.82-0.9 for aqueous solution drops and 0.87 for oil drops (Fuchs, 1964).

Because particle size may vary over four orders of magnitude, characterizing particulate matter in terms of particle distributions is convenient and, more specifically, a continuum of size variations. The total number of particles is defined as

$$N = \int_0^\infty n(D_p)\,dD_p \qquad (2.1)$$

where $n(D_p)$ represents the size distribution function for particle size. A normalized size distribution function is then defined as $\tilde{n}(D_p)=n(D_p)/N$, where $\tilde{n}(D_p)dD_p$ is the fraction of the total number of particles per cubic metre of air having diameters in the range of D_p to D_p+dD_p.

Until the early 1970s, the two most common types of frequency distributions used by atmospheric scientists were Junge's (1955) power law distribution for particle size and the log-normal distribution for mass. Junge's power law is of the form

$$\frac{dN}{dD} = AD^{-k} \tag{2.2}$$

where A and k are constants. Although it was valid for number distributions, Clark and Whitby (1967) found this function to be inadequate for describing surface and volume distributions. Limitations were also identified in the log-normal distribution (Fuchs, 1964), in that it was adequate only when particulate matter was sampled perfectly.

Recognizing the weaknesses with the two established methods, Whitby et al. (1972) instead expressed the size distributions in terms of the logarithm of the diameter, obtaining

$$\frac{dN}{d\log D_p} = n(\log D_p) \tag{2.3}$$

for number distributions,

$$\frac{dS}{d\log D_p} = n_s(\log D_p) \tag{2.4}$$

for surface area distributions and

$$\frac{dV}{d\log D_p} = n_v(\log D_p) \tag{2.5}$$

for volume (or mass) distributions, where S and $n_S(\log D_p)$ are surface area and surface area distribution function, and V and $n_V(\log D_p)$ are volume and volume distribution function, respectively. An advantage of presenting the data in this form is that the area under the curve is proportional to the quantity (number, surface area or volume) in the given size interval. For a more detailed description of particle size distributions, the reader is referred to Seinfeld (1986).

A well-known example of number, surface area and volume distributions obtained by Whitby (1975) during a smog episode in Pasadena, California, in 1969 is presented in Figure 2.1. The respective ordinates are $dN/d\log D_p$, $dS/d\log D_p$ and $dV/d\log D_p$, and the abscissa is $\log D_p$. Figure 2.1 shows that in an urban environment, size distributions may be multimodal, depending on the quantity involved. Number distributions exhibit a single mode, with a maximum near 0.01 µm. Surface area distributions exhibit one or two modes, with a primary maximum near 0.2 µm. Volume or mass distributions are characterized by two modes, with maxima near 0.3 and 10 µm, and a third mode if sampling takes place near a strong source of fresh nuclei.

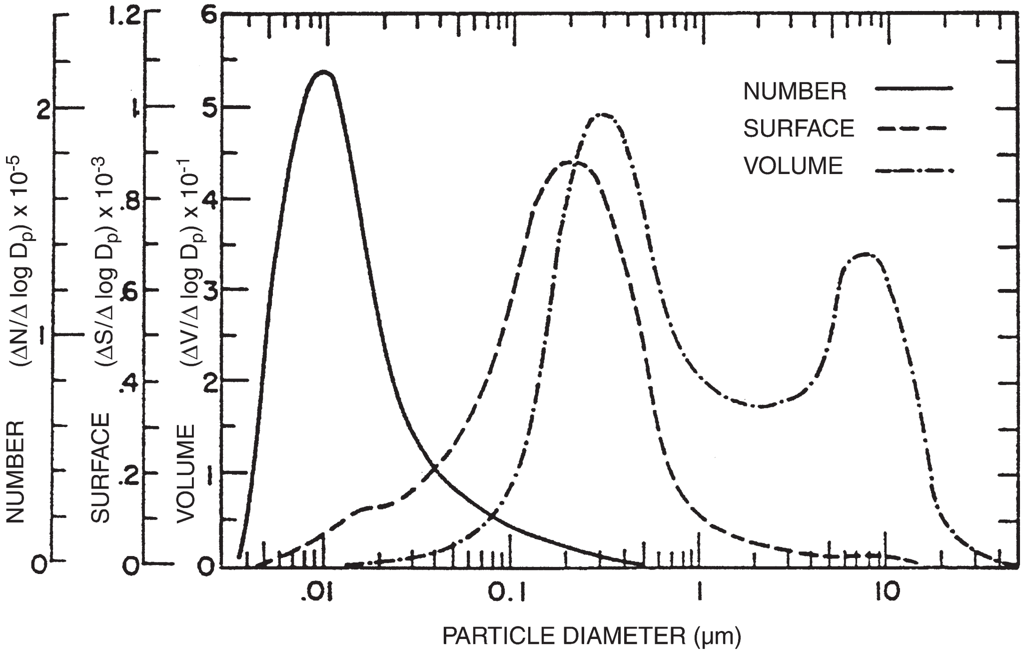
These modes reflect the different source types and the different transformation mechanisms at work in the atmosphere. They are generally identified as follows:

(a) nuclei mode: $D_p < 0.1$ µm,
(b) accumulation mode: 0.1 µm $< D_p <$ 2 µm, and
(c) *sedimentation* or coarse mode: $D_p > 2$ µm.

Particles in the nuclei mode ($D_p < 0.1$µm), also called Aitken nuclei, are formed primarily from the condensation of hot vapours during combustion processes and from the *nucleation* of atmospheric species to form new particles. Although the greatest concentration of airborne particles is found in the nuclei mode, these particles contribute little to overall particle mass loading. They are subject to random or *Brownian motion* and to *coagulation* processes in which particles collide to yield larger particles. Therefore, the atmospheric residence time of nuclei mode particles is very short.

It has been estimated that the concentration of particles of 0.01 µm average diameter, initially present at levels typical of urban air (10^5 particles per cubic centimetre; or $10^5/\text{cm}^3$), should decrease by a factor of two within about 30 minutes owing to coagulation (Wallace & Hobbs, 1977). This compares with an estimated time of 500 hours for a particle of 0.2 µm diameter initially present in concentrations of $10^3/\text{cm}^3$. Because of rapidly decreasing particle mobility as particle size increases, coagulation processes are limited to particles with diameters less than 0.2 µm.

Figure 2.1 Normalized Frequency Plots of Number, Surface and Volume Distributions for Pasadena Smog in 1969 (from Whitby, 1975)



Particles found in the accumulation mode (0.1 µm < D_p < 2 µm) result from the coagulation of particles in the nuclei mode and from the condensation of vapours onto existing particles that then grow into this size range. The accumulation mode accounts for most of the particle surface area and a sizable portion of the particle mass. It is so-named because removal processes are least efficient in this size range. The atmospheric lifetime of particles in the accumulation mode may be on the order of days to weeks.

The coarse particle mode (D_p > 2 µm) is typically associated with mechanical processes, such as wind erosion that produces dust particles, industrial processes that produce fly ash, and breaking ocean waves that produce sea spray. These processes generally lack the energy to produce very fine particles, as one would find in high-temperature combustion processes. Particles in the coarse mode are efficiently removed by gravitational settling and, as a result, are characterized by short atmospheric residence times, on the order of hours to days. Therefore, although the coarse mode accounts for much of the total mass of ambient PM_{10}, it contributes little to the total number of particles. As a result, little mass is transferred from the accumulation mode to the coarse mode. The coarse mode also contributes little to particle surface area distributions, owing to the small numbers and the small surface area to volume ratios of particles relative to those in the accumulation mode.

Figure 2.2 shows normalized particle number distributions obtained from measurements in several different environments. Urban settings, which are associated with heavy anthropogenic activity, are seen to contain the greatest number of fine particles, whereas desert dust storms contain a large number of giant particles. Variations in particle concentrations are greatest for the smaller and larger particles, reflecting their shorter residence times. To maintain the observed concentration levels, there must be a continuous production of very small and large particles in the atmosphere. All distributions show a rather uniform decrease in concentration beyond a particle size of approximately 0.1 µm, thus masking the fact that considerable particle mass lies at particle sizes greater than 2.5 µm.

To represent contributions to the coarse fraction better, normalized particle volume distributions based on the same data as the aforementioned number distributions are shown in Figure 2.3. Urban particulate matter is shown as exhibiting high mass concentrations in both the fine and coarse fractions. Recent studies over eastern North America confirm that away from immediate sources, particle mass distributions are dominated by particles in fine (0.2-0.5 µm) and coarse (5-30 µm) modes (Leaitch & Isaac, 1991). An exception is near large-particle sources such as the ocean.

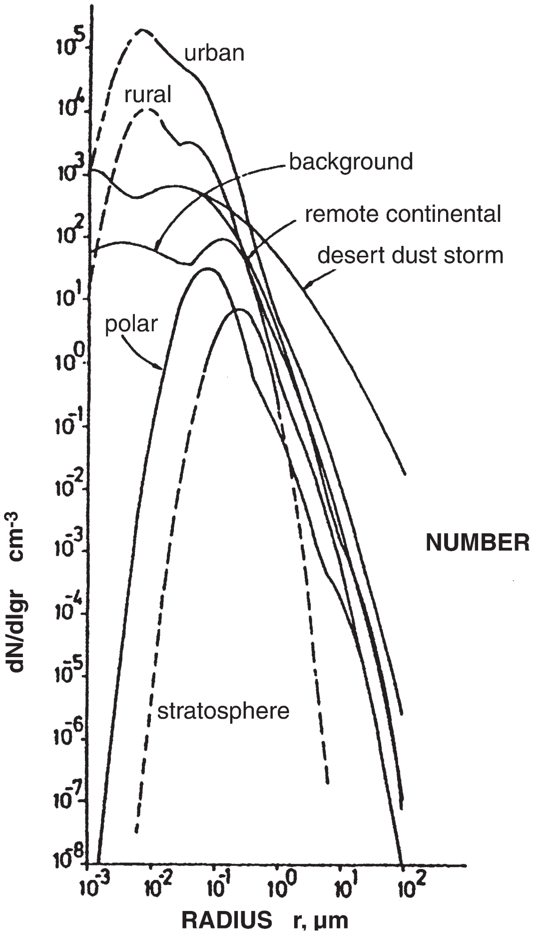


Figure 2.2 Number/Size Distributions Obtained from a Large Set of Measurements from Various Environments (from Jaenicke, 1986)

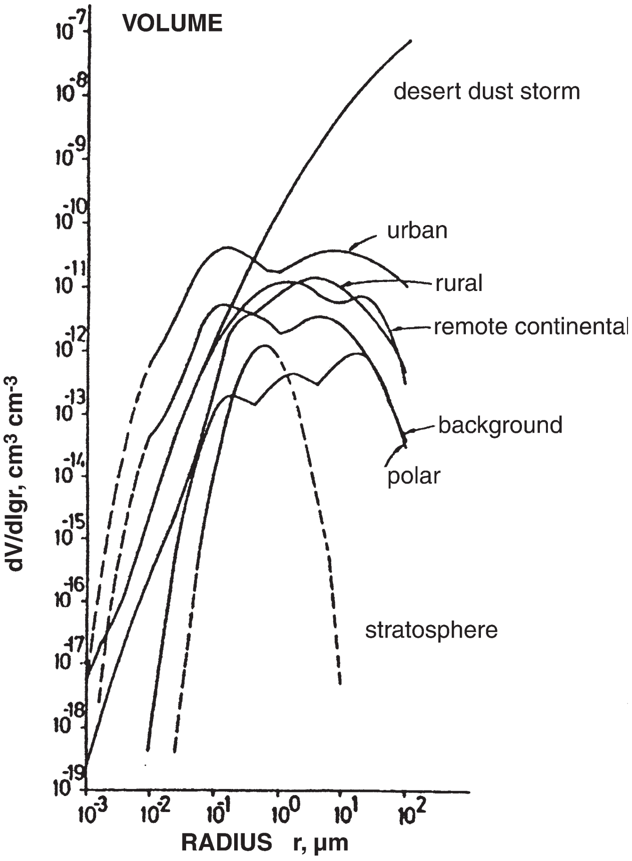


Figure 2.3 Volume Distributions Obtained from a Large Set of Measurements from Various Environments (from Jaenicke, 1986)

2.2 PARTICLE SHAPE AND DENSITY

Particle shape depends on the source type as well as the processes that a particle may undergo once in the atmosphere. Those particles formed by processes of *comminution* (grinding or pulverizing), *attrition* (abrasion or friction) or disintegration will resemble the parent material, while those particles formed by condensation or nucleation will be spherical or of similar simple shape. Condensation is often followed by solidification and formation of chain-like aggregates. Further changes to particle shape may result through processes of *crystallization*, *hydration* (addition of water molecules) and *agglomeration* (formation of a larger, permanent mass in which the individual particles can still be identified). In Table 2.2, the main categories of particle shape are identified and related to particle source type and contribution to total sample size.

Any given shape may include fine and coarse fractions from the same source type of material, (e.g., fly ash). Particles observed in urban areas are highly irregular in shape (Katrinak et al., 1993). Combustion particles also tend to be highly irregular in shape, although exposure conditions (e.g., combustion temperature) will modify the particle shape. Estimates of the specific surface area of coal fly ash are 3-20 times lower than experimental values when the particles are assumed to be nonporous spheres (Rothenberg, 1980).

Particle density (mass per unit volume) will affect both the motion and behaviour of a particle in the atmosphere. The density of airborne particles has been estimated to range from 0.5-6.5 g/cm^3 (Corn, 1976b). Those particles formed through attrition will have the same density as the parent material, whereas processes of oxidation, hydration and

Table 2.2 Particle Shapes (from Stern, 1976)

Shape	Percent by Weight in Sample		Particle Source Types
	Range	Average	
spherical	0-20	10	smoke, pollen, fly ash
irregular/ cubical	10-90	40	mineral, cinder
flakes	0-10	5	mineral, epidermis
fibrous	3-35	10	lint, plant fibre
condensation flocs	0-40	15	carbon, smoke, fume

agglomeration will alter particle density. Those particles containing many void spaces, as is typical of agglomerates, may have a density less than one-tenth that of the parent material, as shown in Table 2.3, which compares floc or apparent particle density with the true density of the parent material.

2.3 BULK MATERIAL PROPERTIES

The physical state and growth of particles in the atmosphere are affected by such bulk material properties as chemical composition, vapour pressure, hygroscopicity and deliquescence (US EPA, 1982a). Refractive indexes, together with particle size, will affect particle scattering of light and therefore atmospheric visibility.

Because the hygroscopic or water-attracting nature of particles affects such characteristics as particle size, shape, refractive index, pH and reactivity, further discussion of this property is warranted. Strictly hygroscopic compounds such as sulphuric acid (H_2SO_4) *monotonically* increase in size with increasing relative humidity. Particles containing deliquescent *salts* such as ammonium bisulphate (NH_4HSO_4) and ammonium sulphate [$(NH_4)_2SO_4$] remain dry with increasing relative humidity until the deliquescence point, which corresponds to the water vapour pressure of the saturated salt solution, is reached. This transition is marked by a sudden uptake of water and a corresponding increase in particle size to form droplets of concentrated solution. Laboratory and field experiments show that sulphate particle size increases with increasing relative humidity (Koutrakis and Kelly, 1993). Growth rates of 50% in the mass median aerodynamic diameter (MMAD) of sulphate-, nitrate- and ammonia-containing particles (from 0.27 to 0.42 µm) have been observed as relative humidity is increased from 40 to 70% (Countess et al., 1981). As light scattering is most efficient for particles in the size range of 0.1-1.0 µm, reaching a maximum between 0.3 and 0.7 µg, particle growth through deliquescence has a large potential impact on atmospheric visibility.

Table 2.3 Particle Densities of Metal Oxide Agglomerates (from CARB, 1982, based on Whytlaw-Gray and Patterson, 1932)

Material	Floc Density (g/cm^{-3})	True Density (g/cm^{-3})
Silver	0.94	10.5
Mercury	1.70	13.6
Cadmium Oxide	0.51	6.5
Magnesium Oxide	0.35	3.6
Mercuric Chloride	1.27	5.4
Arsenic Trioxide	0.71	3.7
Lead Monoxide	0.62	9.4
Antimony Trioxide	0.63	5.6
Aluminum Oxide	0.18	3.7
Stannic Oxide	0.25	6.7

Particles may also undergo a sudden release of water with decreasing relative humidity. This is termed *efflorescence*, and the associated relative humidity is called the efflorescence point. Deliquescence and efflorescence points for various compounds are presented in Table 2.4. The latter typically occur at relative humidities 30% below the deliquescence point (US EPA, 1982a).

An example of a deliquescent compound is $(NH_4)_2SO_4$, the fully neutralized ammonium salt of H_2SO_4, which undergoes a solid-liquid transition at about 80% relative humidity. Below this point, the oxidation of SO_2 to H_2SO_4 takes place predominantly in the gas phase, with H_2SO_4 condensing onto particle matter. Above this point, SO_2 readily dissolves in the sulphate droplets and is oxidized to form particle sulphate. Further discussion of this mechanism can be found in Section 2.7.

Table 2.4 Deliquescence and Efflorescence Points of Salt Particles (based on US EPA, 1982a, Countess et al., 1981)

Composition	Deliquescence (% RH)	Efflorescence (% RH)
NaCl	75.7	43
KCl	84.3	53
NaCl-KCl	73.8	38
$(NH_4)_2SO_4$	79.5	~36
$(NH_4)_3H(SO_4)_2$	69.0	–
$(NH_4)HSO_4$	39.0	–
$2NH_4NO_3•(NH_4)_2SO_4$	56.4	–
NH_4NO_3	62.0	–

2.4 PARTICLE SURFACE PROPERTIES

Small particles are characterized by a large surface area relative to their mass, which is further increased with the presence of surface irregularities and internal pores. Under most atmospheric conditions, particles smaller than 0.1 µm diameter are known to contain significant amounts of water. Therefore, gas-liquid phase interactions are considered important on these small particles (Lodge et al., 1981).

Other surface properties of importance include electrostatic charging, adhesion and the influence of surface films (US EPA, 1982a). Electrostatic charging and adhesion can provide means of particle detection, measurement and collection. Organics such as carboxylic acids, alcohols, esters and aldehydes can form coatings on fine particles (Gill et al., 1983). As many of these coatings are surface active (surfactants), they may influence how the particle grows in a humid environment. Exposure to organic gases appears to retard the evaporation of water droplets, thereby increasing their persistence in the atmosphere (Chang et al., 1980). Carbon black particles, which are normally hydrophobic (i.e., have an aversion to water), were found to absorb large amounts of water (20-40% of dry particle mass) when coated with an organic surfactant (Andrews and Larson, 1993).

2.5 PARTICLE FORMATION AND GROWTH

Two basic processes are involved in particle formation: grinding or atomization, and nucleation of *supersaturated* vapours. Grinding and atomization are mechanical processes that result in the direct discharge of particles to the atmosphere. Owing to the nature of the formation process, these particles are typically found in the coarse mode. Examples include windblown dust and sea spray.

Nucleation of supersaturated vapours results from the molecular agglomeration of supersaturated vapours, either without foreign particles and ions (homogeneous nucleation) or in their presence (heterogeneous nucleation). Examples of homogeneous nucleation include the formation of H_2SO_4 by reaction of the hydroxyl radical (OH) with SO_2 and the formation of carboxylic acids by reaction of ozone with olefins. The condensation of hydrocarbon vapours onto carbon particles during the cooling of automobile exhaust and the condensation of H_2SO_4 molecules onto fly ash during the cooling of power plant plumes are examples of heterogeneous nucleation.

Particle growth may occur through particle-particle interactions or gas-particle interactions. Particle-particle interactions involve the coagulation of two particles to form one larger particle. Gas-particle interactions include the growth of hygroscopic particles such as sulphates and nitrates through absorption of water vapour; the absorption and adsorption of pollutant gases such as SO_2, nitrogen dioxide (NO_2) and hydrocarbons, followed by chemical reactions to yield such products as sulphate (SO_4^{2-}), nitrate (NO_3^-)and organic compounds; and the condensation of low-vapour-pressure molecules formed in gas-phase reactions such as H_2SO_4 and organic compounds. These growth processes are generally limited to particles less than 1 µm in diameter.

2.6 PARTICLE TRANSPORT AND REMOVAL

Mechanisms for particle transport and removal are dictated by particle size. Coarse particles are typically emitted close to the surface and are quickly removed through gravitational effects (sedimentation) or inertial effects (impaction).

For particles less than 1 µm in diameter, sedimentation is not an effective means of removal. Instead, the main removal mechanisms are:

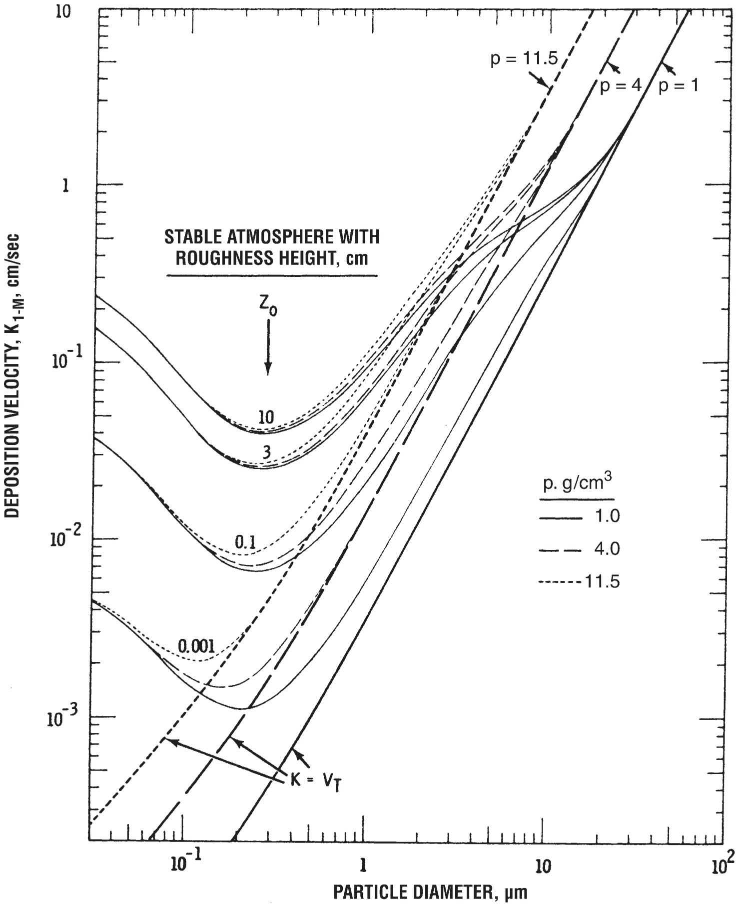
(a) dry deposition – the removal of chemical species or particles from the atmosphere at the air-surface interface, and

(b) precipitation scavenging – the removal of chemical species or particles from the atmosphere by interaction with precipitation.

Dry deposition is typically expressed in terms of the dry deposition velocity v_d. v_d is the downward flux, F, of a chemical species or particle divided by the concentration of that species $c(x, y, z_1, t)$ at some height z_1 above the surface (typically 1-2 m). Dry deposition can be viewed as a multistage process involving: (1) turbulent transport of a chemical species or particle from the boundary layer to the surface laminar sublayer; (2) diffusion across the surface laminar sublayer to the surface; and (3) uptake by the surface (Seinfeld, 1986). Factors that influence transport to the surface laminar sublayer include wind speed, atmospheric stability and surface roughness. Transport to the surface depends on molecular properties affecting diffusion across the laminar sublayer. Surface uptake may be assumed to be immediate once contact is made, although surface properties such as moisture content and canopy structure will affect resuspension (Sehmel, 1980). Superimposed on the rate of deposition is the particle settling velocity due to gravitational effects. Deposition velocities predicted by Sehmel (1980) for a stable atmosphere as a function of particle diameter, aerodynamic surface roughness (z_o) and particle density (ρ) are presented in Figure 2.4. Clearly, the lowest deposition velocities are predicted for particles in the accumulation mode (i.e., 0.1-1.0 µm). Sehmel (1980) notes that predictions by Sehmel and Hodgson (1978) for an unstable atmosphere show increased deposition velocities relative to those for a stable atmosphere. However, this increase is small relative to the effects of particle diameter, friction velocity and surface roughness. Given the many factors involved in the characterization of dry deposition, estimating deposition rates is an onerous task. For a more detailed review of the dry deposition process, the reader is referred to Sehmel (1980) or Seinfeld (1986).

Removal through precipitation scavenging may take place through in-cloud or below-cloud processes. “Rain-out” is an in-cloud process in which particles serve as cloud condensation nuclei (CCN) or are captured in the formation of cloud droplets. To act as CCN at 1% supersaturation, the particles must be at least 0.1 µm in radius if wettable but water-insoluble and at least 0.01 µm in radius if water soluble. Forest fires are thought to be major sources of CCN, whereas windblown dust and sea salt particles are considered minor sources. Sulphates have been identified as a common constituent of CCN. “Wash-out” is a below-cloud process in which particles are scavenged by falling precipitation. Particles greater than 2 µm in diameter are the most efficiently removed by this process. Globally, it is estimated that precipitation scavenging accounts for about 80-90% of the mass of particles removed from the atmosphere (Wallace & Hobbs, 1977). Improvements in visibility following precipitation events are generally attributed to precipitation scavenging. For a more detailed discussion of scavenging processes, the reader is referred to US EPA (1982a).

Figure 2.4 Predicted deposition velocities at 1 m for u=20 cm/s and particle densities of 1, 4 and 11.5 g/cm^3. V_T is terminal settling velocity (Sehmel, 1980).



2.7 CHEMICAL CHARACTERISTICS

In the preceding sections, the formation and removal processes affecting the fine and coarse fractions of particulate matter have been discussed and have been shown to be distinctly different. It is not surprising, therefore, that the chemical species found within the fine and coarse fractions should also vary significantly.

A schematic presenting an idealized aerosol mass distribution and the typical segmentation of chemical species among the fine and coarse fractions is shown in Figure 2.5. The major components of the fine fraction include sulphate, nitrate, ammonium, lead and inorganic and organic carbon compounds. These particles are generally of primary anthropogenic or secondary origin, although forest fires are known to be a large natural source of particulate matter in the fine fraction. Particles in this size range tend to be acidic in nature.

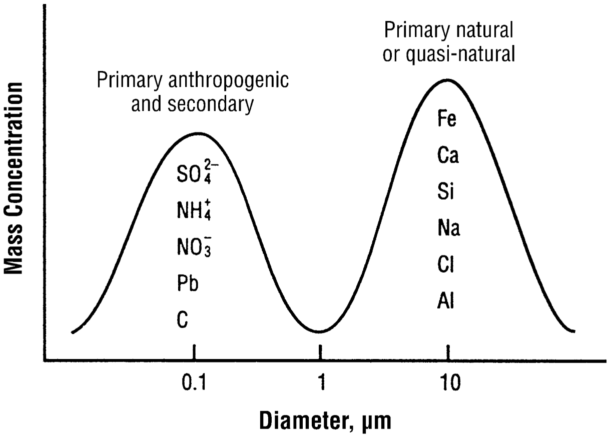
The coarse fraction consists primarily of materials that are common to the earth's crust (oxides of iron, calcium, silicon and aluminum) and sea salt spray (sodium and chloride). Particles of this size range are typically basic in nature.

Some chemical species such as nitrates and chlorides may be found in both the fine and coarse fractions. Trace metals such as nickel, tin, vanadium, copper, zinc, antimony and manganese are also variable. The following sections provide a detailed description of the more common chemical species associated with PM.

2.7.1 Elemental Carbon

Inorganic or elemental carbon (EC), also known as graphitic or black carbon, is a product of the incomplete combustion of carbon-based materials and fuels, and is solely primary in origin. The predominant sources of EC include fossil fuel combustion and biomass burning (Penner et al., 1993).

Figure 2.5 Idealized Volume (mass) Distribution of Fine and Coarse Particles in an Urban Atmosphere, and Associated Chemical Composition (from Seinfeld, 1986)



EC particles are typically less than 1 µm in diameter. Size distribution measurements of EC in ambient air and vehicular emissions have been found to exhibit a bimodal distribution with peaks in the range of 0.05-0.12 µm and 0.5-1.0 µm (Venkataraman and Friedlander, 1994). Because EC particles are both very small and very inert, they can remain in the atmosphere for extended periods before being removed by scavenging processes. This poses a potential health problem, as these particles can penetrate deeply into the lungs and act as adsorption sites for toxic pollutants. A characteristically large surface area together with its impurities makes EC the principal light-absorbing aerosol species, with the potential to affect both visibility and climate (Charlock and Sellers, 1980; Charlson et al., 1992). It is estimated that EC is responsible for more than 90% of light absorption and 25-45% of overall visibility reduction (Hamilton and Mansfield, 1991), as described in chapter seven.

2.7.2 Organic Carbon

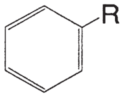
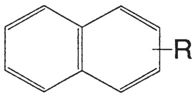
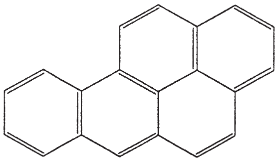
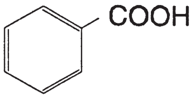
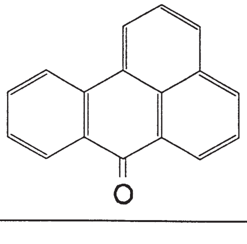
Organic carbon (OC) particulate matter can be directly released to the atmosphere or produced via secondary gas-to-particle conversion processes. It is predominantly found in the fine fraction (Van Vaeck and Van Cauwenberghe, 1978). Surprisingly, meat-cooking operations, paved road dust and fireplaces have been estimated to account for more than 50% of fine OC particle emissions in an urbanized core of the Los Angeles Basin (Hildemann et al., 1994). The associated organic species have been found to number in the hundreds (Rogge et al., 1991, 1993a, 1993b, 1993c). The major classes of OC compounds found in urban particulate matter are summarized in Figure 2.6. Alkanes in the range of C_{17}-C_{36}, alkenes, and aromatic and polycyclic aromatic hydrocarbons (PAH) are typically primary in nature (Seinfeld, 1986). Oxidized hydrocarbons such as acids, aldehydes, ketones, quinones, phenols and esters may be primary or secondary in nature. Nitro derivatives of organic compounds and heterocyclic sulphur compounds have also been identified in organic particulate matter.

PAH compounds are some of the most well-studied of the organic compounds, as certain species such as benzo[a]pyrene have been identified as potential carcinogens. Rogge et al. (1991, 1993a, 1993b, 1993c) identified PAH compounds in particulate emissions from vehicle exhaust, road dust, charbroiler and meat cooking operations and natural gas home appliances. Ambient measurements in Barcelona, Spain (Aceves and Grimalt, 1993) revealed that airborne PAH levels measured in very fine (<0.5 µm) particulate matter were more than fifty times higher than those levels found in coarse (>7.2 µm) particles. Measurements of PAH in ambient air and vehicular emissions were found to exhibit bimodal distributions similar to that for EC, with peaks in the range of 0.05-0.12 µm and 0.5-1.0 µm (Venkataraman and Friedlander, 1994). The more volatile four-ring PAHs such as fluoranthene, pyrene, benz[a]anthracene and chrysene were found to predominate in the nuclei mode particles while five-ring and larger particles such as benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene predominated in the accumulation mode particles.

Increasing interest has focussed on secondary organic compounds (e.g. Grosjean and Seinfeld, 1989; Grosjean, 1992; Pandis, et al., 1992, 1993), as they are estimated to form a substantial portion of the fine fraction of PM_{10}, with contributions of up to 50% estimated in parts of the Lower Fraser Valley in British Columbia (Lowenthal et al., 1994) and 26-47% estimated for selected areas in the United States (van Houdt, 1990). At the height of a pollutant episode studied in the Los Angeles Basin, secondary formation was estimated to account for approximately 70% of organic particulate matter (Turpin and Huntzicker, 1991).

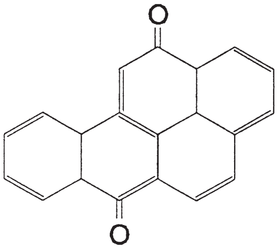
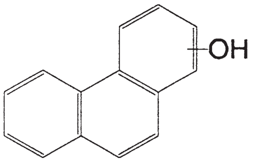
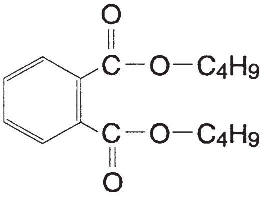
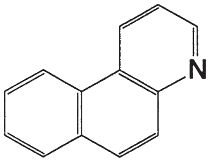
Secondary processes involve the gas-phase oxidation of hydrocarbon precursors by the hydroxyl radical during the day, nitrate radicals during the night, and ozone (O_3) during the day or night (Grosjean, 1992). Based on an examination of the rate constants and of the relative concentrations of electrophiles in urban air, aromatic hydrocarbons, saturated aliphatics (e.g., alkanes, cycloalkanes) and oxygenated aliphatics (e.g., alcohols, esters) are expected to react with the hydroxyl radical. Likewise, alkenes, cycloalkenes and other olefinic compounds such as dienes, terpenes and styrene are expected to react with the hydroxyl and nitrate radicals and ozone. Low-volatility products either nucleate or condense on the surfaces of preexisting particles, yielding particles in the size range of 0.1-1.0 µm. Compounds which yield high-volatility products will be unable to form particulate matter under atmospheric conditions. Such compounds include the C_1-C_6 alkanes, the C_2-C_6 alkenes, benzene and many low-molecular-weight carbonyls, chlorinated compounds and oxygenated solvents (Grosjean and Seinfeld, 1989).

Figure 2.6 Major Classes of Organic Compounds Found In Urban Air (from Daisey, 1980)

Compound Class	Example	Concentration in Urban Air (ng m^{-3})	Location, Date of Measurement(s)
Alkanes	n-$C_{22}H_{46}$	1000-4000	217 U.S. urban stations 1966-67
Alkenes	n-$C_{22}H_{44}$	2000	217 U.S. urban stations
Alkylbenzenes		80-680	West Covina, California July 24, 1973
Naphthalenes		400-500	Pasadena, California September, 1972
Polycyclic aromatic hydrocarbons		6.6	100 U.S. urban stations, 1958-59
		3.2	32 U.S. urban stations, 1986-87
	(Benzo (a) pyrene)	2.1	32 U.S. urban stations 1970
Aromatic acids		90-380	Pasadena, California September 1972
		8	Average U.S. urban prior to 1965
Cyclic ketones		2-48	U.S. urban site January 1968

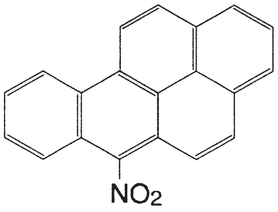
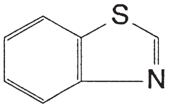
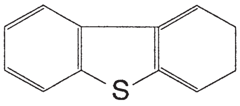
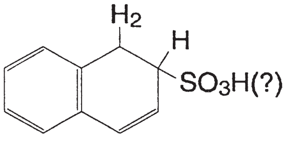
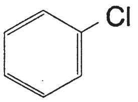
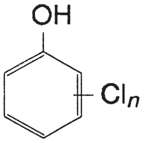
(continued)

Figure 2.6 Major Classes of Organic Compounds Found In Urban Air *(continued)*

Compound Class	Example	Concentration in Urban Air $(ng\ m^{-3})$	Location, Date of Measurement(s)
Quinones		0.04-0.12	Toronto, Ontario 1972-1973
Phenols		~ 0.3	Antwerp, Belgium 1975
Esters		29-132	Antwerp, Belgium 1976
		2-11	New York City 1975
Aldehydes	$CHO(CH_2)_nCHO$	30-540	Pasadena, California September 1972
Aliphatic carboxylic acid	$C_{15}H_{31}COOH$	220	New York City February 1964
		36.5	Antwerp, Belgium January 1976
Aliphatic dicarboxylic acids	$HOOC(CH_2)_nCOOH$	40-1350	Pasadena, California September 1972
Aza-arenes		0.2	Composite 100 U.S. urban sites, 1963
		0.01	New York City 1976
		~ 0.5	Antwerp, Belgium
N-Nitrosamines	$(CH_3)_2NNO$	≤ 0.03-0.96	Baltimore, Maryland August 1975
		15.6	New York City July 1976
Nitro compounds	$CHO(CH_2)_nCH_2ONO_2$	40-1010	Pasadena, California September 1972

(continued)

Figure 2.6 Major Classes of Organic Compounds Found In Urban Air *(continued)*

Compound Class	Example	Concentration in Urban Air (ng m^{-3})	Location, Date of Measurement(s)
Nitro compounds		identified	Prague, Czechoslovakia
Sulfur heterocyclic compounds		0.014-0.02	New York City 1976
		identified	Indianapolis and Gary, Indiana
SO_2-adducts		2-18 nmoles m^{-3}	New York City 1976
Alkylhalides	$C_{18}H_{37}Cl$	~ 20-320	Pasadena, California September 1972
Arylhalides		0.5-3	Pasadena, California 1972
Chlorophenols		5,7-7.8	Antwerp, Belgium 1976

2.7.3 Trace Elements

Highly volatile trace elements such as lead, nickel, arsenic, chromium and cadmium are emitted in vapour form from combustion and other high-temperature industrial processes and quickly condense in the ambient atmosphere. These species are known to concentrate in the fine fraction (Fennelly, 1975). Oxides of silicon, aluminum, iron, potassium, calcium and magnesium are common constituents of the earth's crust and common constituents of the coarse fraction. Sodium from sea spray is also commonly found in the coarse fraction.

Where trace elements exhibit a high abundance relative to other elements in a source profile, they may be used as key-indicating species for that source. Vanadium is a common tracer for heavy oil combustion, whereas zinc is used to identify municipal refuse incinerators (Cheng and Hopke, 1989; Schroeder et al., 1987). Iron is a marker for suspended crustal material (Lyons et al., 1993). Selenium is associated with coal combustion products (Andren et al., 1975). Lead is still used to identify motor vehicles, although with the phase-out of leaded gasoline alternative markers such as PAH compounds are being investigated (Li and Kamens, 1993).

In a review of elemental size distributions for 38 trace metals reported in the literature over the preceding two decades (based exclusively on cascade impactor data), elements with a MMAD of less than 2 µm were found to exhibit bimodal distributions, with a dominant peak in the range of 0.5-1 µm and a secondary peak at 3-5 µm (Milford and Davidson, 1985). This included lead, mercury, selenium, cadmium, antimony, bromine, nickel, arsenic, chromium, zinc and copper. Elements with a MMAD greater than 2 µm exhibited unimodal mass distributions, with the dominant peak at 3-5 µm and little mass below 1 µm in diameter. This included manganese, cobalt, chlorine, iron, potassium, sodium, silicon, aluminum, calcium, magnesium and strontium. More recent measurements made in the Los Angeles Basin reveal trimodal distributions for lead and manganese, with the smallest mode attributed to fresh emissions from motor vehicles and supermicrometre particles attributed to suspended crustal material (Lyons et al., 1993). An intermediate mode (0.5-1.0 µm) was believed to result from the growth of smaller particles.

2.7.4 Sulphate

Sulphate is one of the predominant species in the fine mode. Particle sulphate species found in the atmosphere include the strong acids H_2SO_4 and NH_4HSO_4 and the weak acid $(NH_4)_2SO_4$ (Lipfert et al., 1989). In the eastern United States, where SO_2 emissions from coal- and heavy-oil-fired plants are substantial, it has been estimated that sulphates, associated ammonium ion and water comprise approximately 40-70% of the fine particle mass. These contribute substantially to regional haze problems (Husar and Wilson, 1993). Sulphate contributions of 65% have been observed in southwestern Ontario in the summer (Keeler et al., 1990). Measurements taken during the Canadian Acid Aerosol Measurement Program (CAAMP) study in eastern Canada during 1992-1993 exhibited average sulphate to $PM_{2.5}$ ratios of 0.39, 0.30, 0.35, 0.30, 0.24, 0.36 and 0.27 at Egbert, Kejimkujik, Sutton, Windsor, Montréal, Saint John and Toronto, respectively (Environment Canada, 1994). On average, 32% of the $PM_{2.5}$ was due to sulphate, and 60% of the PM_{10} was due to $PM_{2.5}$. Nationally, composite average sulphate concentrations observed at sites east of Winnipeg are 2.3 times higher than those observed at western sites (Dann, 1994). The regional nature of particulate episodes in eastern Canada is attributed to the long atmospheric residence times of sulphate and the synoptic scale of the meteorological conditions conducive to episode development.

A detailed description of particle sulphate formation mechanisms is found in US EPA (1982a). Briefly, sulphate may be formed through the oxidation of SO_2 in the gas phase or aqueous phase. Gas-phase oxidation is primarily via reaction with the hydroxyl radical (Atkinson and Lloyd, 1984) to form sulphuric acid gas. Because of its low vapour pressure, sulphuric acid gas may nucleate in the presence of water vapour to form sulphuric acid droplets. Sulphuric acid gas may also condense on existing particles or react with ammonia to form the progressively neutralized compounds $(NH_4)HSO_4$ and $(NH_4)_2SO_4$. Calvert and Stockwell (1983) reported a wide range of transformation rates (0.01-5 %/hr of SO_2 concentration), with nighttime rates less than 0.1 %/hr. Their studies indicate that gas-to-particle transformation is controlled by the hydroxyl radical and competing reactions as opposed to SO_2 concentrations. Hydroxyl radical production is related closely to photochemistry. Therefore, the highest rates of transformation are expected to occur during the summer daytime when photochemistry is most active.

Aqueous-phase oxidation by oxygen and hydrogen peroxide is a second important pathway for sulphate production (Saxena and Seigneur, 1987). Reaction with oxygen is dependent on iron and manganese concentrations and on liquid water content, which, in turn, is dependent on relative humidity and background concentrations of sulphate, nitrate and ammonia (Saxena et al., 1986). Reaction with hydrogen peroxide is important at low temperatures when gas solubilities are relatively high. In the presence of fog or clouds, SO_2 can dissolve in droplets, where it undergoes faster aqueous reactions than in the gas phase. In the presence of ammonia, H_2SO_4 is neutralized to form $(NH_4)_2SO_4$. Reactions within the fog droplet are controlled by the solubility of precursor gases, and are generally 10-100 times faster than gas-phase reactions (Watson et al., 1994a).

The size distribution for sulphate particles is associated with the accumulation mode, (Milford and Davidson, 1987). Particles produced through gaseous-phase oxidation are typically smaller (MMAD approx. 0.2 µm) than those produced through aqueous-phase oxidation (MMAD approx. 0.5 µm) (Hering and Friedlander, 1982). This feature is used to study the relative importance of the two formation pathways. The presence of supermicrometre particles in marine environments may be attributed to sea spray (MacIntyre, 1974) or the oxidation of SO_2 originating from biogenically produced dimethylsulphide or anthropogenic sources (Garland, 1981). In continental locations, scanning electron microscopy studies revealed sulphate particles attached to clay and calcite particles and smooth sulphate coatings on clay, calcite and pollen particles, suggesting gas-to-particle conversion (Mamane and Noll, 1985).

MMADs averaged over a number of marine and continental distributions for particle sulphate were calculated to be 2.3 and 0.52 µm, respectively (Milford and Davidson, 1987). This compares with more recent estimates of 0.25-0.31 µm in the continental United States (Bondietti and Papastefanou, 1993).

Sulphate particles may be transported long distances (Pierson et al., 1990; Tanner et al., 1984). For a particle of 0.2 µm MMAD, an atmospheric residence time of 12 days is estimated (Bondietti and Pastefanou, 1993). Usually a residence time of 3-5 days is expected for sulphate particles (US EPA, 1996).

2.7.5 Nitrate

Particle nitrate is an end-product of photochemical reactions involving nitrogen oxides. It has been identified as a major constituent of secondary particulate matter in urban areas in British Columbia (Pryor and Steyn, 1994a) and the western United States (Gray et al., 1988; Chow et al., 1992a, 1992b) and a key contributor to visibility problems in the Lower Fraser Valley (Pryor and Steyn, 1994b), Denver (Groblicki et al., 1981) and Los Angeles (White and Roberts, 1977).

Particle nitrate is formed by reactions involving nitric acid (HNO_3) and either ammonia or preexisting particles. Nitric acid is formed primarily by gas-phase reactions of NO_2 with the hydroxyl radical. Additional HNO_3 is produced at night during the hydrolysis of dinitrogen pentoxide (N_2O_5), which is a by-product of reactions involving NO_2 and the nitrate radical (NO_3). This pathway is ineffective during the daylight hours due to the reactivity of both N_2O_5 and NO_3. Gas-to-particle transformation rates for NO_2 to HNO_3 are rapid compared with those for sulphates, ranging from 1%/hr to 90%/hr (Calvert and Stockwell, 1983). These rates are significant during both the daytime and nighttime, in contrast to gas-to-particle sulphate production which is most active during the daytime. Aqueous-phase reactions involving HNO_3 or NH_4NO_3 are an additional pathway for particle nitrate formation. Studies have shown that in the presence of sufficient ammonia, equilibrium is established between gaseous HNO_3, ammonia and solid-phase ammonium nitrate (NH_4NO_3) (Stelson, 1979; Stelson and Seinfeld, 1982a, 1982b). This equilibrium is strongly influenced by temperature and relative humidity, with particle formation being favoured by low temperatures and higher relative humidities (Russell et al., 1983). However, more recent studies (Wexler and Seinfeld, 1990) have shown that the equilibrium assumption may not hold for lower temperatures or larger particles when the time scales for mass transport are too large. Ammonium nitrate is characterized by high vapour pressures. As a result, ammonia will distill away from NH_4NO_3 in the presence of acidic sites such as less than fully neutralized acidic sulphates.

A further pathway for nitrate formation involves reactions that convert sodium chloride to hydrochloric acid and thermally stable nitrates such as sodium nitrate (Russell and Cass, 1984; Mamane and Mehler, 1987; Pilinis and Seinfeld, 1987; Pio and Harrison, 1987). This mechanism is believed to be the principal source of coarse particle nitrate and is a factor where atmospheric sodium chloride levels are significant. Major sources of sodium chloride include sea salt, road sanding and dry lake beds.

The MMAD for particle nitrate distributions has been reported to range from 0.23-4.2 µm (Milford and Davidson, 1987). However, volatility losses and sampling artifacts may render this data unreliable.

2.8 SUMMARY

PM_{10} refers to all airborne solid and liquid particles, except pure water, that are 10 µm or less in diameter. PM_{10} is generally subdivided into a fine fraction of 2.5 µm or less ($PM_{2.5}$) and a coarse fraction of larger than 2.5 µm, reflecting its multimodal nature. It is further classified as primary (emitted directly into the atmosphere) or secondary (formed in the atmosphere through chemical and physical transformations). Primary particles are found in both the fine and coarse modes, whereas secondary particles such as sulphates and nitrates are found predominantly in the fine fraction.

The behaviour of PM_{10} in the atmosphere is affected by many chemical and physical parameters, including particle size. The theory behind particle size distributions and observations taken from various environments were presented. Particles less than

0.1 µm in diameter (the nuclei mode) are formed primarily from the condensation of hot vapours during combustion processes and from the nucleation of atmospheric species to form new particles. Although the greatest number of airborne particles are found in the nuclei mode, they contribute little to overall particle mass loading. They are subject to Brownian motion and coagulation processes that quickly yield larger particles. Particles in the size range of 0.1-2.0 µm (the accumulation mode) result from the coagulation of particles in the nuclei mode and from the condensation of vapours onto existing particles that then grow into this range. They account for most of the particle surface area and much of the particle mass. The accumulation mode is so-named because removal processes are least efficient in this size range. Particles can remain in the atmosphere for days to weeks. Particles larger than 2.0 µm (the sedimentation or coarse mode) are typically associated with mechanical processes such as wind erosion, industrial processes that produce fly ash, and breaking ocean waves that produce sea spray. These particles are efficiently removed by gravitational settling and remain in the atmosphere for periods of a few hours to a few days. They contribute little to number concentrations but significantly to total particle mass.

Other physical characteristics that affect particle behaviour include particle shape and density, bulk properties such as chemical composition, vapour pressure, hygroscopicity, deliquescence and refractive index, and surface properties such as electrostatic charging and surface films. Deliquescence is of particular interest. As deliquescent materials (e.g., ammonium bisulphate, ammonium sulphate and ammonium nitrate) will grow rapidly when the relative humidity rises above the material's deliquescence point, into a size range that efficiently scatters light and thus contributes to visibility reduction.

The two basic processes involved in particle formation were discussed: grinding or atomization, and the nucleation of supersaturated vapours. Windblown dust and sea spray are produced by the former process, whereas sulphate formation is an example of the latter process. Particle growth may occur through particle-particle interactions such as coagulation, or gas-particle interactions such as the absorption and adsorption of pollutant gases such as sulphur dioxide followed by chemical reactions to yield particulate sulphate. The main removal mechanisms are dry deposition, which involves the removal of particles from the atmosphere at the air-surface interface, and precipitation scavenging, which involves the removal of particles from the atmosphere by interaction with precipitation.

The chemical composition of PM_{10} generally varies between the fine and coarse modes. Usually, the fine mode is characterized by chemical constituents such as sulphate, nitrate, ammonium, lead, elemental carbon, metals, and hundreds of different organic carbon compounds. The coarse mode is characterized by materials typical of the earth's crust (oxides of iron, calcium, silicon and aluminum) and sea spray (sodium and chloride). Sulphates, nitrates, ammonium and a portion of the organic carbon compounds result from secondary reactions, while the remaining materials are typically primary in nature. Size distributions associated with various materials were described.

3 SAMPLING OF PARTICULATE MATTER

Measurements related to current compliance monitoring are expressed in terms of mass. Mass measurements may be made directly or indirectly. Direct (or manual) measurements are made by collecting particles on a pre-weighed filter over a specified period, weighing the soiled filter, and then dividing the gain in mass by the volume of air sampled. Samples are typically collected for a 24 h period, once every six days, as in the National Air Pollution Surveillance (NAPS) network (Dann, 1994). However, different sampling periods and frequencies may be used where required. Examples of manual samplers include high-volume (hi-vol) and dichotomous (dichot) samplers.

Indirect measurements are made using techniques other than gravimetric ones to assess particle properties. These measurements are then related to mass. Tapered element oscillation microbalance (TEOM) and beta-attenuation monitors are examples of indirect methods that have also been automated to provide near real-time measurements of particulate concentrations.

In this chapter, measurement techniques used in Canada and elsewhere are described and compared. Section 3.1 describes direct measurement techniques for TSP, PM_{10} and smaller particulate size fractions, filter media, mass measurements and chemical analyses. Section 3.2 reviews indirect measurement techniques for PM_{10} and its sub-fractions. Section 3.3 describes specialized sampling systems used to provide a more detailed chemical characterization of particulate matter. Personal Exposure Monitors (PEMs) are briefly reviewed in Section 3.4. Siting criteria are discussed in Section 3.5. A summary is provided in Section 3.6.

3.1 DIRECT MEASUREMENTS

For historical reasons, this section begins with a description of the standard technique for total suspended particulate (TSP) measurements even though the document focuses on the smaller size fractions of particulate matter. This is followed by a description of techniques available for PM_{10} measurement: the size-selective inlet (SSI) hi-vol sampler, the dichot sampler and the Partisol sampler. Additional techniques to measure particle fractions smaller than 10 µm are also described. Finally, filter media, mass measurements and chemical analyses are briefly discussed.

3.1.1 TSP

The standard sampler for TSP monitoring is the hi-vol sampler. The hi-vol sampler draws large volumes of air (1132 L/min or 40 cfm) through a 20.3 x 25.4 cm filter. TSP concentrations are calculated based on the net weight gain of the filter and the volume of sampled air. The collected particulate sample may be further analysed for its chemical constituents.

A characteristic feature of the hi-vol sampler is the gabled roof, designed to prevent dustfall on the filter. Because of this design, particle collection efficiency is dependent on both wind speed and wind direction. The 50% cut point (D_{50}) is the particle aerodynamic diameter at which 50% of the particles pass through the inlet and 50% are rejected. The hi-vol sampler has a poorly defined cut point which has been shown to decrease from 50 µm in 2 km/h winds to about 22 µm in 24 km/h winds (McFarland and Rodes, 1979). Positive biases of 10-15% can occur due to passive deposition onto the filter (Bruckmen and Rubino, 1976; Chahal and Romano, 1978; Swinford, 1980).

3.1.2 PM_{10}

To fractionate the sample into specified size ranges such as for PM_{10}, specially designed sampling inlets are used. PM_{10} samplers are designed to have a 50% cut point of 10 µm. The cut point is valid for a specified flowrate, and will change with the inverse square root of the ratio of actual flow to cut point flow.

As shown in Table 3.1, sampler inlets may vary as to the method of fractionation. Cyclonic flow, inertial impaction and virtual impaction are commonly applied separation techniques that are described later in this chapter. Also evident from Table 3.1 is that the 50% cut point varies slightly among sampler models. The

Table 3.1 US EPA-approved Reference and Equivalent Methods for PM_{10} (based on Chow, 1995)

Manufacturer	Operating Principle	d_{50} (m)	Flow Rate (L/min)	PM_{10} Reference Number	Comments
SA or GMW Model 321A	Impactor	10.2	1,133	RFPS-1287-065	2-stage with greased shim
SA or GMW Model 321B	Impactor	9.7	1,133	RFPS-1287-064	2-stage with greased shim
SA or GMW Model 1200	Impactor	9.7	1,133	RFPS-1287-063	Single-stage with greased shim (body hinged)
Wedding PM_{10}	Cyclonic Flow	9.6	1,133	RFPS-1087-062	Inlet cleaning port on top of inlet
SA 254 Medium Volume PM_{10} Inlet	Impactor	10	113	RFPS-0387-071, EQPM-0990-076	Several small screws must be removed to clean.
SA 246B	Virtual Impactor	10.2	16.7	EQPM-0391-081	Plastic cap acts as a hopper to collect large particles

resulting concentration differences due to cut point biases may be amplified because the 10 µm cut point occurs near a maximum in the particle mass distribution.

Dichotomous Sampler

The dichot sampler was the original sampler for inhalable particles. It is modelled after inertial virtual impactors in that it fractionates particles according to their aerodynamic characteristics. The dichot sampler operates at a low sampling rate (16.7 L/min) relative to the hi-vol sampler. Sample air is drawn through an inlet head, and then through a virtual impactor that separates particles into a coarse (>2.5-10 µm) and fine (2.5 µm) fraction. This is achieved by accelerating particles through a nozzle and then drawing 90% of the flow stream off at right angles. The fine particles follow the right-angle flow stream, while the larger particles continue toward the collection nozzle. Particles are collected on 37 mm filters. Separation of the two size fractions minimizes potential interactions between the more acidic fine fraction and the more basic coarse fraction. However, this also requires further care in sample handling and mass determination than required with the SSI samplers. As well, it requires different mass and analytical techniques than used for the hi-vol filters.

Size Selective Inlet High-Volume Sampler

Reflecting the need to monitor inhalable particles, the US EPA commissioned the design of an SSI to retrofit standard hi-vol samplers. The SSI head is round-shaped to allow for unbiased sampling from any direction, in direct contrast to the gabled roof design of the original hi-vol sampler (Hicks and Corr, 1983). Air is drawn through a series of baffles to separate out particles greater than 10 µm in diameter. Similar to the standard hi-vol samplers, units are operated at a flow rate of 1132 L/min (40 cfm) and samples are collected on 20.3 x 25.4 cm fibre filters. The same mass and analytical techniques as used for the TSP filters can be used for the filters from the SSI samplers. A potential disadvantage with respect to these samplers is the self-contamination of the filter through wear of the carbon/graphite brushes against the copper segments of the motor commutator that are part of the internal electrical mechanism.

Partisol Sampler

The Partisol sampler is a manual, low-volume sampler approved by the US EPA as a reference method for PM_{10} (US EPA, 1994a). It consists of a hub station and up to three satellite stations. The hub unit contains a microprocessor with internal data storage, an active flow control system and a pump. All satellite units are fitted with a sample inlet and a 47 mm filter exchange mechanism that may employ quartz fibre, Teflon-coated glass fibre or Teflon filters. Only one unit can operate at a time. Menu-driven software can be used to determine the conditions (e.g., wind speed, wind direction) under which the hub or satellite units are active. It may be fitted with TSP, PM_{10}, $PM_{2.5}$ or PM_{10} inlet heads. Therefore, compared with other manual samplers, it provides added flexibility with respect to sampling inlet, sample collection hardware and pre-programmed operation. Flow is controlled between 3-20 L/min.

Comparability of Direct PM_{10} Measurements

An intercomparison study of the Sierra Andersen (S/A) 321A PM_{10} sampler and the Wedding PM_{10} monitor was conducted by Purdue et al. (1986) in Phoenix, Arizona. Unoiled S/A 321A samplers were found to collect an average of 58% more mass than co-located and uncleaned Wedding samplers. Part of the difference was attributed to cut point bias. However, during extended sampling periods when sampling performance was degraded, the S/A 321A monitor tended to over-sample, while the Wedding monitor tended to under-sample. By periodically cleaning the inlets and oiling the impaction plates of the S/A 321A, differences were reduced to within predictable agreement based on expected mass calculations from wind tunnel inlet effectiveness data and ambient particle mass distribution data.

An intercomparison of various PM_{10} monitors (Wedding, S/A 321B, S/A 1200 and S/A dichot) was carried out in Rillito, AZ during a year-long measurement program (Thanukos et al., 1992). The S/A and Wedding PM_{10} sampler inlets differ in the type of fractionation device used. S/A inlets incorporate a greased impaction surface below a series of impactor jets, while Wedding inlets employ a greased cyclone. Comparison of concurrent measurements by different samplers showed very linearly but significant differences in measured concentrations when all instruments are consistently maintained. In summary, the Wedding samplers recorded the lowest concentrations, followed by the S/A 321B samplers (19.2% higher than the Wedding samplers), the S/A 1200 samplers (28.1% higher than the Wedding samplers), and the S/A dichot samplers (41.6% higher than the Wedding samplers).

In the Canadian national network, Graseby Andersen (formerly Sierra Andersen) dichot and Graseby Andersen SSI samplers are collocated at five sites: Saint John, Ottawa, Edmonton, Vancouver Rocky Point Park and Vancouver West 10th Ave (Dann, 1994). Before 1988, the S/A 321 inlet was used in all the SSI samplers. This inlet was shown to allow large particle pass-through from bounce and/or re-entrainment, resulting in an over-sampling of PM_{10} (Hayes et al., 1988). This was particularly problematic when coarse particle loadings were high. Consequently, the S/A 321 inlets were replaced by Graseby Andersen 1200 inlets in December 1988. Based on samples collected between 1984-1993, mean ratios of PM_{10} concentrations measured with the dichot samplers to PM_{10} concentrations measured with hi-vol samplers ranged from 0.93 at sites in Edmonton and Saint John to 1.17 at the Vancouver West 10th Avenue site (Dann, 1994). Excellent correlation was found between the samplers (0.84-0.95).

3.1.3 Fine Fraction

Similar operating principles used in PM_{10} inlets are applied to inlets designed to collect smaller particle size fractions. However, in contrast to the 10 µm cut point, the 2.5 µm cut point occurs near a minimum in the particle mass distribution, thereby minimizing differences between samplers with cut point biases. In the following, methods applied to the direct measurement of fine particle fractions are described.

Inertial Impactors

Inertial impactors are based on the following principle of operation. An airstream is drawn through a series of nozzles of jets and directed toward a flat impaction plate. The high inertia of larger particles will carry them into the impaction plate, which may be coated with an adhesive or grease to aid collection. Smaller particles will continue with the airstream.

The cascade impactor consists of a series of nozzles and coated impaction plates, called stages, with each stage collecting progressively smaller particles. Size segregation is dependent on sampler geometry and flowrate. Bounce-off, re-entrainment and deposition on lower stages, wall losses, and lack of discreteness are problems encountered with this technique. Sample collection is generally limited to particles of about 0.5 µm or larger, which eliminates a large percentage of urban particulate matter.

Virtual impactors differ from cascade impactors in that the impaction plate is replaced by an opening that directs larger particles to one sampling substrate, and the smaller particles to another. This principle is used in dichot samplers, as previously described. Relative to cascade impactors, the effects of particle bounce-off and re-entrainment are reduced. However, this method requires that part of the total flow (typically 10%) be drawn through the virtual impaction surface. Therefore, correction factors must be applied to the coarse channel flow to account for contamination by the fine fraction.

A low-flow (4 L/min) standard impactor was developed by Marple et al., (1987) for use in the Harvard Six City Study (Dockery and Spengler, 1981a,b). Also called the Harvard impactor, it was designed with 2.5 µm or 10 µm cut points and two identical cascade stages. The purpose of the latter is to produce sharper cut points and to reduce particle bounce resulting from particle overloading. The impactor surfaces are oil-impregnated metal plates to further reduce particle bounce. The Harvard impactor and variations on it have been used in several major indoor particulate monitoring studies: Total Human Environmental Exposure Study (THEES) (Buckley et al., 1988); Particle Total Exposure Assessment Methodology (P-TEAM) (Wallace et al., 1991); and New York State Energy Research Development Authority (ERDA) study (Koutrakis et al., 1992).

To obtain improved size fractionation of smaller particles, several low-pressure impactors have been developed: the Berner impactor (Berner and Lurzer, 1980); the Low Pressure Impactor (Hering et al., 1978; Hering and Friedlander, 1978); the Micro Orifice Uniform Deposit Impactor (MOUDI) (Marple et al., 1981); Model 20-725, Andersen Samplers Inc.; the DRUM (Davis Rotating-drum Universal-size-cut Monitoring impactor) sampler (Raabe et al., 1988). By operating under reduced pressure, the mean free path of the air becomes comparable to particle diameter, thereby reducing the drag on the particle and enhancing particle collection. Size segregation down to cut points of 0.025 µm (Berner and Lurzer, 1980) have been obtained. The Hering and Andersen samplers have very low flow rates of 1 and 3 L/min, respectively. As a result, sampling periods of more than 24 h may be required to collect sufficient sample (Bondietti and Papastefanou, 1993; Lyons et al., 1993).

Cyclone Samplers

Cyclone samplers use an impeller to impose a circular motion to air entering a cylindrical tube. Centripetal force moves the particles toward the walls of the tube. Particles reaching the walls, which may be covered in an oil or grease coating, either adhere to it or drop into a hopper at the bottom of the tube. The inner tube and hopper are cleaned to minimize re-entrainment. They are simple to operate, and can be very compact in design. As a result, cyclone samplers have been applied in a number of personal monitoring applications (e.g., Dockery and Spengler, 1981b; Spengler et al., 1985; and Colome et al. 1992). $PM_{2.5}$ cyclone inlets are also widely used in the IMPROVE monitoring network (Malm, 1994b).

Comparability of Direct $PM_{2.5}$ Measurements

Reflecting the past emphasis on PM_{10} as the particulate fraction of concern, relatively few intercomparison studies have been conducted for $PM_{2.5}$ samplers. To investigate potential sampling methodologies for the fine fraction, Cook et al. (1995) evaluated various $PM_{2.5}$ samplers in Bakersfield, California. Direct measurements were obtained from samplers that included two S/A 241 dichots, a Partisol 200H sampler, an AirMetrics Model 4.1 impactor and a Xontech 920 multi-channel sampler fitted with an AirMetrics 2.5 µm inlet. Indirect measurements (to be discussed more thoroughly in Section 3.3) were obtained with the TEOM Series 1400a monitor, Meteorology Research Inc.'s Model 1550 B nephelometer and the American Iron and Steel (AISI) tape sampler.

Good agreement was observed between the dichot samplers, the Partisol and the Xontech/AirMetrics sampler. Data pairs agreed within 10% of one another, and variability among samplers was less than 15%. The AirMetrics $PM_{2.5}$ unit did not yield good statistical agreement with the other samplers over the full range of particulate concentrations. Limited agreement was observed with the dichot data for concentrations of 20-50 mg/m^3. TEOM data collected at sampling temperatures of 30°C and 50°C were much lower than measurements from other samplers, suggesting volatilization problems due to the heating of the airstream. However, TEOM, AISI and nephelometer data correlated quite well to the other samplers at times, suggesting that these methods may be useful for monitoring $PM_{2.5}$ if strong and consistent relationships with the other samplers can be determined over time.

3.1.4 Filter Media

Filters consist of a woven mat or a permeable membrane that contains microscopic pores. Commonly used filter media for particle sampling are tabulated by Chow (1995), along with the references. No single filter type is suitable for all applications. Filter media used in monitoring activities must display the physical and chemical properties appropriate for the sampling methodology and the laboratory analysis methods used.

Selection should be based on the following considerations: particle sampling efficiency, mechanical stability, chemical stability, temperature stability, blank concentrations, flow resistance and loading capacity, cost and availability. Except for selective filtration, filters should remove more than 99% of the suspended particles drawn through them.

The two most common types of filters are fibre filters and membrane filters. Fibre filters exhibit a low pressure drop and high collection efficiencies for all particle sizes. Examples of fibre filters include those composed of glass fibres, Teflon-coated glass fibres and quartz material. Membrane filters retain particles on the surface of the filter, enabling non-depth analyses such as X-Ray Fluorescence. They generally have higher flow resistence and lower loading capacities than fibre filters, and are also more expensive. They are available in a wide range of materials including Teflon, Polyvinyl Chloride (PVC) and polycarbonate.

Filter materials exhibit varying degrees of reactivity with chemical species. Glass fibre filters adsorb HNO_3, NO_2, SO_2 and organic vapours, resulting in positive sampling artifacts. They are also characterized by high metal blanks. Quartz filters are relatively inert to the adsorption of gases, but passively adsorb organic vapours. Nylon filters exhibit high collection efficiencies for HNO_3. All filters may be subject to losses of volatile species due to changes in ambient temperature, pressure or relative humidity. Most nitrates are expected to be in the gas phase as HNO_3 at temperatures above 30°C, and in the particle phase at temperatures lower than 15°C (Russell et al., 1983). Significant losses (>50%) of nitrate, ammonium and chloride have been observed in glass and quartz fibre filters stored in unsealed containers at ambient temperatures for 2-4 weeks before analysis (Witz et al., 1990). Turpin et al. (1994), found that organic gas adsorption accounted for up to 50% of organic carbon on quartz fibre filters in southern California, and outweighed the amount of organic carbon lost to volatilization. This appears to be in contrast with the findings of Eatough et al. (1993), which showed that the percentage loss of semi-volatile compounds from a quartz filter during sampling accounted for approximately 50% (on average).

To minimize contamination of the filter by the operator, filter holders have been designed so that filters can be loaded and unloaded in a clean environment rather than in the field. Consideration should be given to the material used to construct the filter holder, particularly when measuring reactive components of the particulate matter. Additional consideration should be given to the filter holder configuration. Filter holders are designed as open-face or in-line (Chow, 1995). Open-face holders are without any constrictions upstream of the filter surface. In-line holders consist of a small diameter opening into a small chamber in which the filter is mounted. As a result, in-line filter holders may concentrate particles in the centre of the filter and will bias results where only part of the filter is analyzed. Differences of up to 600% have been reported between chemical measurements made at the middle and edges of filters sampled with in-line holders (Tombach et al., 1987; Fujita and Collins, 1989).

3.1.5 Mass Measurements

To determine particulate concentrations from manual samplers, mass measurement of the exposed filter is required. Minimum requirements for balance sensitivity are as follows: 100 mg for high-volume samplers, 10 mg for medium-volume samplers and 1 mg for low-volume samplers (US EPA, 1996). Measurements are made in a temperature- and humidity-controlled environment. The main interference results from electronic charges that induce non-gravimetric forces between the filter and the balance.

Most of the mass measurements for SSI and dichot samples obtained in the national monitoring network are done by the Pollution Measurement Division, Environmental Technology Centre (ETC) in Ottawa (Dann, 1994). A Mettler M3 or Mettler MT5 electronic microbalance is used. Filters are equilibrated at 23°C±3°C and 43%±5% prior to mass determination. The ETC laboratory uses a polonium 210 radioactive source to control static charge. Local agencies measure SSI samples collected from the Vancouver sites and three of the Saint John sites (Dann, 1994). Local agencies also measure most of the hi-vol filters. Lower detection limits of mass concentration are determined by the repeatability of filter tare weights. For SSI samples, the lower limit is about 2 $\mu g/m^3$. Corresponding limits for dichot samples are slightly lower. Upper limits are dependent on particle size. Small particles will clog the pores of the filter at low concentrations while larger particles will fall off the filter at high concentrations. For hi-vol samplers, the limit is typically in the range of 400-1000 $\mu g/m^3$ (Watson et al., 1989).

3.1.6 Chemical Analyses

Further analytical techniques may be applied to learn the chemical composition of particulate samples.

Various destructive and non-destructive methodologies are available. Chow (1995), lists some of these techniques, along with the associated references. The following discussion, therefore, is meant only to provide a brief introduction of these techniques.

X-ray fluorescence (XRF) and Proton Induced X-Ray Emission (PIXE) spectroscopy are two common techniques that can be used to determine concentrations of elements with atomic numbers from 11 (Na) to 92 (U). Both techniques leave the filter intact, enabling further analyses to be conducted on the filter. Neither requires sample preparation nor extensive operator time.

Inductively Coupled Plasma (ICP) emission spectroscopy and Instrumental Neutron Activation Analysis (INAA) are more expensive analyses than XRF or PIXE, however, they provide low detection limits for several species. INAA requires that the filter be wadded up and then made radioactive, while ICP destroys the filter.

Atomic Absorption Spectrophotometry (AAS) is useful for quantifying Na, Mg, K and Ca concentrations, but requires too great a dilution of the sample when multi-species analyses are required. Ion Chromatography (IC) and Automated Colorimetric (AC) analysis are applied to water extracts of filter samples to determine anion and cation content. IC is commonly used to measure chloride, nitrate and sulphate, while AC is commonly used to measure ammonium and chloride. Techniques developed to measure carbon species include Thermal/Optical Reflectance (TOR), Solvent Extraction Method and Thermal Combustion Method.

At the ETC laboratory, XRF is used for the elemental analysis of particulate samples (Dann, 1994). Lead analyses are conducted using a wavelength XRF spectrometer. Multi-element analyses are conducted using a Kevex 770/8000 energy dispersive X-ray fluorescence (EDXRF) spectrometer. Sulphate and nitrate analyses are done on the extracts of hi-vol and SSI filter cuttings using automated photometric methods. Cuttings are extracted in an ultrasonic bath (40 or 47 kHz) after addition of a wetting agent. Sulphate is determined using the methyl thymol blue method. Nitrate is determined as azo dye after reduction to nitrite.

3.2 INDIRECT MEASUREMENTS

As in Section 3.1, this discussion begins with a description of the historical methods for measuring particulate matter, such as the British Smoke Shade or Black Smoke (BS) sampler. This is followed by descriptions of the US EPA equivalent techniques for PM_{10} measurement (the beta attenuation monitor and the TEOM sampler) and the integrating nephelometer. Finally, a description of single particle samplers used to measure particle size distributions is provided.

3.2.1 Black Smoke Shade

The BS technique has been used in Britain since the early 1900s. Air is drawn at low flow rates (1.5 L/min) through a disc of cellulose fibre filter paper over a 24 h period. The reflectance of the resulting stain is analysed, yielding measurements in BS units. A calibration curve is then used to convert the units to particle mass concentration.

BS measurements are influenced by both the mass and optical properties of smoke. In particular, they are sensitive to the dark, “sooty” component of particulate matter in the size range of $\leq$3.5 to 4.5 µm. Therefore, BS measurements are generally considered a poor indicator of TSP levels. This technique is still being used in the United Kingdom and elsewhere in Europe because it is the main method for determining compliance with the European Community directive on suspended particulate, based on early epidemiological studies using BS data (EPAQS, 1995). The BS technique is also viewed as more accurately reflecting the health risks of smoke from coal combustion (Waller, 1980). It is also relatively simple and economical for routine sampling.

The commonly used relationship between BS measurements and gravimetrically determined concentrations were reported in a 1964 study supported by the Organization for Economic Cooperation and Development (OECD). Equivalent mass concentrations were determined through collocated gravimetric samplers. The US EPA (1982a) is careful to point out that the so-called OECD “high-volume” samplers are different from the US TSP hi-vol samplers. The OECD units were designed to be aerodynamically similar to the smoke shade unit, but had not been characterized for aerosol collection effectiveness. They operate at a sampling rate of 60 L/min, compared to approximately 1500 L/min used in the US model.

A non-linear relationship was found to exist between BS and TSP measurements made with co-located samplers (US EPA, 1982a). TSP measurements were generally 2 or more times higher than corresponding

BS readings, up to BS levels of about 100 µg/m^3. At higher levels, the two measurements tended to converge, with BS/TSP ratios of one at BS levels of 500 µg/m^3 or more. In a review of various European studies (Kretzschmar, 1975; Ball and Hume, 1977; Bailey and Clayton, 1982; Laskus, 1983; Edwards et al., 1983; Willison et al., 1985), Hamilton and Mansfield (1991) observed that background TSP concentrations were 2-4 times higher than the corresponding BS levels. At a roadside site, however, BS levels 3 times higher than the TSP levels were observed. This apparent anomaly was explained by the fact that the soiling factor for diesel-emitted smoke is 3 times higher than that for smoke from coal combustion, upon which the BS calibration chart is based.

3.2.2 Coefficient of Haze (CoH)

CoH is measured using the AISI tape sampler. The fundamental principles of the tape sampler are similar to those of the BS technique. Particles of up to approximately 5 µm in aerodynamic diameter are collected in a 25 mm spot on filter paper tape that is periodically (usually hourly) advanced to allow for collection of the next sample. The opacity of the stain is measured by the transmittance of light through the stained area. The result is expressed as optical density or CoH units per 1000 linear feet of air sampled. The CoH unit is 100 times the optical density of the deposit that allows 50% of light transmittance. The optical density is calculated as the log of the ratio of the light transmission through clean filter paper to that through the sample. Measurements can be made automatically, enabling hourly concentrations to be recorded.

The precision and accuracy of this method depends on the precision and accuracy of the air flow rate, filtration efficiency and optical system (Lodge, 1989). The lower limits of detection for optical density are about 0.05. Upper limits are about 0.30, which represents a 50% attenuation of the incident light.

Similar to BS measurements, CoH measurements are more representative of the fine, light-absorbing components of particulate matter such as soot particles. Conversion to units of mass therefore requires the use of a co-located gravimetric device. In a comparison of measurements from co-located CoH and dichot samplers in an urban Toronto location, a correlation of 0.75 was found between the $PM_{2.5}$ fraction and the CoH measurements, and one could not be interpolated from the other (Hicks and Corr, 1983). Fairley (1990) looked at the relationship between CoH and PM_{10} measurements in Santa Clara County from 1980 to 1986. The analysis was restricted to the winter months (November-January) of 1985 and 1986, when CoH levels were typically 3-4 times higher than in the summer months. Median CoH-to-PM_{10} ratios of 1.87 and 1.64 and corresponding correlation coefficients of 0.79 and 0.81 were reported for 1985 and 1986, respectively.

3.2.3 Beta Attenuation Monitor

The beta attenuation monitor, also called the beta-gauge monitor, has been used in Europe and Japan for several years. Mass determination is based on the attenuation that a beta-ray particle undergoes as it passes through an exposed filter. The beta attenuation monitor can provide hourly concentrations, based on a 55 min sampling period followed by calibration and measurement periods. The filter material is on a roll that can be automatically advanced. Therefore, compared with gravimetric techniques, filter handling is minimized, and therefore the potential for filter contamination reduced. Errors due to the loss of small fragments from the filter edges do not affect measurements; therefore, these monitors may be a better measure of lightly loaded samples than gravimetric techniques (US EPA, 1982a). The particle mass detection limit is about 5 µg/m^3 for a 1 h average.

A consideration in the use of beta attenuation monitors is that it requires a radioactive source. Further considerations are that the filter must be oriented in exactly the same way for each mass determination; changes in air density and atomic number of the collected particulate matter affect calibration; and the instrument is very expensive. Absorption of water by the filter material has been cited as a source of error (Lawrence Berkely Laboratory, 1975). The presence of a significant number of large particles has also been found to affect the precision and accuracy of measurements (US EPA, 1982a). Chemical characterization of the particulate matter requires the use of a co-located manual sampler.

Field comparisons of beta attenuation and hi-vol PM_{10} monitors have been done in Denver (Arnold et al., 1992) and in Citrus Heights, CA (Shimp, 1988). In the Denver study, a Wedding beta attenuation monitor reported 24 h average PM_{10} concentrations that were 19% lower than those measured by a Wedding hi-vol PM_{10} sampler. In the Citrus Heights study, the beta attenuation monitor averaged concentrations that were 6% less than collocated Sierra-Andersen Model 321a hi-vol PM_{10} samplers.

3.2.4 Tapered Element Oscillation Microbalance (TEOM)

In contrast to the previously described monitoring methods, the TEOM sampling method allows for the continuous measurement of PM_{10} concentrations. It has been approved as an equivalent PM_{10} monitoring method in the United States (US EPA, 1990), and is finding widespread application in various provinces (MELP, 1995; OME, 1995). It can also been fitted with a $PM_{2.5}$ sampling inlet (Rupprecht et al.,1995).

The TEOM instrument operates under the following principles. Ambient air is drawn in through a heated air inlet and an exchangeable filter cartridge that sits on the end of the tapered tube. The filtered air then goes through a hollowed tapered tube which is maintained in oscillation in a clamped-free mode. An automatic flow controller directed by the system's microprocessor maintains the sample flow at a constant rate. As particulate matter gathers on the filter cartridge, the tube's natural frequency of oscillation decreases. The electronics system continually monitors this frequency. Based upon the direct relationship between mass and frequency, the instrument's microprocessor computes the total mass accumulation on the filter, as well as the mass concentrations and mass rate, in real time. A more detailed description is contained in Patashnick and Rupprecht (1991).

Sample air is typically drawn in at a flow rate of 16.7 L/min, and a flow splitter channels a 3 L/min portion to be filtered. To standardize sampling and weighing conditions, the filter and the airstream passing through it are heated to 50°C, ensuring that the filter is always above the dew point and thereby minimizing water uptake.

In acceptance testing carried out in Birmingham, Alabama in 1990, three TEOM instruments were co-located with three reference PM_{10} hi-vol samplers (Meyer, 1993). The 24 h averages from each sampler correlated well (correlation coefficient of 0.977). The precision of replicate TEOM measurements (1 $\mu g/m^3$) was reported to be better than that of the reference samplers (1.8 $\mu g/m^3$). In testing done in Essen, Germany using two production version Series 1400a monitors, a minimum detection limit of 3.4 $\mu g/m^3$ was estimated for 1 h averages and 1.3 $\mu g/m^3$ for 24 h averages (RWTUV, 1994).

An evaluation of co-located TEOM and manual PM_{10} samplers by state and regional air agencies in the western United States showed that the TEOM data were consistently lower than that obtained by the manual samplers (Moore and Barthelmie, 1995). Mean percent differences ranged from -14% (all pairs greater than 20 $\mu g/m^3$) to -38% (all pairs greater than 150 $\mu g/m^3$). An analysis of approximately 1,000 pairs of TEOM-manual method data showed a -14% mean percent difference during the woodheating season and a -6% difference during the non-woodheating season. These results suggested greater losses of VOCs due to volatilization when woodburning emissions are more significant.

Concerns have been raised over the high sampling temperature used in the TEOM. Meyer et al. (1992) showed that the high sampling temperature may result in the partial volatilization of organic compounds such as those found in woodsmoke. A woodsmoke exposed quartz filter baked in a drying oven at 50°C showed a loss in mass of more than 25% after 4 hours of exposure, and 50% after 3 days. The blank control filter showed a loss of 14% after 3 days. Rupprecht & Patashnick (1993) suggested that lower sampling temperatures (e.g., 30°C) may be used to reduce these potential volatilization losses in situations where the contributions from volatile or semi-volatile components are expected to be significant. However, this is recommended only where outdoor temperatures do not exceed 25°C more than 5% of the time.

The effect of sampler temperature and flow rate was investigated by Meyer et al. (1995), in Salt Lake City, Utah during December 1994. A PM_{10} high-vol sampler was co-located with two TEOM monitors, one operating at 50°C and 3 L/min flow rate and the other at 30°C and 1 L/min flow rate. Face velocities of 41 cm/s were estimated for the hi-vol sampling, and 44 cm/s and 15 cm/s for the higher- and lower-volume TEOM instruments. In a comparison of the TEOM instrument operating at 30°C with that operating at 50°C, the authors reported a ratio of 2.23 (±0.22) for the month of December. This finding suggests that by lowering the equilibration temperature by 20°C and reducing the flow rate by a factor of 3, more than 2 times as much PM_{10} is retained on the filter. Comparisons of the two TEOM instruments with the hi-vol PM_{10} sampler produced ratios of 1.66 (±0.34) and 0.74 (±0.14), respectively, indicating a wide variation among the samplers used. More significantly, these findings suggest that the reference sampler does not measure all of the ambient PM_{10}.

3.2.5 Integrating Nephelometers

The integrating nephelometer is commonly used in visibility studies. It measures the optical scattering coefficient from the light scattered by particles and gases in the air, integrated over a wide range of angles. It is composed of an enclosed volume painted black, a light source on one side of the volume, and a light detector looking through the volume. The light received by the detector is that which has been scattered within the volume. Those particles in the size range of 0.3-0.7 µm are the most efficient at scattering visible light.

The range and sensitivity of integrating nephelometers are dependent on the individual instrument optics, electronic design and mode of operation. However, particle scattering coefficients can typically be measured over the range of approximately 1×10^{-6} to 1×10^{-2} m^{-1}, and commercial instruments typically have a sensitivity of about 0.5×10^{-6} m^{-1} (Lodge, 1989).

Larson et al. (1992), found that in woodsmoke-impacted areas, where the fine particle mode is expected to dominate, weekly averaged nephelometer measurements showed a high degree of correlation (r^2=0.945) with ambient $PM_{2.5}$ measurements. However, while relative loadings of $PM_{2.5}$ can be inferred from the backscatter measurements, this instrument is relatively insensitive to larger particles.

3.2.6 Single Particle Samplers

The measurement of particle size distributions is useful for studies involving particle sizing and collection transport and transformation, source characterization, and particle sizing and collection device performance (US EPA, 1996). Whereas cascade impactors can obtain particle distributions in terms of mass, single particle counters obtain distributions based on particle count. By making assumptions regarding particle shape and density, surface area and volume distributions may then be calculated.

The three most commonly used types of single particle samplers are aerodynamic particle sizers, electrical mobility analyser and optical particle counters (OPC's). Each is briefly described below.

Aerodynamic particle sizers use two parallel laser beams to measure the velocity lag of particles suspended in accelerating air flows (APS 3310, TSI. Inc., St. Paul, MN). Particle velocity is a function of particle diameter as long as the particle Reynolds number, Rep, which describes the gas flow around a particle, remains small (Wilson and Liu, 1980). As Rep increases, particle density and shape become additional factors.

This instrument generally allows a rapid and precise measurement of the aerodynamic size of most particles, and is typically applied in studies where particle diameters are larger than 0.5 µm. Inaccuracies may be encountered in measuring the aerodynamic diameter of non-spherical particles, due to the high acceleration in the instrument's acceleration nozzle (Baron et al., 1993). Coincidence errors, in which two particles are detected as a single particle, may be experienced at high particle concentrations (Heitbrink et al., 1991).

In electrical mobility analyzers, particles with a known charge distribution migrate through an electric field. Particle mobility is related to particle size. Electrical mobility analyzers are generally limited to studies where particle size is in the submicrometre range and particles are approximately spherical in shape. Examples of this technology are the electrical aerosol analyser (EAA) (Whitby and Clark, 1966) and the differential mobility analyzer (DMA) (Knutson and Whitby, 1975a, b).

The EAA uses unipolar diffusion charging and measures the integrated band of mobility. Standard data reduction tables are used to relate particle size, particle charge and electrical mobility under standard conditions. Yeh (1993) describes two major limitations with respect to EAAs. First, a minimum exists in the electrical mobility for given diffusion charging conditions as a function of particle size. This minimum lies between 1.0 and 2.0 µm particle diameter. To avoid errors in electrical mobility measurements due to larger particles, use of an aerosol preclassifier such as an impactor is recommended where particle diameters larger than 1.0 µm are expected. The second item of note is that because the reduction tables are valid only for standard operating conditions, any deviations from these conditions may lead to errors.

The DMA uses an equilibrium charge state of the particles, which is considered more stable than the distribution obtained from unipolar diffusion charging, and measures the extracted narrow band of mobility. As a result, the DMA has better resolution than the EAA. In addition, Yeh (1993) shows that the theoretical basis for predicting the equilibrium charge distribution is better understood and more accurate than that for diffusion charging theory. A limitation of the DMA is with respect to the neutralizer required to bring particle charge distribution to Boltzmann equilibrium. Radioactive sources such as a-emitters 241Am or 210Po and b-emitter 85Kr are commonly used as neutralizers. Yeh (1993) cites studies by Leong et al. (1983) and Winklmayr et al. (1990) as indicating that radiolytic processes can result in the formation of ultrafine particles, thereby arising as an artifact in size measurements.

OPCs measure the light scattered by individual particles traversing a light beam. The signals are processed in a multi-channel analyser, where light flashes are converted into electrical pulses. Number concentration is then derived from the count rate of the pulses and particle size is derived from the pulse height. OPCs are typically used to measure the number of particles in the size range of 0.1-50 µm. In the submicrometre range, counting efficiency decreases with decreasing particle size. In a review of OPC instruments, Gebhart (1993) reports that instruments using incandescent light count particles of 0.3-2 µm diameter with an efficiency of less than 20%. Better performance is observed with laser instruments, which typically exhibit a counting efficiency of 100% for particle diameters down to 0.1 µm. OPCs can experience coincidence errors and counter saturation at high particle concentrations.

3.3 PARTICLE SAMPLING SYSTEMS

To provide the type of detailed chemical analysis required for source apportionment studies, specialized particle sampling systems have been developed. They typically consist of multiple inlets, denuders and filters in parallel or series. A range of filter media is also typically used to optimize analyses for various chemicals. However, the care required to maintain these systems and the costs required to carry out the laboratory analyses limit their general application.

The University of California at Davis designed a specialized device for a cooperative visibility monitoring effort in Class I areas of the United States (Eldred et al., 1988). The study was known as the Interagency Monitoring of Protected Visual Environments (IMPROVE) and the samplers have since been called IMPROVE samplers. These units have been applied throughout North America, with intensive studies carried out in the Lower Fraser Valley (Sakiyama, 1994; Pryor and Barthelmie, 1996).

Many different sampling systems have been developed or modified for specific studies, including the Southern California Air Quality Study (SCAQS) (Fitz et al., 1989), and the Valley Air Quality Study (VAQS) (Chow et al., 1993b). Chow (1995) provides a list of several filter-based particle sampling systems and cites references to the associated research studies.

3.4 PERSONAL EXPOSURE MONITORS

Personal exposure monitors (PEMs) are sampling devices worn on the body to estimate an individual's exposure to air pollutants. As such, they provide a better representation of what individuals actually breathe than do fixed outdoor monitors or even indoor monitors. Due to the nature of their application, PEMs must meet a number of additional criteria relative to fixed-location samplers: low noise; light weight; portability; rugged design; ease of operation; adequate battery lifetime to meet sampling requirements; and comparability with fixed-location monitors. PEM design is typically based on cyclone or impactor samplers. Because of the lower flow rates and poorer flow controllers used in these devices, they are believed to have poorer precision than ambient samplers (Wiener and Rodes, 1993).

Lioy et al. (1990) employed a single-stage PM_{10} impactor called a lollipop during Phase II of the Total Human Environmental Exposure Study (THEES). The sampler was designed to collect particles on 25 mm filters at a flow rate of 4 L/min. During performance tests, five side-by-side personal impactors were operated close to three 10 L/min Indoor Air Sampling Impactors (IASI) (Marple et al., 1987) and one dichot sampler. Correlation coefficients near 1 were obtained, suggesting that within the test limits, the prototype samplers provided accurate estimates of PM_{10} concentrations. The Particle Total Exposure Assessment Methodology (PTEAM) study used a PM_{10} impactor designed by the University of Minnesota to operate with 37 mm filters and a flow rate of 4 L/min (Wiener et al., 1990). During the large-scale field study, PEM measurements taken from a central outdoor site averaged about 5% lower than 85 paired measurements made with co-located dichot samplers (Wallace et al., 1991).

Colome et al. (1992) used cyclone samplers (SKC Inc., Fullerton, CA) as PEMs in a study involving primarily asthmatics in Orange County, California. The cyclone had a 50% cut point of approximately 5 µm and excluded particles larger than 7 µm. A portable constant-flow battery-operated pump was used. The cyclone and pump assembly operated with 37 mm

Teflon filters at a flowrate of 2 L/min. In a comparison with PM_{10} measurements made concurrently with a Marple PM_{10} sampler (Marple et al., 1987), nearly 90% of the variation in PM_{10} mass was explained by the PEM measurements. Colome et al. (1992) concluded that for this application, the cyclone sampler provided a good and inexpensive measure of PM_{10} mass.

3.5 SITING CRITERIA

Monitoring data obtained from fixed samplers represent pollution levels at an individual site and not necessarily levels representative of an entire community. Each site is unique with respect to sensor location, surrounding structures and land use patterns, local meteorology, sources and other parameters that will affect measured pollution levels. Therefore, knowledge of site characteristics is important when comparing pollution levels among different sites.

Site documentation for the NAPS monitoring network has been compiled by Environment Canada (1988). A description of the site and nearby sources, a site map and photographs are provided for each station.

In the NAPS network, stations are sited based on population, a demonstrated need for monitoring or other special pollution problems of national importance, such as long-range pollutant transport (Environment Canada, 1988). Based on the station class and location, recommended criteria are provided for the spatial scale of representativeness. Additional requirements for probe siting are provided for the various criteria air pollutants. As such, requirements for particulate monitoring refer to TSP and not PM_{10}, but are applicable to the latter. Criteria include the following:

- probe height 2-15 m above ground,
- distance from supporting structure >2 m (horizontal),
- distance from trees >20 m,
- distance from sampler to obstacle such as buildings must be at least twice the height of the obstacle protruding above the sampler,
- unrestricted air flow in 3 out of 4 cardinal wind directions,
- no furnace or incineration flues should be nearby and
- spacing from roads varies with height of monitor.

More information on individual sampler locations is provided in Chapter 5 (Table 5.3).

3.6 SUMMARY

Reflecting the wide spectrum of physical and chemical characteristics associated with particulate matter, several techniques are available to determine directly or indirectly mass concentrations of particulate matter. Therefore, it is important to understand the capabilities and limitations of the various methods, and to be able to relate the measurements made by one method to another.

Methods that are currently used to directly measure the mass concentration of PM_{10} in the atmosphere include SSI samplers, dichot samplers and Partisol samplers. $PM_{2.5}$ measurements are available through dichot and Partisol samplers and also various cyclone samplers and virtual impactors developed to monitor smaller size fractions. In each case, air is drawn through a filter over a known period. Further speciation of the collected material is possible through analysis of the soiled filter. Samplers may vary as to inlet design, operating flow rates and collection media. Intercomparison studies of PM_{10} samplers show that inter-sampler differences are minimized to within predicted levels when the samplers are regularly maintained. Good agreement has been observed between dichot, Partisol and Xontech/AirMetrics samplers for $PM_{2.5}$ measurements.

Indirect methods measure parameters other than mass that can be later converted to obtain units of mass concentration. The BS sampler and the tape sampler employ somewhat similar methodologies. In both cases a filter or tape is exposed to the atmosphere for a set time, after which the reflectance or transmittance of light through the soiled substrate is measured and related back to mass. Both methods are most sensitive to the light-absorbing fractions of particulate matter in the range of 0 to about ≤ 3.5 - 4.5 µm in diameter and, as such, are poor representatives of PM_{10}, except where this component dominates.

Automated indirect methods approved by the US EPA include the beta-attenuation (or beta-gauge) monitor and the TEOM monitor. In the beta-attenuation monitor, mass determination is based on the attenuation that a beta-ray particle undergoes as it passes through an exposed filter. In the TEOM, air is drawn through a filter and down a tapered tube, which will oscillate at a frequency that can be related to mass collected on the filter. Both can provide almost real-time measurements. Both have shown a tendency to underestimate concentrations obtained from manual samplers. There are some concerns that the high TEOM sampling temperature (30°C or 50°C) can result in the loss of semi-volatile species such as nitrates and various organic compounds, as observed in woodsmoke-impacted areas during the wintertime. These underestimates are particularly significant when sampling for $PM_{2.5}$. The integrating nephelometer measures the scattering of light by particles, and can provide a relative measure of $PM_{2.5}$ loadings in areas where fine particles dominate.

Sampling systems developed for the IMPROVE, VAQS and SCAQS programs are examples of systems that use multiple inlets, denuders and filters to enable detailed chemical analyses to be carried out. Although PEMs are worn on the body and are therefore more representative of what an individual breathes, they represent unique challenges in that they require compact, lightweight and portable design that gives results comparable to ambient samplers.

4 SOURCES OF PM

PM may be discharged directly to the atmosphere from a broad range of sources, both natural and anthropogenic, or it may be produced in the atmosphere via secondary reactions. As discussed in Chapter 2, the size and chemical composition of the particles formed will reflect the parent materials and the formation processes involved. High-temperature combustion processes and secondary reactions typically produce particles in the fine fraction ($D_p \leq 2.5$ µm), while natural and anthropogenic sources involving mechanical processes contribute more greatly to the coarse fraction ($D_p > 2.5$ µm).

Table 4.1 (from Chow, 1995) identifies the dominant size fraction and chemical species associated with various source types. There is a clear distinction in both particle size and chemical composition between those particles derived from fugitive dust sources, and those resulting from high-temperature combustion processes. Fugitive dust sources characteristically emit coarse particles that are predominantly composed of crustal elements such as Si, Al, K, Ca and Fe. In contrast, combustion and metal refining processes emit fine particles that are high in organic and elemental carbon, SO_4^{2-} NH_4^+ and NO_3^-.

In the following, the major sources of PM_{10} are discussed. Sources contributing more significantly to the fine fraction are described in Section 4.1, and those contributing more to the coarse fraction are described in Section 4.2. Precursors to secondary particles are discussed in Section 4.3. Provincial and national emission estimates are presented in Section 4.4, and associated uncertainties are described in Section 4.5. A summary is provided in Section 4.6.

4.1 PRIMARY SOURCES OF THE FINE FRACTION

4.1.1 Prescribed Burning and Wildfires

Prescribed burning is used as a tool for hazard reduction, site preparation, wildlife habitat improvement, disease and insect control and ecosystem maintenance (Smith and Stoneman, 1992). Particle emission rates vary depending on fuel type and on the phase of combustion (flaming, smoldering, or a combination of the two). Total particle emissions have been found to increase by a factor of 2 - 4 in going from flaming to smoldering (Susott et al., 1991). Prescribed burning and wildfires are a major source of fine particles in western North America (Lamn et al., 1992).

Generally, 90% of particles from prescribed fires are less than 10 µm in diameter, and approximately 70% are less than 2.5 µm in diameter (Lamn et al., 1992). However, the actual size distribution of particles will vary depending on the rate of energy release of the fire. In lower-intensity fires, a normal distribution with a peak near 0.3 µm is observed (Ward and Hardy, 1984). In high-intensity fires, a bimodal distribution is observed, characterized by peaks near 0.03 µm and 35+ µm. The larger particles reflect the increased mechanical turbulence present in such fires.

The fine fraction consists of approximately 40-70% organic carbon material, 2-15% graphitic carbon, and the remainder inorganic ash material (Ward and Blakely, 1992). A variety of PAHs have been identified in the organic fraction, including anthracene, phenanthracene, benz[a]anthracene, chrysene, fluoranthene, and benzo[a]pyrene. Potassium is the most abundant trace metal in the plumes. Measurements show that K, S and Cl are highest during flaming stages, and Al, Si, Ca and Fe tend to increase during the smoldering phase (Susott et al., 1991).

4.1.2 Residential Wood Combustion

Residential wood combustion (RWC) is a major source of wintertime particle emissions in communities where there is a high density of woodstove users and they are subject to persistent temperature inversions and therefore poor air dispersion. Several studies on RWC have been conducted in the United States: Puget Sound, Washington (Maykut and Fry, 1992), Mammoth Lakes, California (Ono and Taylor, 1992), Medford, Oregon (Hough et al., 1992), Libby, Montana (Morris et al., 1992; Manderino et al., 1992), Denver, Colorado (Schwayder, 1992), and Waterbury, Vermont (Sexton et al., 1985). Similar studies in Canada are limited. Crozier and Manna (1988)

Table 4.1 Characterization of PM$_{10}$ from Various Sources (based on Chow, 1995)

Source Type	Dominant Particle Size	Chemical Abundances in Percent Mass			
		< 0.1%	0.1 to 1%	1 to 10%	> 10%
Motor Vehicle	Fine (0 to 2.5 µm)	Cr, Ni, Y, Sr, Ba	Si, Cl, Al, Si, P, Ca, Mn, Fe, Zn, Br, Pb	Cl$^-$, NO$_3^-$, SO$_4^{2-}$, NH$_4^+$, S	Organic Carbon (OC), EC
Vegetative Burning	Fine	Ca, Mn, Fe, Zn, Br, Rb, Pb	NO$_3^-$, SO$_4^{2-}$, NH$_4^+$, Na$^+$, S	Cl$^-$, K$^+$, Cl, K	OC, EC
Residual Oil Combustion	Fine	K$^+$, OC, Cl, Ti, Cr, Co, Ga, Se	NH$_4^+$, Na$^+$, Zn, Fe, Si	V, OC, EC, Ni	S, SO$_4^{2-}$
Incinerator	Fine	V, Mn, Cu, Ag, Sn	K$^+$, Al, Ti, Zn, Hg	NO$_3^-$, Na$^+$, EC, Si, S, Ca, Fe	Si
Coal-Fired Boiler	Fine	Cl, Cr, Mn, Ga, AS, Se, Br, Rb, Zr	NH$_4^+$, P, K, Ti, V, Ni, Zn, Sr, Ba, Pb	SO$_4^{2-}$, OC, Ec, Al, S, Ca, Pb	Si
Oil-Fired Power Plant	Fine	V, Ni, Se, AS, Br, BA	Al, Si, P, K, Zn	NH$_4^+$, OC, EC, Na, Ca, Pb	S, SO$_4^{2-}$
Smelter Fine	Fine	V, Mn, Sb, Cr, Ti	Cd, Zn, Mg, Na, Ca, K, Se	Fe, Cu, AS, Pb	S
Antimony Roaster	Fine	V, Cl, Ni, Mn	SO$_4^{2-}$, Sb, Pb	S	None reported
Paved Road Dust	Coarse (2.5 to 10 µm)	Cr, Sr, Pb, Zr	SO$_4^{2-}$, Na$^+$, K$^+$, P, S, Cl, Mn, Zn, Ba, Ti	Elemental Carbon (EC), Al, K, Ca, Fe	(OC), Si
Unpaved Road Dust	Coarse	NO$_3^-$, NH$_4^+$, P, Zn, Sr, Ba	SO$_4^{2-}$, Na$^+$, K$^+$, P, S, Cl, Mn, Ba, Ti	OC, Al, K, Ca, Fe	Si
Construction	Coarse	Cr, Mn, Zn, Sr, Ba	SO$_4^{2-}$, K$^+$, S, Ti	OC, Al, K, Ca, Fe	Si
Agriculture Soil	Coarse	NO$_3^-$, NH$_4^+$, Cr, Zn, Sr	SO$_4^{2-}$, Na$^+$, K$^+$, S, Cl, Mn, Ba, Ti	OC, Al, Mg, K, Ca, Fe	Si
Natural Soil	Coarse	Cr, Mn, Sr, Zn, Ba	Cl$^-$, Na$^+$, EC, P, S, Cl, Ti	OC, Al, Mg, K, Ca, Fe	Si
Lake Bed	Coarse	Mn, Sr, Ba	K$^+$, Ti	SO$_4^{2-}$, Na$^+$, OC, Al, S, Cl, K, Ca, Fe	Si
Marine	Fine and coarse	Ti, V, Ni, Sr, Zr, Pd, Ag, Sn, Sb, Pb	Al, Si, K, Ca FE, Cu, Zn, Ba, La	NO$_3^-$, SO$_4^{2-}$, OC, EC	Cl$^-$, Na$^+$, Cl, Na

investigated the effects of RWC on air quality in Cranbrook, British Columbia.

Approximately 95% of particles emitted from woodstoves are reported to be less than 0.4 µm in diameter and therefore almost entirely in the fine fraction (Rau and Huntzicker, 1984).The MMAD of particles generated from wood-burning fireplaces is approximately 0.17 µm (Dasch, 1982).

Woodstove emissions are predominantly consisting of organic carbon, elemental carbon and sulphate, with trace amounts of potassium, chloride and nitrate. More than 100 different organic compounds have been identified in woodsmoke. A major constituent of the PM_{10} fraction is polycyclic organic material (POM) which results from the incomplete combustion of hydrocarbons. This group includes PAHs, polycyclic heterocyclic compounds and various derivatives. PAH emission rates from woodstoves are substantially higher than from prescribed burning and fireplaces. Softwood combustion has been found to emit more elemental carbon than hardwood combustion which is primarily composed of organic compounds (Dasch, 1982).

Elemental potassium-to-iron ratios ranging from 15-230 have been found in woodsmoke, while most other sources exhibit ratios of <0.35 (Wolff et al., 1981;Watson, 1979).This observation is used to trace particle emissions to woodsmoke sources.

4.1.3 Transportation Sources

The transportation sector has been identified as a large source of PM, generating emissions through fuel combustion and engine wear. Motor vehicles also generate PM through tire and brake wear and the resuspension of road dust.

Particle emissions from on-road motor vehicles are typically subdivided into the following types: exhaust, tire wear, brake lining and road dust. Both gasoline and diesel vehicles produce particle emissions that are almost entirely <10 µm and predominantly in the fine fraction. In studies carried out in the United States, an estimated 89% and 92% of particle emissions from light-duty gasoline and diesel vehicles were smaller than 2.5 µm (Cooper et al., 1987). Comparable studies in Canada are lacking. As Canadian vehicles differ as to onboard emission controls and fuel characteristics, emission characteristics may differ from their US counterparts.

Measurements show that mass emission rates from diesel trucks are 6-100 times higher than those from gas automobiles (Hildemann et al., 1991a; NRCC, 1982; Williams et al., 1989), while noncatalyst cars emit more submicrometer particles than catalyst cars (Hildemann et al., 1991a). The size distribution for the submicrometre fraction of automobile emissions is unimodal and peaks at about 0.1 µm, although bimodal distributions are also observed (Hildemann et al., 1991a). Diesel truck emissions also exhibit a unimodal size distribution in the submicrometer range, peaking around 0.2 µm.

Chemical analyses of fine (<2 µm) particles in exhaust from noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks currently in use in the Los Angeles area have identified more than 100 different organic compounds. These compounds include n-alkanes, n-alkanoic acids, benzoic acids, benzaldehydes, PAH, oxy-PAH, steranes and pentacyclic triterpanes (Rogge et al., 1993a). Chemical composition typically shows wide vehicle-to-vehicle variation. The organic carbon component has been estimated to account for 38-75% of the fine particle mass, while the elemental carbon component accounts for 4-37% of the total (Hildemann et al., 1991b). PAH and oxy-PAH emissions are highest from noncatalyst-equipped automobiles, while n-alkanoic acid emissions are higher from automobiles equipped with catalytic converters (Rogge et al., 1993a). Heavy duty diesel trucks emit four times as much PAH as catalyst-equipped vehicles, but nearly seven times less PAH than noncatalyst-equipped vehicles. Heavy-duty diesel trucks also emit substantial quantities of n-alkanes and n-alkanoic acids. Bromine is found in trace amounts (3%) in noncatalyst vehicle exhaust (Hildemann et al., 1991b). Particle sulphate is also found in trace amounts (4%) in vehicle exhaust. Diesel engines, which use a large amount of excess oxygen, have a greater tendency to form sulphates than gasoline engines (ASEP, 1997). However, the larger contribution is through the conversion of SO_2 emissions from vehicular exhaust to secondary particles. Reflecting the higher fuel sulphur content found in diesel fuel compared with gasoline (i.e., up to a factor of four difference), higher SO_2 emissions are observed from the diesel vehicle fleet as compared with the gasoline vehicle fleet (e.g., MELP, 1995; ASEP, 1997). Vehicular exhaust is also a large source of NO_x emissions that may convert in the atmosphere to particle nitrate.

Additional primary mobile particle emissions are attributed to tire wear, brake linings and re-suspended fugitive dust. Analyses have shown that brake dust consists primarily of iron and organic carbon compounds (11% each), magnesium (8%), barium and silicon (7% each), sulphates (3%) and elemental carbon (3%) (Hildemann et al., 1991b). Similar analyses of tire dust show that organic carbon (15%) and elemental carbon (36%) are the dominant constituents. However, a large fraction of the total mass is not accounted for in these estimates.

Particulate lead (from the octane enhancer tetraethyl lead) and bromine (from the lead scavenger ethylene dibromide) have traditionally been used to identify particle emissions from automobiles. However, leaded gasoline was phased out in Canada and in many parts of the United States in 1990. With the phase-out of leaded gasoline, new tracer species have become necessary. In Canada, methylcyclopentadienyl manganese tricarbonyl (MMT) has been used as an octane enhancer in gasoline since 1977. Combustion results in the formation of various oxides of manganese. In a study carried out in Montreal, Loranger and Zayed (1992) found that ambient manganese levels appeared to correlate well with traffic density in an urban setting. However, the difficulty in using manganese as a tracer for gasoline vehicles is that other sources of manganese exist in the environment, such as crustal material. Steranes and pentacyclic triterpanes, which have been extensively used in geochemistry as petroleum markers, are introduced into vehicular emissions via engine oil. These compounds have been identified as potential markers for internal combustion engines in Southern California (Rogge et al., 1993a). Different PAH signatures have been used to differentiate among emissions from spark ignition engines, diesel engines and residential wood combustion (Li and Kamens, 1993). In an airshed where emissions are predominantly from motor vehicles and residential wood combustion, several VOCs were identified as potential tracers for motor vehicle emissions, including xylenes; methylcyclohexane; 2- and 3-methylhexane; 2,3,4- and 2,2,4-trimethylpentane; and 2-methylpentane (Zweidinger et al., 1990).

4.1.4 Fossil Fuel Combustion

Fuel combustion typically includes all boilers, heaters and furnaces associated with utilities, industry, and commercial/institutional and residential establishments. It also includes residential wood combustion. Emissions from fuel combustion processes are dependent on many factors, including the type of fuel burned, the source type and the type of emission controls employed.

Coal is a slow-burning fossil fuel characterised by a high ash content. The combustion of coal is a large source of PM in the utility and industrial sectors. Emissions depend in part on the type of coal burned and its ash content. For instance, the combustion of low-ash coal yields less PM than that of high-ash coal. Major chemical constituents of PM from coal combustion include oxides of silicon, aluminum and iron, with lesser amounts of sulphur, magnesium, potassium and calcium. Particles <1 µm in diameter are enriched in volatile elements such as arsenic, antimony, selenium and gallium, indicative of material vaporized during combustion (Markowski and Filby, 1985). The presence of selenium is of particular note, as coal combustion is estimated to be the largest source of atmospheric elemental selenium in the United States, with contributions of 60-85% of anthropogenic emissions (NAS, 1976; Eimutis et al., 1978). As the selenium content of coal is an order of magnitude greater than that of oil, this observation is used to discriminate between air masses originating over coal-burning areas in the Midwestern United States, and those originating over oil-burning regions of the east coast (Spengler and Thurston, 1983). During the summer of 1986 in southern Ontario, a study of transported acid PM identified coal combustion as the largest single contributor (75%) to the fine particle mass (Keeler et al., 1990).

The predominant types of fuel oil burned by combustion sources are distillate oils and residual oils. Distillate oils, including Nos. 1 and 2 fuel oil, are more volatile and less viscous than residual oils. They contain little nitrogen or ash and less than 0.3% sulphur by weight. They are used mainly in domestic and small commercial applications. Residual oils, including No. 5 and No. 6 (Bunker C) fuel oil, contain significant quantities of ash, nitrogen and sulphur. The sulphur content of high-sulphur No.6 fuel oil is 3.97% by weight. They are used in utility, industry and large commercial applications. Measurements of emissions from an industrial-scale boiler burning No. 2 fuel oil showed a bimodal mass distribution, with peaks near 0.05 µm and 0.5 µm (Hildemann et al., 1991a). The mass distribution of particles resulting from heavy oil combustion was found to be shifted toward larger particle sizes, with peaks near 0.18 µm and 5.7 µm (Buerki et al., 1989). Analysis of the larger-diameter mode revealed spherical particles containing many holes, which is typical of fly ash.

Particle emissions from distillate oil fired boilers are typically carbonaceous in nature and dependent on the completeness of combustion. Emissions from residual oil combustion are high in carbon and sulphur levels and depend on oil sulphur content. Low-sulphur residual oils have a lower viscosity and reduced asphaltene, ash and sulphur content, resulting in better atomisation and fuel combustion. Usually, the combustion of distillate oils produces less PM than that of heavier residual oils. Reduced boiler loads may also contribute to decreased particle emissions.

Trace elements associated with oil combustion include cadmium, cobalt, copper, nickel, vanadium, sodium and iron. Vanadium is considered the key indicating species of residual oil combustion. In the United States, an estimated 90% of vanadium emissions are attributed to the combustion of residual oil (NAS, 1974). Although coal also contains some vanadium, its levels are much less than those found in residual oil.

4.1.5 Nonferrous Metal Industries

Nonferrous industries include the smelting of metals other than iron, and include the production of copper/nickel, lead/zinc and aluminum. PM from metal smelters is typically enriched in the so-called chalcophilic elements (e.g., sulphur, copper, zinc, arsenic, selenium, silver, cadmium, indium and gold) compared with the feed material. Emissions from copper smelters in particular have been found enriched in copper, arsenic, selenium, cadmium and indium. These characteristic chemical profiles have been used to identify the plumes and PM from individual smelters (Small et al., 1981).

Aluminum smelters are sources of various particle fluorides (cryolite, aluminum fluoride, calcium fluoride, chiolite), alumina and ferric oxide. They are also a source of vaporized organic compounds and sulphur dioxide, which later may be involved in secondary particle production. Particle emissions from lead smelters are composed of a range of materials, including lead oxides, quartz, limestone, iron pyrites, iron-lime silicate slag, arsenic and other metallic compounds. Much of the PM from zinc smelters is from the zinc roasters, in which zinc sulphide concentrate is converted to an impure zinc oxide called calcine. Emissions from such operations as crushing, grinding and material transport may also contribute fugitive emissions.

4.1.6 Pulp and Paper Industry

In chemical wood pulping, cellulose is extracted from wood by dissolving the lignin that binds the cellulose fibres together. Kraft, sulphite, neutral sulphite semi-chemical (NSSC) and soda (US EPA, 1992) are four major processes for chemical wood pulping. Particle emissions from Kraft pulp mills are primarily from the recovery furnace, the lime kiln and the smelt dissolving tank. They consist mainly of sodium salts and some calcium salts from the lime kiln, and are caused by carryover of solids and sublimation and condensation of the inorganic chemicals. Except for uncontrolled emissions from the lime kiln, particle diameters are predominantly less than 2.5 µm. In sulphite mills, a major source of PM is the absorption system used to recover SO_2 in the recovery furnace exhaust. Auxiliary power boilers fuelled by coal, oil or bark/wood residues may also be large sources of particle emissions in pulp mills.

4.1.7 Wood Products Industry

This industry involves the processing of wood-derived products. It includes sawmills and plywood and veneer manufacture. Plywood manufacturers are a source of both PM and organic matter. The major source is the veneer dryer, which emits various condensable and volatile organic compounds from the wood (US EPA, 1992). The condensable organic fraction consists largely of wood resins, resin acids and wood sugars that cool outside the stack to temperatures below 21°C and combine with water vapour to form a blue haze, a water plume or both. The volatile fraction consists of terpenes and, for gas-fired dryers, natural gas components. Plywood manufacturers may also be a source of fugitive emissions as sawdust and other small wood particles, primarily from plywood cutting and sanding operations.

4.2 PRIMARY SOURCES OF THE COARSE FRACTION

4.2.1 Windblown Dust

The action of the wind on soils and crustal materials results in the gradual erosion of the parent material, producing particles that become suspended in the atmosphere. The size distribution is typically bimodal in nature, with maxima reported at 1-10 µm and 50 µm (Gillette, 1980). More than 90% of the mass is greater than 1 µm in diameter (Gillette, 1980; Houck et al., 1989).

In a review of mass balance studies in the United States, Chow (1995) found that approximately one-half of PM_{10} consists of geological material, but only about 10% is $PM_{2.5}$. Reflecting the composition of the earth's crust, soil-derived material is typically composed of seven major elements: silicon, aluminum, iron, sodium, potassium, calcium and magnesium. Actual composition will vary from site to site; however, silicon, aluminum, iron and calcium are typically used as key indicators of soil-derived material (e.g., Lowenthal et al., 1994). Because the atmospheric concentrations of many trace elements tend to be a factor of 10-1000 times higher than expected from the physical dispersion of crustal material, enrichment factors are sometimes used to help identify the source of the PM. Enrichment factors are typically defined as the ratio of the airborne concentrations of element *x* to aluminum, divided by that in crustal rock. Ratios near unity suggest that crustal weathering is the source of element *x*, while ratios much larger than unity indicate noncrustal sources (Milford and Davidson, 1985).

4.2.2 Marine

Size distributions of marine particles are characterized by two distinct modes separated by a minimum in the range of 0.2-0.3 µm radius. The fine mode (<0.2 µm radius) comprises 90-95% of the particles but only about 5% of the particle mass. It consists primarily of non-sea salt sulphate (Fitzgerald, 1991). The coarse mode (>0.5 µm radius) comprises 90-95% of the total mass, but little of the total number of particles. This fraction is composed primarily of sea salt particles, which are generated at the surface of the ocean by the bursting of whitecap bubbles. Each bursting bubble produces about 1-10 jet drops and hundreds of film drops. Most jet drops have a radius of less than 10 µm, while most film drops have a radius smaller than 1 µm (Woolf et al., 1988). Depending on the relative humidity, the drops become either sea-salt particles or sea-salt solution droplets. Larger particles (>10 µm radius) known as spume drops are produced from the mechanical disruption of wave crests by the wind. Spume droplet formation becomes significant at wind speeds greater than 10 m/s (Wang and Street, 1978; Monahan et al., 1986). Sea salt particles are primarily composed of water and dissolved and suspended materials such as sodium chloride, potassium, calcium, organic compounds, sulphates and carbonates.

4.2.3 Vegetation

Vegetation-derived particles may be primary or secondary in nature. Seeds, pollen, spores, leaf waxes and resins are examples of particles emitted directly to the atmosphere. Particle size typically ranges from 1 to 250 µm (Warneck, 1988), with spore size between 5-10 µm (Corn, 1976b). Secondary particles are formed via reactions involving natural VOC's such as alpha- and beta-pinene released from vegetation (e.g., Hatakeyama et al., 1989; Zhang et al., 1992, Pandis et al., 1992). Further discussion of secondary particles is found in Section 4.3.

4.2.4 Road Dust

Road dust represents several source contributions ranging from vehicle exhaust, worn tires and brake linings particles, dirt from construction sites, blowing garden soil, leaves and other plant materials.

Sanding material has been shown to contribute almost half the PM_{10} emissions during the late winter/early spring snow melt in Telluride, Colorado (Dresser and Baird, 1988). Fine particle (<2 µm) paved road dust has been identified as the third largest source of fine organic carbon particle emissions in the Los Angeles Basin (Hildemann et al., 1994). Studies in the Denver metropolitan area show that PM_{10} emissions from clean, and paved roads account for about 40-70% of total PM_{10} (Zimmer et al., 1992).

Chemical analyses of paved road dust in the Los Angeles Basin show that the major chemical constituents include organic carbon compounds (13%), silicon (12%), iron (6%), aluminum (6%), calcium (4%), potassium (2%) and sulphate and elemental carbon (1% each) (Rogge et al., 1993b). Vehicular emissions, tire dust and vegetative detritus respectively contribute 7.6%, 1.6% and a minimum of 2.2% of the total fine road dust, and 32.7%, 4.3% and 5.3% of the organic component. Relative to ambient PM, road dust deposits are more typically enriched in mechanically generated fine particles such as leaf dust and soil dust, which deposit more readily by sedimentation or impaction. They contain hundreds of organic compounds, including n-alkanes (C_{19}-C_{39}), n-alkanoic acids (C_6-C_{32}), n-alkanal (C_{28}, C_{30}, C_{32}), n-alkanols (C_{26}, C_{28}), benzoic acid and its alkyl-substituted homologues, PAH and oxy-PAH, steranes, triterpanes, pesticide and insecticide residues and monoterpenoids.

4.2.5 Agriculture

Agricultural crops (wind erosion and tillage), dairy operations, feedlots and agricultural burning are potential sources of PM. Particle emissions from dairies and feedlots are typically larger than 2.5 µm and contain higher levels of organic carbon, nitrate and ammonium than agricultural soils (Houck et al., 1989). These chemical constituents are concentrated in the finer size fractions, indicating the importance of secondary organic and ammonium nitrate formation resulting from agricultural emissions.

Agricultural burning is performed for waste reduction, sanitation and maintenance purposes (Freeburn and

Schmitt, 1992). In contrast to other agricultural operations, agricultural burning (wheat and barley stubble) has been found to produce fine particle emissions, with an estimated 82% smaller than 2.5 µm and 93% smaller than 10 µm (Houck et al., 1989).These emissions are high in organic carbon, elemental carbon, chlorine and potassium.

4.3 SECONDARY PARTICLES

Secondary particle formation is dependent on many chemical reactions and transformations taking place in the atmosphere. The principal precursor gases involved in secondary particle formation include SO_2, NO_x, organic compounds and ammonia, which undergo reactions to yield such products as NH_4HSO_4, $(NH_4)_2SO_4$, various condensible organic compounds and NH_4NO_3.

The mechanisms for particle formation involving SO_2 and NO_x were described in Chapter 2. Briefly, sulphate is formed through the oxidation of SO_2 in the gas phase or aqueous phase. Gas-phase oxidation is primarily via reaction with the hydroxyl radical to form sulphuric acid gas, which may nucleate in the presence of water vapour to form sulphuric acid droplets. Sulphuric acid gas may also condense on existing particles. Important sources of SO_2 include the nonferrous mining and smelting sector and electric power generation. Particle nitrate is formed from reactions involving HNO_3 and either ammonia or pre-existing particles. Nitric acid is formed primarily from gas-phase reactions with the hydroxyl radical. Motor vehicles and electric power generation are large sources of NO_x. Estimates of both SO_2 and NO_x emissions are provided in Section 4.4.

Mechanisms for organic particle formation are less well understood. The potential for a particular VOC species to be involved in secondary particle formation will depend on the ease with which it can be oxidized and the volatility of its byproducts. Grosjean and Seinfeld (1989) used the results of smog chamber experiments to estimate the fraction of VOC converted into particles. This dimensionless number is called a fractional aerosol coefficient (FAC). Based on the compiled FACs, the most potent particle precursors were aromatic hydrocarbons, higher-molecular-weight olefins and cyclic olefins, and higher-molecular-weight paraffins including cycloalkanes. Applying this methodology to VOC emission estimates for a smog episode in Southern California, Grosjean (1992) determined that aromatics such as toluene, xylene and various substituted benzenes, and various VOCs associated with biogenic emissions yields the greatest quantity of secondary organic PM. In contrast, alkanes with up to six carbon atoms, all alkenes with up to six carbon atoms, benzene and many low-molecular-weight carbonyls, chlorinated compounds and oxygenated solvents do not form particles under atmospheric conditions.

Biogenic sources have long been associated with the blue haze observed in forested areas (Went, 1960). The study of the degradation pathways of biogenic hydrocarbons is an important and current problem in atmospheric chemistry (Zhang et al., 1992). Major VOC types emitted by biogenic sources include isoprene from deciduous trees and the monoterpenes alpha- and beta-pinene from coniferous trees (Lamb et al., 1986). Smog chamber studies have shown that the oxidation of isoprene contributes little to particle formation (Pandis et al., 1991). This finding is attributed to the high vapour pressure of the products of formation. In similar studies involving alpha-pinene (Hatakeyama et al., 1989; Zhang et al., 1992) and beta-pinene (Pandis et al., 1992; Hatakeyama et al., 1989; Zhang et al., 1992), measurable particle yields were detected. It was concluded that alpha- and beta-pinene could contribute to particle formation in areas with high vegetative coverage (Pandis et al., 1992).

Ammonia is the most common alkaline component in the atmosphere. It neutralizes such atmospheric acids as HNO_3, H_2SO_4 and hydrochloric acid (HCl) to yield several salts, including NH_4NO_3, $NH_4\,HSO_4$, $(NH_4)_2\,SO_4$ and ammonium chloride (NH_4Cl). For acid rain falling over large parts of Europe, up to 70% of the original acid is neutralized by ammonia (EMEP/CCC, 1984). Ammonia is emitted from many sources, including combustion processes, refinery operations, chemical fertilizer manufacture and application, chemical plants, steel mill coke ovens and decomposing livestock wastes. Livestock operations are typically the major source of ammonia emissions, contributing more than 50% of ammonia emissions in the South Coast Air Basin (Russell et al., 1983) and more than 80% in Europe (Buijsman et al., 1987). Similar estimates for Canadian sources are not available.

4.4 EMISSION ESTIMATES

Emission inventories are typically prepared using several methodologies, including:

- actual source measurements,
- emission factors applied to surrogate activities,
- raw data from industry and government agencies, and
- engineering estimates based on a fundamental understanding of the emission source.

The availability of actual source measurements is typically limited to large industrial facilities, due to the large costs associated with sampling programs. Particle emission estimates are obtained through noncontinuous sampling studies, and so provide only a snapshot of emissions for a particular set of plant operating conditions. Consequently, average emission factors are more commonly applied. Emissions may be calculated using the following formula:

$$E = \sum_i A_i \cdot F_i \cdot (1 - C_{eff,i})$$

where E is the emission estimate, A_i is the activity rate for source i, F_i is the emission factor for source i and $C_{eff,i}$ is the efficiency of control measures applied to a source i. For a point source, a typical activity rate would be per volume of fuel used, while a corresponding emission factor would be tonnes of pollutant per volume of fuel used.

In the 1990 national emission inventory for criteria contaminants (which included TSP but not PM_{10}), standard and nonstandard emission factors were used for 46.0 and 41.7%, respectively, of the calculations (Deslauriers, 1996b). Provincial permit information was used for 7.4% of the calculations. Emissions based on source testing or other measurements, material balance using engineering expertise and knowledge, specific reports and other methods accounted for less than 2% each of the total calculations.

Standard emission factors were derived from the 5th edition of the US EPA publication AP-42 (US EPA, 1996). For on-road vehicles, emission factors for gaseous pollutants (in units of gm/mi) were calculated from the Canadian version of the US EPA Mobile5 model, designated M5C. Corresponding TSP emission factors were based on standard factors in AP-42.

Biogenic emissions were estimated using CANBEIS (Canadian Biogenic Emission Inventory System), a modeling system based on the US EPA's system PC-BEIS (Personal Computer Biogenic Emission Inventory System). CANBEIS integrates the programs developed to estimate emission factors with a Geographical Information System (GIS) called SPANS, which includes land use and land cover information.

To estimate contributions from PM_{10} and smaller size fractions, additional speciation factors were applied to TSP emission estimates. These speciation factors were largely based on those included in the US EPA SPECIATE database (Radian Corp., 1993).

Estimates of primary particle emissions in Canada for the year 1990 have been prepared for PM, PM_{10}, $PM_{2.5}$ and $PM_{2.5\text{-}10}$ (Deslauriers, 1996b). Contributions from the major source categories are listed in Table 4.2. Sources considered in each category include the following:

- industrial: coal industry, pulp and paper industry, nonferrous mining and smelting, iron and steel production, wood industry and mining and rock quarrying,
- Nonindustrial fuel combustion: commercial and residential fuel combustion, residential fuel wood combustion and electric power generation,
- transportation: gasoline and diesel vehicles and trucks, propane-powered vehicles, railroads, marine craft, aircraft and tire wear,
- incineration: wood waste and other types of incineration,
- biogenic: forest fires,
- miscellaneous sources: structural fires, pesticides and fertilizer application, cigarette smoking and the marine cargo handling industry.

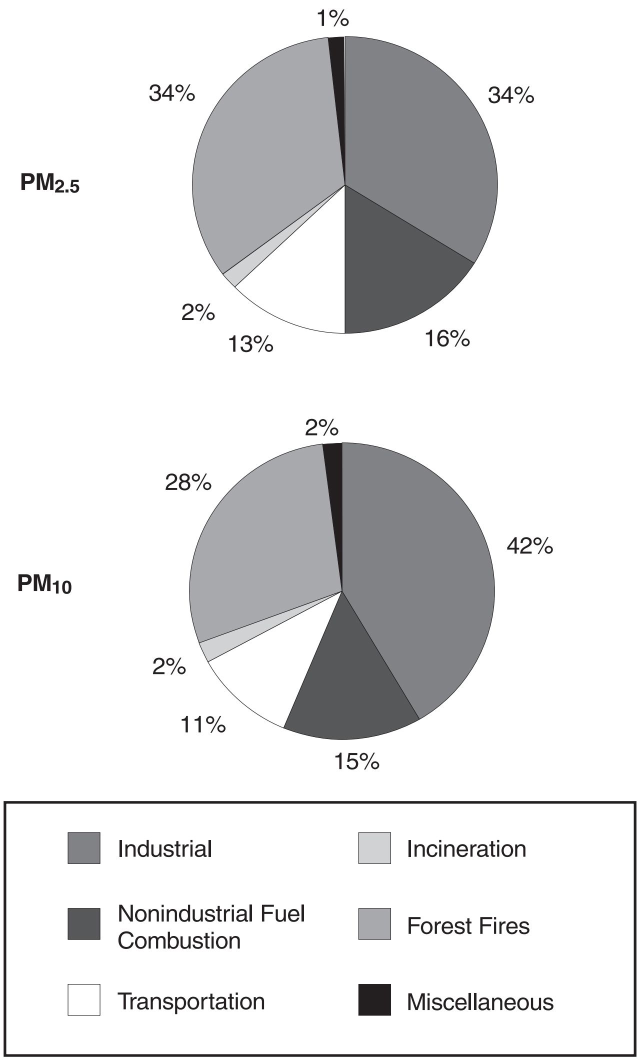
Emission estimates for open sources such as paved and unpaved roads, construction sites, agricultural and prescribed burning are currently under revision, and so excluded from Table 4.2. In 1990, an estimated 1.0 Mt of PM_{10} was emitted from primary sources excluding open sources. $PM_{2.5}$ accounted for approximately 75% of this total. Emission estimates for PM_{10} and $PM_{2.5}$ are further summarized in Figure 4.1. The source sector breakdown for PM_{10} emissions is as follows: 42% industrial sources, 28% forest fires, 15% nonindustrial fuel combustion, 11% transportation and 2% each incineration and miscellaneous sources. The corresponding breakdown for $PM_{2.5}$ emissions shows equally large (34%) contributions from forest fires and industrial sources, and

Table 4.2 1990 Emissions of PM in Canada (Deslauriers, 1996a)

Category/Sector*	PM tonnes	$PM_{2.5}$ tonnes	$PM_{2.5-10}$ tonnes	PM_{10} tonnes
Industrial Sector	810,366	270,182	178,509	448,691
Nonindustrial Fuel Combustion	272,842	126,513	31,041	157,554
Transportation	133,489	101,493	13,896	115,389
Incineration	34,248	13,683	5,128	18,811
Forest Fires	293,123	263,811	26,381	290,192
Miscellaneous	30,430	11,026	7,105	18,131
TOTAL	**1,574,498**	**786,708**	**262,060**	**1,048,768**

*Open sources and secondary particles are not included.

Figure 4.1 Summary of PM_{10} and $PM_{2.5}$ Contributions, 1990. Open sources and secondary particles are not included.

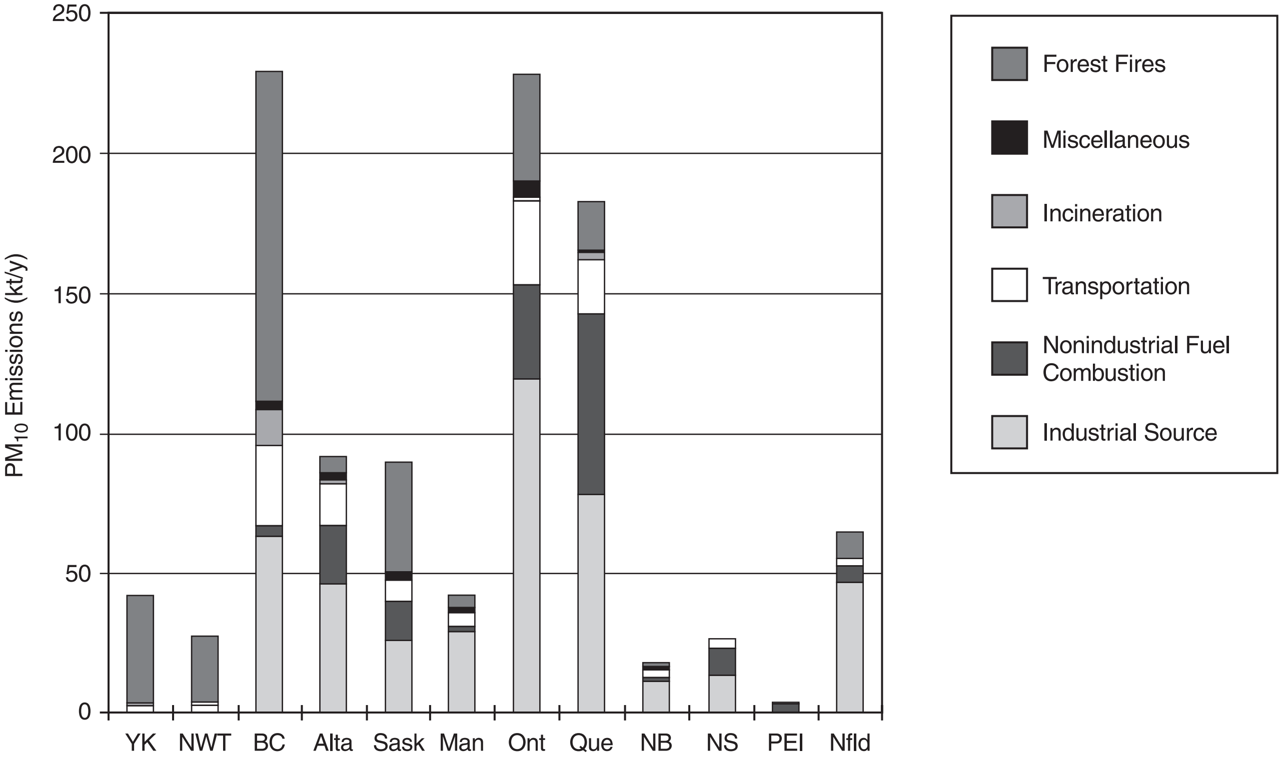


smaller contributions from nonindustrial fuel combustion (16%), transportation (13%), incineration (2%) and miscellaneous sources (1%).

Provincial estimates of PM_{10} emissions for 1990 are summarized in Figure 4.2. Nonindustrial fuel combustion (primarily residential wood combustion) is the dominant source in Prince Edward Island. In BC and Saskatchewan, emissions from forest fires comprise the largest percentage of provincial PM_{10} totals, with contributions from industrial sources also significant. Elsewhere, industrial sources are the largest contributors to provincial PM_{10} emissions. The transportation sector is also a large contributor in British Columbia, Alberta, Ontario and Quebec, whereas nonindustrial fuel combustion is a major source in Alberta, Saskatchewan, Ontario, Quebec and Nova Scotia.

Although excluded from the above figures, preliminary estimates show that fugitive dust sources account for a high percentage of PM_{10} emissions in most provinces (Deslauriers, 1996b). This agrees with findings in the US, where emissions from fugitive dust and miscellaneous sources are estimated to be a factor of 16 higher than emissions from industrial and transportation sources (US EPA, 1994b). Unpaved and paved roads and construction/mining and quarrying sites account for more than 70% of these emissions. In Canada, an estimated 65 Mt of total PM is attributed to open sources (Deslauriers, 1996a), of which more than 90% is from roads and construction sites. These sources are generally episodic in nature, being highly dependent on meteorological conditions such as wind speed and precipitation. For example, 24-hour emission estimates for a day in which wind gusts exceeded

Figure 4.2 Summary of Provincial PM_{10} Emissions, 1990. Open fugitive sources and secondary particles are not included.



96 km/h accounted for 20% of annual fugitive dust emissions in the Coachella Valley, CA (South Coast Air Quality Management District, 1994). As a result, fugitive dust emission estimates exhibit considerable year to year variability. Some concerns have been raised regarding the validity of emission inventory estimates for fugitive dust emissions, owing to discrepancies with estimates obtained from receptor modeling studies. For example, Lowenthal et al. (1994) report that fugitive dust emissions based on inventory estimates accounted for 85% of total PM_{10} emissions in the South Coast Air Basin (SoCAB) of Southern California. In comparison, geological contributions (including road dust, natural soils, agricultural soils and construction material) based on a receptor modeling study in the SoCAB ranged from 15-30% in the summer and from 10-17% during the fall (Watson et al., 1994b).

Also, excluded from aforementioned emission estimates are secondary particles. Unlike fugitive dust emissions, secondary particles are predominantly found in the fine fraction. Limited studies in the Lower Fraser Valley indicate that secondary particles (sulphates and nitrates) comprise up to approximately 50% of $PM_{2.5}$ in parts of the region during the summer months (Pryor and Steyn, 1994a). A source apportionment study in downtown Toronto (Lowenthal, 1997) shows that secondary sulphate and nitrate contribute 33% and 6%, respectively, to $PM_{2.5}$ concentrations measured at the Evans Street site between August-October 1995. In a review of several receptor modeling studies in the western US, Lowenthal (1997) found that secondary sulphate contributions to $PM_{2.5}$ ranged from 1.2% in Phoenix, AZ to 41.8% in Steubenville, OH. Secondary nitrate contributions ranged from undetectable levels in Steubenville, OH to 49.5% in Rubidoux, CA.

Emission estimates for the precursor species SO_2, NO_x and VOCs are included in national and provincial inventories and summarized in Table 4.3 (based on Deslauriers, 1996a). Similar estimates for NH_3 are not available. Precursor emission rates should not be misconstrued as being directly proportional to secondary particle production. As discussed in Section 2.7, secondary particles are the product of various chemical and physical transformations taking place in the atmosphere that may be highly nonlinear.

Table 4.3 Emission of Common Pollutants for Canada 1990 (from Deslauriers, 1996a)

	Emissions in Tonnes		
Category/Sector	**SO_2**	**NO_x**	**VOC**
Industrial Sources			
Abrasive Manufacture	3,490	214	1,758
Aluminum Production	31,967	3,173	834
Asbestos Production	1,748	895	45
Asphalt Production	434	260	2,206
Bakeries		4	3,459
Cement and Concrete Manufacture	31,171	29,372	186
Clay Products	164	292	26
Coal Industry	2,857	1,824	2,457
Crude Oil Production	67,187	2,952	4,390
Ferrous Foundries	1,875	30	1,106
Grain Industries		10	1
Iron and Steel Production	69,514	29,069	27,294
Iron Ore Mining and Beneficiation	45,978	6,809	562
Mining and Rock Quarrying	3,854	3,243	142
Natural Gas Processing	247,532	117,489	3,664
Nonferrous Mining and Smelting	1,401,425	54,594	329
Oil Sands	148,211	15,855	30
Other Chemicals	13,740	15,102	2,818
Other Petroleum and Coal Products	557	458	116
Paint & Varnish Manufacturing	1	9	1,236
Petrochemical Industry	3,291	12,990	28,662
Petroleum Refining	132,647	33,466	82,264
Plastics & Synthetic Resins Fabrication	424	354	12,477
Pulp and Paper Industry	141,717	61,388	20,165
Upstream Oil & Gas Operations		3,159	541,874
Wood Industry	3,479	5,419	15,958
Other Industries	66,665	85,322	88,575
Category total:	**2,419,926**	**483,751**	**842,836**
Nonindustrial			
Commercial Fuel Combustion	19,368	24,192	1,055
Electric Power Generation	690,201	252,356	2,280
Residential Fuel Combustion	29,245	34,971	2,616
Residential Wood Combustion	1,119	5,462	250,526
Category total:	**739,933**	**316,982**	**256,478**

continued

Table 4.3 Emission of Common Pollutants for Canada 1990 (from Deslauriers, 1996a) – ***continued***

	Emissions in Tonnes		
Category/Sector	**SO_2**	**NO_x**	**VOC**
Transportation			
Aircraft	1,332	18,506	7,252
Heavy-duty Diesel Vehicles	32,334	324,277	36,555
Heavy-duty Gasoline Trucks	173	11,943	11,445
Light-duty Gasoline Trucks	3,786	95,323	137,294
Light-duty Gasoline Vehicles	9,378	294,501	441,800
Light-duty Diesel Trucks	2,323	2,610	1,088
Light-duty Diesel Vehicles	2,408	1,959	679
Marine	48,410	47,346	32,174
Motor Cycles	19	540	3,023
Off-road Use of Diesel	17,271	271,643	27,763
Off-road Use of Gasoline	1,498	47,153	95,747
Propane Powered Vehicles	7	2,803	1,674
Railroads	14,317	134,143	6,599
Tire Wear			815
Category total:	**133,255**	**1,252,748**	**803,908**
Incineration			
Other Incineration	2265	2659	2594
Wood Waste Incineration	487	4882	52898
Category total:	**2,751**	**7,541**	**55,492**
Miscellaneous			
Application of Surface Coatings		4	177,520
Cigarette Smoking			
Dry Cleaning		1	11,985
Fuel Marketing			96,654
General Solvent Use		9	289,888
Marine Cargo Handling Industry			1
Pesticides and Fertilizer Application		746	42,113
Structural Fires		514	2,376
Category total:		**1,275**	**620,538**
TOTAL FOR CANADA	**3,295,867**	**2,062,297**	**2,579,051**

*The Carbon Black Sector was grouped under the Other Industries Sector to protect confidentiality of information.

In 1990, an estimated 3.2 Mt of SO_2 were discharged from anthropogenic sources in Canada (Deslauriers, 1996a). The largest contributor was the industrial and manufacturing sector, which was responsible for approximately 70% of SO_2 emissions. Emissions from copper and nickel smelting alone accounted for 40% of these emissions.

NO_x emissions are a by-product of combustion activities. In 1990, an estimated 2.1 Mt of NO_x was emitted from anthropogenic sources in Canada. Transportation accounted for 60% of this amount, and stationary fuel combustion an additional 16%.

Anthropogenic VOC emissions result from the incomplete combustion of fuel and from evaporative losses. Approximately 2.6 Mt of VOCs were discharged in Canada in 1990. Industrial sources (predominantly the oil and gas sector) and the transportation sector respectively accounted for 33% and 31% of this amount. Miscellaneous sources such as fuel marketing, solvent use and the application of surface coatings accounted for a further 24%.

4.5 UNCERTAINTIES IN EMISSION ESTIMATES

Uncertainties in emission inventories may be introduced through several ways, including

- partial inclusion of all sources,
- inappropriate emission factors applied,
- temporal variations in sources not considered (e.g. activity rates assumed to be constant with time) and
- poor characterisation of control efficiencies.

Although uncertainty estimates are unavailable for the 1990 PM_{10} or TSP inventory, estimates were made for 1990 CO, NO_x and SO_x emissions (McCann, 1995). These estimates were based on a mix of classical methods and scientific judgment. Calculated uncertainties are as shown in Table 4.4. Uncertainties vary across individual source sectors, and from sector to sector. For example, NO_x emissions from electrical generation were generally based on stack testing, flue gas rate measurements and analytical techniques. The associated uncertainty was estimated to be ±8%. In contrast, emissions from area fuel sources, which were based on US EPA emission factors, were estimated to have an uncertainty of ±50%. Even greater uncertainties can be expected for emission estimates for open sources, due to the very limited amount of published research for these emission factors (Deslauriers, 1996a).

Table 4.4 Estimated NO_x, SO_x and CO Uncertainties (from Deslauriers, 1996a)

Pollutant	Current Data Total	Percentage Uncertainty
SO_x		
All Sectors	3,235	± 5
NO_x		
Non-Transportation Sector	802	*
MOBILE5C	718	*
Other Gasoline User	47	*
Other Transport (c)	459	± 30
Total NO_x	2,026	±20
CO		
Non-Transportation Sector	2,651	± 30
MOBILE5C	5,645	±25
Other Gasoline User	1,441	±20
Other Transport (c)	*	
Total CO	10,004	±30

(a) Excludes miscellaneous categories, forest and other fires.

(b) Confidence levels 95% for SO_x, and NO_x, 85% for CO.

(c) 3,000 tonnes due to taxis and propane vehicles not included.

*could not be determined.

4.6 SUMMARY

Particle emissions result from both natural and anthropogenic activities. Examples of natural sources include sea salt, windblown dust, volcanic emissions, vegetation and wildfires. Important anthropogenic sources include the industrial sector, nonindustrial fuel combustion, prescribed burning, and transportation. Particles may be discharged directly into the atmosphere (primary) or formed in the atmosphere through various chemical and physical transformations (secondary).

The size and chemical composition of the particles formed will reflect the parent materials and the formation processes involved. High-temperature combustion processes and secondary reactions will yield particles predominantly in the fine fraction. Natural and anthropogenic sources involving mechanical processes contribute more greatly to the coarse fraction. The physical and chemical characteristics of particle emissions from various sources were described.

National emission estimates for primary PM_{10} emissions and contributions to the fine and coarse fractions were presented. Excluding open fugitive dust sources, an estimated 1.2 Mt of PM_{10} was emitted directly to the atmosphere in 1990. The fine fraction accounted for almost three-quarters of this amount. On a national scale, significant sources of PM_{10} include industrial sources (36%), biogenic sources (24%), prescribed burning (15%), nonindustrial fuel combustion (13%) and transportation (9%). $PM_{2.5}$ contributions show a similar breakdown, except that the portion from biogenic sources rises to 28% and that from industrial sources decreases to 29%. Preliminary estimates show that emissions from open fugitive dust sources such as paved and unpaved roads, construction sites and agricultural operations account for a high percentage of PM_{10} emissions in most provinces. Limited studies in the Lower Fraser Valley of British Columbia show that secondary particles may account for a significant fraction of $PM_{2.5}$ during the summer months.