



**Australian Government**

**Department of the Environment and Heritage**

# **Health Impacts of Ultrafine Particles**

## **Desktop Literature Review and Analysis**

**A consultancy funded by the Australian Government  
Department of the Environment and Heritage**

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## GLOSSARY

<b>Accumulation Mode Particles</b>	<ol style="list-style-type: none"><li>1. Particles with the diameters between about 0.04 and 1 <math>\mu\text{m}</math>.</li><li>2. A mode in the atmospheric particle size distribution, formed primarily by coagulation of smaller particles.</li></ol>
<b>Absorption</b>	Penetration of a substance into the body of another substance
<b>Acute</b>	Refers to severe symptoms and a rapid onset and progressive change to an organism leading to a crisis in a relatively short period of time, measured in seconds, minutes, hours, or days, following exposure to a health hazard.
<b>Acute Exposure</b>	Refers to a single, short-term exposure to a toxic substance. Acute exposures are characterised as lasting no longer than 1 day.
<b>Acute Health Effect</b>	An effect that develops either immediately or a short time after exposure.
<b>Adiabatic</b>	A body is said to undergo an adiabatic change when its condition is altered without gain or loss of heat.
<b>Adsorption</b>	The condensation of gases, liquids, or dissolved substances on the surfaces of solids
<b>Adverse Health Effect</b>	Abnormal or harmful effect to an organism (e.g., a person) caused by exposure to a chemical. It includes results such as death, other illnesses, altered body and organ weights, altered enzyme levels, etc.
<b>Aerodynamic Diameter</b>	Refers to the size of particles. It is the diameter of a sphere of unit density that behaves aerodynamically (has the same settling velocity in air) as the particle of the test substance. It is used to compare particles of different size, shape, and density, and to predict where in the respiratory tract such particles may be primarily deposited.

<b>Air Contaminant</b>	Any particle matter, gas, or combination thereof, other than water vapour
<b>Air Pollutant</b>	Any substance in air that could, in high enough concentration, harm humans, animals, vegetation, or material. Pollutants may include almost any natural or artificial composition of airborne matter capable of being airborne. They may be in the form of solid particles, liquid droplets, gases, or in combination thereof. Generally, they fall into two main groups: (1) those emitted directly from identifiable sources and (2) those produced in the air by interaction between two or more primary pollutants, or by reaction with normal atmospheric constituents, with or without photoactivation.
<b>Air Pollution</b>	The presence of contaminants or pollutant substances in the air that interfere with human health or welfare, or produce other harmful environmental effects.
<b>Air Pollution Episode</b>	A period of abnormally high concentration of air pollutants, often due to low winds and temperature inversion that can cause illness and death.
<b>Air Quality Criteria</b>	The levels of pollution and lengths of exposure above, which adverse health and welfare effects may occur.
<b>Air Quality Standards</b>	The level of pollutants prescribed by regulations that are not to be exceeded during a given time in a defined area.
<b>Airborne Particles</b>	Total suspended particulate matter found in the atmosphere as solid particles or liquid droplets. Chemical composition of particles varies widely, depending on location and time of year.
<b>Ambient Air</b>	The external air environment (does not include the air environment inside buildings or structures).
<b>Ambient Measurement</b>	A measurement of the concentration of a substance or pollutant within the immediate environments of an organism; taken to relate it to the amount of possible exposure.

<b>Asthma</b>	A respiratory disease caused by spasmodic contraction of the bronchioles in the lungs. Characterised by attacks of wheezing, shortness of breath and/or coughing and resulting in difficult breathing.
<b>Bias</b>	A systematic error introduced through some aspect of the study design. It cannot be controlled for in the analysis and efforts must therefore be made to prevent it through good study design and data collection.
<b>Black smoke</b>	Surrogate for suspended particles used in UK and is defined according to a special measuring procedure, indicating the density of blackness on a certain filter system.
<b>Carbonaceous particles</b>	Particles consisting mostly of carbon compounds.
<b>Cardiovascular</b>	A medical term that refers to the heart and blood vessel system.
<b>Cardiovascular and Blood Toxicity</b>	The adverse effects on the heart or blood systems, which result from exposure to toxic chemicals.
<b>Chronic</b>	Refers to a change to an organism over a long period of time, measured in weeks, months, or years following repeated exposure to a health hazard.
<b>Chronic Exposure</b>	A long-term exposure to a toxic substance.
<b>Chronic Health Effect</b>	Refers to an adverse health effect that develops slowly over a long period of time or from prolonged exposure to a health hazard without implying a degree of severity.
<b>Coarse particles</b>	Particles with the diameter between 2.5 and 10 $\mu\text{m}$ .
<b>Combustion</b>	A chemical reaction in which a material combines with oxygen with the evolution of heat: “burning”. The combustion of fuels containing carbon and hydrogen is said to be complete when these two elements are all oxidised to carbon dioxide and water. Incomplete combustion may lead to (1) appreciable amounts of carbon remaining in the ash;

(2) emission of some of the carbon as carbon monoxide; and  
(3) reaction of the fuel molecules to give a range of products of greater complexity than that of the fuel molecules themselves (if these products escape combustion they are emitted as smoke).

**Community time series epidemiology**

Epidemiological studies that assess the impact of exposures on day-to-day variation in health events within a community.

**Confounder**

Variable that influences a health effect apart from air pollution. In particular, a confounder is associated with the exposure and the outcome and effect estimates would be biased if the variable would be neglected in the analyses.

**COPD (chronic obstructive pulmonary disease)**

A disease process that decreases the ability of the lungs to perform ventilation. Diagnostic criteria include a history of persistent dyspnea on exertion, with or without chronic cough, and less than half of normal predicted maximum breathing capacity. Diseases that cause this condition are chronic bronchitis, pulmonary emphysema, chronic asthma, and chronic bronchiolitis.

**Diesel exhaust**

Diesel exhaust emissions contain hundreds of chemical compounds, which are emitted partly in the gaseous phase and partly in the particulate phase of the exhaust. The major gaseous products are carbon dioxide, oxygen, nitrogen, and water vapour; carbon monoxide, sulfur dioxide, nitrogen oxides, and hydrocarbons and their derivatives are also present. Benzene and toluene are present in the lower range (percentage weight) in the gaseous part of the hydrocarbon fraction. Other gaseous exhaust compounds are low-relative-molecular-mass polycyclic aromatic hydrocarbons. A main characteristic of diesel exhaust is the release of particles at a rate about 20 times greater than that from gasoline-fuelled vehicles. The particles are composed of elemental carbon, organic compounds adsorbed from fuel and lubricating oil, sulfates from fuel-sulfur, and traces of metallic components. Most of the total particulate matter occurs in the submicrometre range, between 0.02 and 0.5  $\mu\text{m}$ .

**Dose**

The amount of a chemical substance to which a person has been exposed or adsorbed into the body.

<b>Dose response</b>	A relationship in which a change in the amount, intensity, or duration of an exposure is associated with either an increase or decrease in risk of a specified health outcome.
<b>Dose-Response Assessment/ Relationship</b>	The amount of a chemical that an organism (such as a person) is exposed to is called the dose, and the severity of the effect of that exposure is called the response. A dose-response assessment is a scientific study to determine the relationship between dose and response, and how much dose is correlated with how much response.
<b>Emission</b>	Release of pollutants into the air from a source.
<b>Epidemiology</b>	Science concerned with the study of disease in a general population. Determination of the incidence (rate of occurrence) and distribution of a particular disease (as by age, sex, or occupation), which may provide information about the cause of the disease.
<b>Exposure</b>	(1) The time integral of the concentration of a toxicant, which is in the immediate vicinity of various ports of entry (such as lung, gastro-intestinal tract and skin). (2). Qualitatively, contact between a potentially harmful agent and a receptor (e.g., a human or other organism) that could be affected. Exposure may be short term (acute) or long term (chronic).
<b>Exposure Assessment</b>	The process of measuring or estimating the intensity, frequency, and duration of human exposures to an agent currently present in the environment or of estimating hypothetical exposures that might arise from the release of new chemicals into the environment.
<b>Exposure Limits</b>	Established concentrations which, if not exceeded, will not generally cause adverse effects to the exposed population.
<b>Fine Particles</b>	Particles with the diameter smaller than 2.5 $\mu\text{m}$ .
<b>Forced expired volume in one second</b>	The volume expired in the first second (FEV <sub>1</sub> ) of maximal expiration after a maximal inspiration and is a useful measure of how quickly full lungs can be emptied.

<b>Hazard Evaluation</b>	A component of risk evaluation that involves gathering and evaluating data on the types of health injuries or diseases that may be produced by a chemical and on the conditions of exposure under which such health effects are produced.
<b>Hazard Assessment</b>	Evaluating the effects of a stressor or determining a margin of safety for an organism by comparing the concentration, which causes toxic effects with an estimate of exposure to the organism.
<b>Hazard Identification</b>	Determining if a chemical or a microbe can cause adverse health effects in humans and what those effects might be.
<b>Hazardous air pollutants</b>	(1) Chemicals that cause serious health and environmental effects, (2) According to law, a pollutant to which no ambient air quality standard is applicable and that may cause or contribute to an increase in mortality or in serious illness.
<b>Health hazard</b>	Evidence based on scientific data (human or animal) that acute or chronic effects might occur.
<b>Heterogeneous nucleation</b>	Formation of droplets on condensation nuclei
<b>Homogeneous nucleation</b>	Formation of droplets in the absence of condensation nuclei; also called self-nucleation.
<b>Immunosuppression</b>	Decrease in the immune response.
<b>In vitro</b>	In glass, referring to a study in the laboratory usually involving isolated organ, tissue, cell, or biochemical systems.
<b>In vivo</b>	In the living body, referring to a study performed on a living organism.
<b>Inflammation</b>	The response of the tissues of the body to injury, infection or irritation. Its chief symptoms are redness, heat, swelling, and pain.

<b>Inhalation</b>	Breathing into the lungs of a (contaminated) substance in the form of a gas, vapour, fume, mist, or dust.
<b>Interaction</b>	Modification of the toxic effects of one substance by another. Depending on the substances involved, the effects of interaction can be amplified or mitigated.
<b>Mass concentration</b>	The concentration of particles in air expressed as mass per unit volume.
<b>Mobile sources</b>	Motor vehicles and other moving objects that release pollution; mobile sources include cars, trucks, buses, planes, trains, motorcycles and gasoline-powered lawn mowers. Mobile sources are divided into two groups: road vehicles, which include cars, trucks and buses, and non-road vehicles, which include trains, planes and lawn mowers.
<b>Morbidity</b>	Sickness or illness; departure from a state of physical or mental well-being.
<b>Mortality</b>	Death.
<b>Mortality Rate</b>	The proportion of a population that dies during a specified time period. Also referred to as the death rate.
<b>Mutagen</b>	A chemical substance or physical effect capable of inducing transmissible changes in the genetic material of a living cell that results in physical and functional changes in the descendants. Depending on the type of cells affected, ova or spermatozoa, both male and female can be affected. Mutations can lead to birth defects, miscarriage, or cancer.
<b>Nanoparticles</b>	Particles below 50 nm in diameter (0.05 $\mu\text{m}$ ).
<b>Nucleation Mode</b>	Particles with the diameters between approximately 0.003 and 0.03 $\mu\text{m}$ .
<b>Panel study</b>	An epidemiological or toxicological study performed with volunteers.

<b>Particulate Matter (also particles)</b>	Generally refers to all airborne pollutants, which are not gases. Particulate matter can include droplets of liquids or solid matter.
<b>Personal Air Samples</b>	Air samples taken with a pump that is directly attached to the worker with the sampler placed in the worker's breathing zone.
<b>Personal Measurement</b>	A measurement collected from an individual's immediate environment.
<b>Pollutant</b>	Generally, any substance introduced into the environment that adversely affects the usefulness of a resource or the methods for estimating health of humans, animals, or ecosystems.
<b>Pollution</b>	Generally, the presence of a substance in the environment that because of its chemical composition or quantity prevents the functioning of natural processes and produces undesirable environmental and health effects.
<b>Polynuclear Aromatic Hydrocarbons</b>	A class of chemicals typically formed by burning and common in the environment. PAHs are also common to petroleum products and oil. Although most of these compounds are harmless or mildly toxic, some are carcinogenic.
<b>Primary Particles</b>	Particulate matter originated from direct air emissions.
<b>Regression</b>	Statistical term to describe methods for estimating the relationship between a dependent (response) variable Y and one or more independent (explanatory) variables X.
<b>Respirable Particle</b>	Particles able to penetrate and deposit in the lower bronchioles and alveolar region.
<b>Peak expiratory flow</b>	The maximal expiratory flow rate (PEF) achieved and this occurs very early in the forced expiratory manoeuvre.

<b>Respiratory Toxicity</b>	Adverse effects on the structure or function of the respiratory system caused by exposure to a toxic chemical. Respiratory toxicants can produce a variety of acute and chronic pulmonary conditions, including local irritation, bronchitis, emphysema and cancer.
<b>Risk</b>	The probability that damage to life, health, and/or the environment will occur as a result of a given hazard (such as exposure to a toxic chemical). Some risks can be measured or estimated in numerical terms (e.g., one chance in a hundred).
<b>Risk Characterization</b>	An organised process used to evaluate, summarize, and communicate information about the likelihood of adverse health or ecological effects from particular exposures to a toxic chemical in the environment, i.e. how individuals or populations may be affected. It includes discussion of the kind of evidence it uses and how strong that evidence is. Risk characterization is the final step in the process of risk assessment.
<b>Risk Assessment</b>	An organised process used to describe and estimate the amount of risk of adverse human health effects from exposure to a toxic chemical (how likely or unlikely it is that the adverse effect will occur). How reliable and accurate this process is depends on the quantity and quality of the information that goes into the process. The four steps in a risk assessment of a toxic chemical are hazard identification, dose-response assessment, exposure assessment, and risk characterization.
<b>Risk Management</b>	The process of actually trying to reduce risk, e.g., from a toxic chemical, and/or of trying to keep it under control. Risk management involves not just taking action, but also analyzing and selecting among options and then evaluating their effect.
<b>Secondary Particles</b>	Particulate matter formed in the atmosphere by chemical reactions of gases, particularly sulfur dioxide, nitrogen oxides, ammonia and volatile organic compounds.

<b>Soluble Organic Fraction (SOF)</b>	The organic fraction of diesel particles. Includes heavy hydrocarbons derived from the fuel and from the engine lubricating oil. The term “soluble” originates from the analytical method used to measure SOF, which is based on extraction of particulate matter samples using organic solvents.
<b>Total Carbon</b>	The sum of the elemental carbon and organic carbon associated with diesel particles.
<b>Total Particulate Matter</b>	The total particulate matter emissions including all fractions of diesel particles, i.e. the carbonaceous, organic, and sulfate particles.
<b>Toxicant</b>	A substance capable of causing human injury or damage to living body tissue, impairment to the central nervous system, severe illness, and, in severe cases, death. A poison.
<b>Toxicity</b>	The degree of danger posed by a substance to human, animal or plant life.
<b>Toxicology</b>	Scientific discipline involving the study of the actual or potential danger presented by the harmful effects of substances (poisons) on living organisms and ecosystems, of the relationship of such harmful effects to exposure, and of the mechanisms of action, diagnosis, prevention and treatment of intoxications.
<b>Ultrafine Particles</b>	Particles with diameters smaller than 0.1 µm.
<b>Vital capacity</b>	The maximum volume of air which can be exhaled or inspired during either a forced (FVC) or a slow (VC) manoeuvre.
<b>Volatile Organic Compounds</b>	Hydrocarbon-based emissions released through evaporation or combustion.

**Volatile Organic Fraction**

The organic fraction of diesel particulate matter as determined by vacuum evaporation. It may or may not be equivalent to the SOF fraction. Depending on the exact analytical procedure, the VOF may include the organic material (SOF) as well as some of the sulfate particles which, being composed primarily of hydrated sulfuric acid, are also volatile.

**Volatile Organic Substance**

Any organic substances, mixture of organic substances, or mixture of organic and inorganic substances which have vapour pressures or sums of partial pressures of substances of 0.02 pounds per square inch (one millimeter of mercury) absolute or greater measured at standard conditions of atmospheric pressure and a temperature of 60 degrees Fahrenheit.

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## ACRONYMS AND ABBREVIATIONS

A	Alveolar
AM	Alveolar Macrophages
BALF	Bronchoalveolar Lavage Fluid
BD-AM	Beagle Dogs Macrophages
CAPS	Concentrated Ambient Air Particles
CB	Carbon Black
CFA	Coal Fly Ash
CMD	Count Median Diameter
CNG	Compressed Natural Gas
CO	Carbon Monoxide
COPD	Chronic Obstructive Pulmonary Disease
CP	Coarse Particles
CPC	Condensation Particle Counter
CS	Conventional Sulfur
DECSE	Diesel Emission Control – Sulfur Effects
DEP	Diesel Exhaust Particles
DMA	Differential Mobility Analyser
DMPS	Differential Mobility Particle Sizers
DPF	Diesel Particle Filters
DPM	Diesel Particulate Matter
EAS	Electrical Aerosol Spectrometer
EC	Elemental Carbon
ECG	Electrocardiograph
EELS	Electron Energy Loss Spectroscopy
ELPI	Electrical Low Pressure Impactor
EnTOX	The National Research Centre for Environmental Toxicology
EPA	Environment Protection Authority
ER	Emergency Room
FP	Fine Particles
FVC	Forced Vital Capacity
FEV <sub>1</sub>	Forced Expiratory Volume in 1 Second
GAM	Generalised Additive Modelling
GM-CSF	Granulocyte-Macrophage Colony-Stimulating Factor

HAP	Hazardous Air Pollutants
HBEC	Human Bronchial Epithelial Cells
HC	Hydrocarbons
HEAPSS	Health Effects of Air Pollution on Susceptible Subpopulation
HEI	Health Effect Institute
HRTEM	High Resolution Transmission Electron Microscope
HVCI	High-Volume Cascade Impactor
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ILAQH	International Laboratory for Air Quality and Health
IPL	Isolated Perfused Rat Lung
LAS-X	Optical Laser Aerosol Spectrometer
LS	Low Sulfur
MARK	Mitogen-Activated Protein Kinase
MAS	Mobile Aerosol Spectrometer
MC	Mass Concentration
MCT	Monocrotaline
MI	Myocardial Infarctions
MIU	Medical Institute of Environmental Hygiene
MMAD	Mass Median Aerodynamic Diameter.
MMD	Mass Median Diameter
µg	Micrograms ( $10^{-6}$ grams)
µg/m <sup>3</sup>	Microgram per cubic metre
µm	Micrometres ( $10^{-6}$ metres)
NAAQS	National Ambient Air Quality Standard
NACN	Acetyl Cysteine
NASA	National (US) Aeronautics And Space Administration
NAG	N-Acetyl Glucosaminidase
Nano-TDMA	Nano-Tandem Differential Mobility Analyser
NC	Number Concentration
NF	Nuclear Factor
Nm	Nanometres ( $10^{-9}$ Metres)
NMD	Number Median Diameter
NMHC	Non-Methane Hydrocarbons

NMHC	Non-Methane Hydrocarbons
NO	Nitric Oxide
NO <sub>2</sub>	Nitrogen Dioxide
NOPL	Naso-Oro-Pharyngo-Laryngeal
NO <sub>x</sub>	Oxides of Nitrogen
NYC	New York City
O <sub>3</sub>	Ozone
OECD	Organisation for Economic Cooperation And Development
OFA	Oil Fly Ash
OPC	Optical Particle Counters
PAH	Polycyclic Aromatic Hydrocarbons
Pb	Lead
PDTTC	Pyrrolidine Dithiocarbamate
PEF	Peak Expiratory Flow
PH	Pulmonary Hypertension
PIXE	Particle Induced X-Ray Emission Spectroscopy
PM	Particulate Matter
PM <sub>0.1</sub>	Mass Concentration of Particles with an Aerodynamic Diameter Less Than or Equal to a Nominal 0.1 Micrometres (Ultrafine Particle).
PM <sub>1</sub>	Mass Concentration of Particles with an Aerodynamic Diameter Less Than or Equal to a Nominal 1 Micrometres (Submicrometre Particles).
PM <sub>2.5</sub>	Mass Concentration of Particles with an Aerodynamic Diameter Less Than or Equal to a Nominal 2.5 Micrometres (Fine Particles)
PM <sub>10</sub>	Mass Concentration of Particles with an Aerodynamic Diameter Less Than or Equal to a Nominal 10 Micrometres (Coarse Particles).
Ppm	Parts Per Million
PTFE	Polytetrafluoroethylene
QHSS	Queensland Health Scientific Services
QUT	Queensland University of Technology
ROR	Reactive Oxygen Radicals
SAS	Statistical Analysis Software
SEM	Scanning Electron Microscopy
SHR	Spontaneously Hypertensive Rats

SMPS	Scanning Mobility Particle Sizers
SO <sub>2</sub>	Sulfur Dioxide
SOF	Soluble Organic Fraction
STEM	Scanning Transmission Electron Microscope
SWCL1	Swedish Class 1 Diesel
TB	Tracheobronchial
TEM	Transmission Electron Microscopy
TEOM	Tapered Element Oscillating Microbalance ®
THC	Total Hydrocarbons
TIMS	Thermal Ionisation Mass Spectrometry
TPM	Total Particulate Matter
TSP	Total Suspended Particles
UFCB	Ultrafine Carbon Black
UFP	Ultrafine Particles
UKULSD	UK Ultra Low Sulfur Diesel
ULTRA	The European Project “Exposure And Risk Assessment For Fine And Ultrafine Particles In Ambient Air”. The Studies were Carried Out in Amsterdam, The Netherlands, Erfurt, Germany, And Helsinki, Finland, During Winter and Spring 1998-1999.
ULS	Ultra Low Sulfur
ULSD	Ultra Low Sulfur Diesel
UN/ECE	United Nations/European Commission on The Environment
Urbd	Urban Dust
US EPA	United States Environmental Protection Agency
VOF	Volatile Organic Fraction
WHO	World Health Organization
XPS	X-Ray Photoelectron Spectroscopy
XRF	X-Ray Fluorescence Spectroscopy

## 1. EXECUTIVE SUMMARY

### 1.1 PROJECT

A desktop literature review and analysis of health impacts of ultrafine particles was commissioned by the Australian Department of Environment and Heritage with the following purpose:

- In relation to the health effects of ultrafine particles:
  - establish the state of knowledge; and
  - develop recommendations on the research priorities for Australia to address the information gaps for this issue.
- In relation to the link between the sulfur content of diesel fuels and the number of ultrafine particles in diesel emissions:
  - establish the state of knowledge; and
  - develop recommendations on the research priorities for Australia to address the information gaps for this issue; and
  - develop recommendations on appropriate management responses.

### 1.2 ULTRAFINE PARTICLES: SOURCES, PROPERTIES, AND OCCURRENCE

Ultrafine particles have been defined as those, which are smaller than 0.1 micrometre ( $\mu\text{m}$ ). It should be kept in mind, however, that the divisions between ultrafine and larger particles, similar to the other divisions between different particle size classes, are somewhat arbitrary. On the one hand there are no rigid boundaries created by nature between these size classes, but on the other hand all natural sources (as opposed to laboratory generators) generate particles with a certain range of diameters – polydisperse particles – therefore there is no sharp boundary delineating the contribution of particles from a given particle source.

#### What is known?

1. Particles in the ultrafine, and more generally, submicrometre ranges are generated mainly from combustion, gas to particle conversion, nucleation processes or photochemical processes, with some of them being primary (emitted directly by the source) and some secondary in nature (formed in the air from the precursors emitted by the sources).
2. In terms of numbers, the vast majority of airborne particles are in the ultrafine range. The total mass of the ultrafine particles is, however, often insignificant in comparison with the mass of a small number of larger particles, with which most of the mass of airborne particles is associated. The biggest contribution to the particle surface area in turn, is from particles somewhat above the ultrafine size range.
3. Chemical composition of particles is multi-factorial and depends on particle source as well as post-formation processes. The most important chemical properties of particles include elemental composition, inorganic ions and carbonaceous compounds (organic

and elemental carbon). Primary particles generated from combustion processes consist mainly of soot, which is formed from hydrocarbons burning under fuel-rich conditions. The main chemical constituents of secondary particulate matter in urban locations commonly include sulfuric acid and ammonium sulfate, ammonium and other nitrates and organic compounds. There is also a whole suite of trace metals associated with ultrafine particles. Chemical composition of particles differs significantly from place to place and depends on the type of the local sources, relative contributions from the sources and in the case of internal combustion sources, on the fuels on which the sources operate.

4. Since ultrafine particles reach high concentrations in terms of their numbers but their mass is often very small, measurements of particles in ultrafine or broader, submicrometre ranges are more commonly based on particle number rather than mass concentration. Particle number concentration and number size distribution are usually measured in real time, while particle mass concentration, mass size distribution and morphology, require that samples are first collected, and then the properties investigated under laboratory conditions, using appropriate instrumentation. In general, the instrumentation used for particle number concentration and size distribution measurements is complicated and expensive, as the particles which they investigate, can range down to molecular sizes. Analysis of particle chemical composition is almost entirely conducted using sophisticated laboratory instrumentation, which again, requires that a representative sample be collected.
5. Since the sources contributing to the formation of particles in the ultrafine (and more generally, the submicrometre range) and coarse particle size ranges are different, correlation between fine and coarse airborne particles is frequently absent. Furthermore, the ultrafine particle size range tends to dominate particle number size distribution whereas the coarse particle size range tends to dominate the particle mass size distribution. The degree of correlation between particle number and mass depends on specific local conditions, of which the degree of contribution from different sources is of key importance. In general, from the measurements of particle mass, only limited information, or no information at all can be obtained about particle number and vice versa.
6. Particle number concentration levels in clean environments are usually of the order of a few hundred particles/cm<sup>3</sup>. Clean environments for the purpose of this report are those, which are not influenced by human activities. In urban environments, background particle number concentrations range from a few thousand to about twenty thousand particles/cm<sup>3</sup>. Background concentrations mean the concentrations measured at monitoring stations, which are not influenced by a nearby emission source. Near roads and in the tunnels, vehicular traffic constitutes the most significant urban source of particle number, and particle number concentrations can be ten times higher or more than the background, and can reach or exceed levels of 10<sup>5</sup> particles/cm<sup>3</sup>. This is in contrast to PM<sub>10</sub> and PM<sub>2.5</sub> mass concentrations, which near roads have been shown to be no more than 25 – 30% above background level (calculated as the difference between the maximum at the road and the background levels). Therefore, people living and working in close proximity to an urban arterial road are likely to be exposed to levels of ultrafine particles well above ‘normal’ ambient levels and only to somewhat elevated PM<sub>10</sub> and PM<sub>2.5</sub> levels.

7. Particle number concentration, like the concentration of gaseous pollutants and other surrogates for very small particles, decreases significantly with distance from the road. The relationship between concentration and distance is usually approximated by exponential (or power law) decay. The concentration decreases to the urban background levels at a distance usually not greater than about 300 m from the road.

### **Recommendations for future work**

While there is a general understanding of sources generating ultrafine particles, the range of the particle concentration levels encountered in different environments, the general nature of their chemical composition and the dispersion in atmospheric systems, the two main areas, which require further work include:

1. Developing national and local databases and knowledge of ultrafine particles. This includes local and national:
  - Concentration levels of ultrafine particles and time series of the concentrations.
  - Chemistry of ultrafine particles
  - Source contribution and inventory of primary and secondary ultrafine particles
  - Relationships between different particle metrics (for example particle number and PM<sub>2.5</sub> concentrations). While most commonly there is only a limited relationship or no relationship, in some local environments such relationships may exist.

Since all the above ultrafine particle characteristics vary from place to place and depend on a myriad of local conditions, time and season, this local and national knowledge is essential to conduct local risk assessment and for identifying local control and management strategies.

2. Standardisation of measurement techniques and study designs. There is no standardisation in relation to the instruments or techniques used for investigation of ultrafine particles, and therefore it is often difficult to compare the results reported by different studies. Much more developmental work is needed, to enable cheaper, reliable and repeatable measurements of particle number concentrations in submicrometre range, down to the size of a few nanometres.

## **1.3 ULTRAFINE PARTICLES AND HEALTH**

### **Epidemiological studies**

A number of recent epidemiological studies have addressed the association between ambient ultrafine particle concentrations and mortality or morbidity of urban populations. The number of these studies is however relatively small (8). Moreover, the vast majority of these studies were conducted in the framework of the European “Exposure and risk assessment for fine and ultrafine particles in ambient air” (ULTRA) program by the same teams of researchers from Finland, Germany, and the Netherlands.

The studies reviewed are limited to the investigations of the acute health effects of short-term exposure, which evaluate the impact of day-to-day variation in ambient pollution on health. These studies have correlated morbidity and mortality with daily pollution levels. The general approach of these studies was to compare the effects of ultrafine particles to those of fine particles. Study outcomes span the range from mortality counts of populations to changes in specific parameters or biomarkers in individuals. The main findings of the reviewed studies can be summarised as follows:

1. A study conducted in Germany on daily mortality showed comparable and independent increases in mortality in association with fine and ultrafine particles.
2. The mortality data suggest that fine particles have immediate health effects whereas ultrafine particles have more delayed effects. Immediate effects seem to be attributable to respiratory disease mortality whereas delayed effects are based on an increase in cardiovascular disease mortality.
3. Panel morbidity studies with asthmatic subjects indicate that both fine and ultrafine particles are associated with the respiratory health of the exposed population. A decrease of respiratory function (e.g., peak expiratory flow) and an increase in symptoms and medication use are associated with elevated concentrations of ultrafine particles, independently from fine particles.
4. There is an indication that the acute effects of the number of ultrafine particles on respiratory health are stronger than those of the mass of the fine particles.
5. The acute effects of ultrafine particles on respiratory health of adult asthmatics are more severe than those found for children with asthma symptoms.
6. Inflammatory events in the lungs develop over a time scale ranging from hours to days. It is likely that a lag time exists between exposure to ultrafine particles and the acute respiratory health effects of the exposed population. Cumulative effects over 5 days seem to be stronger than same-day effects.
7. There is an association between exposure to ultrafine particles and cardiovascular morbidity in the population with chronic heart diseases. A panel study among subjects with coronary heart disease indicated that there are independent associations between both fine and ultrafine particles and the probability of specific electrocardiogram changes used as an indicator of myocardial ischemia (ST segment depression). The study report increased odds ratios for 45 subjects ranging from 1.03 to 3.29 with 95% confidence intervals ranging from 0.54 to 6.32.

*In conclusion:* Both fine and ultrafine particles appear to affect health outcomes such as mortality and respiratory and cardiovascular morbidity and appear to do so independently of each other. However, the database at present is too limited (both in numbers of studies and numbers of subjects) and geographically restricted, to allow clear conclusions on the mode of action or generalization to other settings. Further studies are currently under way but more studies in other settings need to be initiated to improve our understanding of ultrafine particles and health outcomes.

## Clinical studies

The following conclusions are based on a limited review of the literature relating to controlled exposure studies.

1. *Dosimetry*: There are inconsistent findings in respect of insoluble ultrafine particles crossing the air-blood barrier of the lung to enter the systemic circulation. Data suggest that for any concentration of ambient air ultrafine particles, populations with moderate to severe chronic obstructive pulmonary disease (COPD) will receive an increased dose of airway/lung-deposited ultrafine particles relative to persons with normal health.
2. *Lung Function*: A modest but statistically significant increase in Airway Resistance across groups of healthy and asthmatic subjects with no significant change in FVC (Forced Vital Capacity) and FEV<sub>1</sub> (Forced Expiratory Volume) following diesel exhaust inhalation was reported in one study. The other studies summarised found no change in lung function parameters following exposure to ultrafine particles. Results of controlled exposure studies of effects of ultrafine particles on lung function as measured by plethysmography and spirometry have not been consistent.
3. *Inflammation*: Chemical speciation may be important to the promotion of an inflammatory airway response by ultrafine particles in normal healthy individuals. Magnesium oxide fume, sulfuric acid aerosol and sodium chloride aerosol appear not to generate an inflammatory response. Inhalation exposure to concentrated ambient air particles, diesel exhaust particulate matter and zinc oxide fume have consistently produced neutrophil infiltration of the bronchial airway. Neutrophil infiltration is an indicator of inflammation. Apart from neutrophil infiltration of the bronchial airways and related markers of inflammation at this site, the studies have not shown a consistent pattern of inflammatory response to ultrafine particle inhalation. Acute inflammation is the body's response to tissue injury and a defence against invasion by an infectious organism. Inflammation involves highly complex and dynamic cellular processes and interactions involving the activation and subsequent control and termination of the inflammatory response. These control processes include control over the rates of synthesis and release of cytokines and other proteins that govern the translocation, activation and function of leukocytes. Blood, bronchial biopsies and bronchoalveolar lavage samples represent a snapshot of this time-varying biological environment. Apparent inconsistencies across studies may be due to differences in the elapsed time between exposure and sample collection.
4. *Plausible biological mechanism for associations between ultrafine particles and health effects*: Findings of upregulation of adhesion molecules on airway vascular endothelial cells amongst healthy subjects and elevated fibrinogen concentrations in peripheral blood provides some support for cardiovascular mortality and morbidity. The absence of any worsening of asthma or any other indicator of inflammation amongst asthmatics is difficult to reconcile with epidemiological studies.

## **Toxicology**

The general conclusions from these studies are that there are complex interrelationships between ultrafine particles and materials adsorbed onto them. There are very few studies, which examine particles on their own. Studies have shown that cytokines are produced by these particles as mediators of the inflammatory response. The complex interrelationships between these cytokines have not yet been demonstrated in appropriately designed experimental studies.

All of the studies available to us demonstrate that the primary determinant of the effect of ultrafine particles is their number and their surface area and not the weight of particles present. This means that the traditional use of PM weight measures is inappropriate in evaluation of the likely biological effects of ultrafine particles.

### **Recommendations for priorities for future Australian studies to address gaps in knowledge in the area of health effects of ultrafine particles in general and in the Australian context**

Knowledge has been gained from the epidemiological studies reported to date and improved scientific understanding of the characteristics and dynamics of ultrafine particles in atmospheric systems compared to a few years ago. Future exposure/epidemiological studies are likely to provide much clearer answers on the associations between ultrafine particles and health outcomes. The design of such studies can now target the specifics of ultrafine particles, which differ from other size fractions and characteristics of ambient particulate matter. The recently published World Health Organization “Guidelines for concentration and exposure-response measurement of fine and ultrafine particulate matter for use in epidemiological studies” (WHO 2002), is an example of the progress in understanding how ultrafine particle specifics should be dealt with in study design to provide the most useful data relevant to study outcomes. Specific recommendations for future health outcome studies include:

1. Studies should be conducted over longer periods of observation. This relates both to studies of acute and to studies of short-term effects. Such studies with longer periods of observation would enable comparisons to be made between periods likely to have high exposure and periods likely to have low exposure. Longer periods of observation would also allow an evaluation of the lag phase between exposure and effect.
2. Study designs and statistical approaches used should be such that the effects related to particle size of interest (<0.1 micrometres) could be decoupled from other characteristics of the particles or complex pollutant mixtures.
3. Studies should be conducted with larger sample sizes. Larger samples would enable better modelling of the role of age, sex, and other demographic and clinical variables in the effect of ultrafine particles on the outcome of interest. In addition, studies should specifically target potentially susceptible subgroups such as for example children and provide information on the susceptibility on relevant groups of the population.

4. Taking note of the reported differences in ultrafine particle concentrations and other characteristics between different geographical locations (resulting from the differences in the local sources, their strength and characteristics, meteorology, topography, etc), as well as the differences in demographic, socio-economic and urban use factors, etc, it is expected that the type and the magnitude of the responses will differ between different locations. Therefore it is recommended that health outcome studies should be conducted in selected places in Australia to quantify the relationship between exposure to ultrafine particles and health outcomes in an Australian setting. The outcomes of such studies would provide appropriate guidance to the decision makers on the most desirable steps in controlling exposure to ultrafine particles in Australia.

#### **1.4 LINK BETWEEN SULFUR CONTENT OF FUEL AND ULTRAFINE PARTICLES**

##### **Nanoparticle formation and emissions in diesel combustion process**

###### *1. Size and concentration of nucleation mode particles*

- The nucleation mode extends through sizes from 3 to 30 nm (0.003-0.03  $\mu\text{m}$ ). This range places nucleation mode particles entirely within the nanoparticle range.
- The maximum concentration of nucleation mode particles occurs at 10-20 nm.
- The nucleation mode, depending on the engine technology and particle sampling technique, typically contains only 0.1-10% of the total PM mass, but it often includes more than 90% of the total particle count. Sometimes the nucleation mode particles represent as much as 99% of the total particle number.

###### *2. Chemical Properties:*

- The nature of nucleation mode particles continues to be the subject of laboratory research.
- Nucleation mode particles and accumulation mode particles are externally mixed across a wide size range, with the chemical components being distributed between two particle types: (a) “less volatile” particles, probably comprised of an elemental carbon core with a small organic component; and (b) “more volatile” particles.
- The volatility of the diesel nanoparticles was found to resemble that of C<sub>24</sub>-C<sub>32</sub> normal alkanes, which implies a significant contribution of lubricating oil to these particles.
- The organic component of total diesel particles and nucleation mode particles appears to be comprised predominantly of unburned lubricating oil, whereas the fuel contribution to the total organic component appears to be relatively small, no more than 20 % and probably much less.

3. *What influences the nucleation mode particles:*

- The nucleation mode is much more sensitive to engine operation, dilution and sampling conditions than is the accumulation mode.
- Cold temperatures favored nucleation mode formation.
- The formation of nanoparticles from particle precursors is influenced by the residence time in the dilution tunnel or exhaust system. Short residence time in the exhaust and sampling system prior to dilution favor nanoparticle formation, while short residence time in the dilution system suppresses nanoparticle growth.
- Storage and release of volatile material in the exhaust system, and prior engine operating history influence the formation of nucleation mode particles.

4. *Control and mitigation:*

- Engine technology effects were observed to be larger than fuel effects for accumulation mode particles, which reflected the observations for particle mass. Fuel effects were observed to be greater than engine technology effects for nucleation mode particles, which reflected the observation for particle numbers.
- Diesel particle filters (DPFs) can effectively remove accumulation mode (solid) particles from the exhaust, but can emit volatile precursors that lead to nanoparticle formation and a large nucleation mode under high load conditions.

**Influence of the fuel sulfur level on nanoparticle formation**

1. Sulfuric acid nanoparticles form as a result of condensation of hydrated sulfuric acid. They are formed from gaseous precursors as temperature decreases in the exhaust system, and after mixing with cold air, be it in the laboratory dilution tunnel or in the ambient air. The diameter of the original nucleus is believed to be about 1 nm.
2. Fuel sulfur enhances nucleation but is not the major component of the nucleation mode.
3. Nanoparticles are more easily formed when fuels with high sulfur content are used, but under some engine conditions, such as light load, nucleation mode formation is independent of fuel sulfur content and heavy hydrocarbons such as those found in lubricating oil could play a major role.
4. Particle number emissions with low sulfur fuels (below 50 ppm) can be up to 100 times lower than with high sulfur fuels (500 ppm), while the particle mass emissions remain almost the same.
5. The reduction of particle number emissions with reduced fuel sulfur content is greater in engines that emit a smaller concentration of accumulation mode particles, smaller mass emissions (new technology vehicles or vehicles with DPFs).
6. The reduction in particle number emission with the reduction of sulfur level will not show any statistically significant change as the vehicles reach a certain age.

## **Recommendations for future investigations**

1. All of the studies except one examined only several vehicles/engines from a limited fleet with most of the engines of a newer design. In order to assess the magnitude of the problem an investigation should be designed to better represent the current and future fleets.
2. New engine designs and after-treatment technologies will present new particle production challenges and solutions. These should be investigated.
3. The reduction of fuel sulfur level is very often accompanied by a significant change in other fuel properties such as aromatic content and volatility. In many of the studies, so far, these parameters were not decoupled. The specific influence of fuel and lubricants should be studied by testing matrices where key parameters of interest, such as sulfur, volatility and aromatic content are decoupled.
4. The effect of not only fuel but also lubricant sulfur content should be studied to determine the influence of this parameter on the formation and emissions of nanoparticles.
5. Further work is required to develop sampling and measurement standards for particle size and number so that comparable datasets can be produced. For this purpose assessment and adaptation of the existing instruments and techniques should be conducted.

## **Recommendations on Management Response**

Since sulfates are just one of several components of the particle mass (PM) emissions, lowering fuel sulfur levels has only limited potential as a means of PM control. The reduction of diesel fuel sulfur levels from 3000 ppm to 500 ppm, as legislated in the U.S. in 1994, yielded relatively large benefits of about 0.04-0.08 g/bhp-hr PM reduction. However, a further reduction of fuel sulfur from the 500 ppm to lower levels has only small incremental PM reduction benefit of about 0.008-0.016 g/bhp-hr. The main benefit in reducing sulfur levels further below 500 ppm towards 50 ppm and lower will be in the reduction in particle number emissions. This reduction will be in the number of particles emitted in the nanoparticle range. Further, to achieve EUROIV and even EUROIII standards of emissions new diesel emission control technologies have to be implemented (aftertreatment devices such as DOC, DPF, etc.). The influence of the sulfur level on the emission of nanoparticles with after-treatment devices is still unknown.

Previous studies have shown that the reduction of nanoparticle emission with the reduction of fuel sulfur level below 500 ppm depends on the age/mileage of the vehicle. In order to assess the scale of the problem for the whole Australian diesel fleet more data are needed on the reduction of nanoparticle emission as a function of age/mileage of the vehicles. The only available scientific data come from a single study, which was conducted on only one type of vehicle present in the diesel fleet (buses).

## **2. PURPOSE AND SCOPE OF THE REPORT**

### **2.1 THE PURPOSE OF THE REVIEW**

A desktop literature review and analysis of health impacts of ultrafine particles was commissioned by Australian Department of Environment and Heritage with the following purpose:

- In relation to the health effects of ultrafine particles:
  - establish the state of knowledge; and
  - develop recommendations for research priorities for Australia to address the information gaps for this issue.
- In relation to the link between the sulfur content of diesel fuels and the number of ultrafine particles in diesel emissions:
  - establish the state of knowledge; and
  - develop recommendations for research priorities for Australia to address the information gaps for this issue; and
  - develop recommendations for appropriate management responses.

### **2.2 THE SCOPE OF THE REVIEW**

As specified by the Australian Department of Environment and Heritage, work to achieve the objectives of this study was summarised as follows:

- Undertake a literature search to identify relevant high quality studies that have been conducted, are underway or are proposed on:
  - the health impacts of ultrafine particles; and
  - the relationship between the sulfur content of diesel fuels and the number of ultrafine particles in diesel emissions.
- Consult widely with stakeholders as needed within Australia and overseas to identify relevant research and obtain views on information gaps and research priorities for both topics.
- Conduct a literature review for both topics, fully referencing all material and using only information from recognised research.
- Recommend priorities for future Australian studies designed to address information gaps on both topics.
- In relation to the link between the sulfur content of diesel fuels and the number of ultrafine particles in diesel emissions:
  - assess the scale of the problem; and

- make recommendations for management responses considered necessary, taking into account the existing framework for managing air quality in Australia.

### 3. PREPARATION AND ORGANISATION OF THE REPORT

#### 3.1 GENERAL COMMENTS ABOUT THE REPORT

To better understand the material presented in this report and its relation to the overall scope of work, two specific points are emphasised:

##### **Terminology used**

The focus of this report is on one specific size fraction of airborne particle matter, which is *ultrafine particles*, defined as those with diameters below 0.1  $\mu\text{m}$ . Particles in this size range are monitored usually in terms of their number concentration (number of particles per unit volume of air). The monitoring instruments available for number concentration monitoring, usually, however, do not have cut-off points of 0.1  $\mu\text{m}$ . This means that they do not measure concentrations of particles that are just within diameters below this value. Most commonly, as explained in section 4.3, they measure concentrations in a much broader window, covering some fraction of the *submicrometre* range (particle sizes below 1 micrometre or even broader than this). Under most circumstances, ultrafine particles constitute the main contribution to the total particle concentration of such windows (see section 4.2). However, it would be technically incorrect to refer to such measurements or investigations as dealing with ultrafine particles only. In most cases, the correct terminology in relation to ambient atmospheric measurements or to exposure and epidemiological studies is particle number concentration within the specified size range investigated. Similarly, in relationship to the investigations of particle formation in the process of diesel combustion and the role of fuel sulfur content on this process, the division most commonly used is not between ultrafine particles and larger, but between particles belonging to nucleation or accumulation modes. This division is directly related to particle formation mechanisms and, consequently, their chemistry. All nucleation mode particles are ultrafine particles: however, only some fraction of accumulation mode particles is within the ultrafine range, while the rest is outside this range. It was required in this report that correct terminology was to be used to avoid confusion on one hand; but, on the other hand, it was also required that the role of ultrafine particles, within the overall size windows investigated and in relation to different modes was clearly explained.

##### **Exclusion from the report**

- Since the focus of the report is on ultrafine particles, or as explained above, in a more general sense, on particle number concentration, studies on particle mass concentrations, most commonly,  $\text{PM}_{10}$  or  $\text{PM}_{2.5}$  and health effects due to exposures to these particle size fractions are not discussed in this report. In a number of places in this report, however, references are made to other particles size ranges for various purposes. For example in chapter 3, a general overview is provided of airborne particle matter and all particle sizes are discussed in this context.
- In the review of the links between health effects and ultrafine particles, studies that did not directly investigate ultrafine particles or their specific, well-defined,

components or fractions or studies that linked health effects to complex mixtures of pollutants are excluded. The authors of this report are of the opinion that even if ultrafine particles were important components of such mixtures, the absence of good characterisation and quantification of the composition of the mixtures means that the effects related to ultrafine particles cannot be decoupled. The effects from ultrafine particles cannot be decoupled from the effects of other components of the mixtures on the one hand, and from possible synergistic (or antagonistic) effects in different components of the mixture on the other hand. These could be different to those caused by ultrafine particles.

## 4. OVERVIEW OF ULTRAFINE PARTICLES

Airborne particulate matter is a complex mixture of particles ranging in size over five orders of magnitude: from molecular dimensions to the sizes that are distinguishable with the naked eye. The particles may be in liquid or solid state and may differ in other physical properties such as shape, surface area, electrical charge, light scattering properties, etc. In addition, there are substantial differences in particle chemical properties and thus in the toxicological and carcinogenic effects they cause. These effects depend primarily on the origin of the particles, and thus on their sources; but they also depend on post-formation processes.

Before discussing health effects related to human exposures to ultrafine particles and the relationship between the sulfur content of diesel fuels and the number of ultrafine particles in diesel emissions – the foci of this report – it was considered important to provide some background information on ultrafine particles and to discuss these particles in the broader context of all airborne particulate matter.

This chapter provides a brief overview of the key aspects necessary to develop a general understanding of airborne particles. It includes classification into different size fractions, source contribution to various size fractions and source identification. It also includes the physical and chemical properties of the particles and their behaviour in atmospheric systems, particularly during transport from the emission sources. A review of measuring methods for ultrafine particles and more generally in relation to particle number concentration is also provided. Finally, the current state of knowledge on ultrafine particles is summarised.

### 4.1 PARTICLE CLASSIFICATION BY SIZE

Various classifications and terminologies have been used to define particle size ranges. The division most commonly used is between **fine** and **coarse particles**, with the boundary between these two fractions being widely accepted as 2.5  $\mu\text{m}$ . Fine particles are smaller than this and coarse particles are larger. **Ultrafine particles** have been defined as those smaller than 0.1  $\mu\text{m}$ . Another classification is into **submicrometre** particles, which are smaller than 1  $\mu\text{m}$ , and **supermicrometre** particles, which are larger than 1  $\mu\text{m}$ . The terminology that has been used in the wording of the ambient air quality standards, and also for characterization of indoor and outdoor particle mass concentrations includes the **PM<sub>2.5</sub>** and **PM<sub>10</sub>** fractions. PM<sub>2.5</sub> (fine particles) is the mass concentration of particles with aerodynamic diameters smaller than 2.5  $\mu\text{m}$ . PM<sub>10</sub> is the mass concentration of particles with aerodynamic diameters smaller than 10  $\mu\text{m}$  (more precisely the definitions specify the inlet cut-offs for which 50% efficiency is obtained for these sizes). There have been references made in the literature to PM<sub>1</sub> or PM<sub>0.1</sub> fractions, which imply mass concentrations of particles smaller than 1 and 0.1 micrometres, respectively. These terms should be used with caution, as particles below 1 micrometre, and, even more importantly, those below 0.1 micrometres, are more commonly measured in terms of their number rather than their mass concentrations (as discussed below). Therefore these terms are misleading.

A classification, which is related to particle formation mechanisms, but which also implies particle size range, is the division of the size distribution into modes, which

correspond to peaks within particle size distributions. The location of such modes is variable, depending on the specific sources and other local atmospheric conditions. Particles can be classified into the following modes:

- **Nucleation mode:** particles in this mode are formed by nucleation of atmospheric gases in a supersaturated atmosphere and their size is of the order of nanometres.
- **Accumulation mode:** particles in this mode originate from primary emissions as well as through gas to particle conversion, chemical reactions, condensation and coagulation.
- **Coarse mode:** particles generated by mechanical processes.

It should be kept in mind that the divisions between the different particle size classes are somewhat arbitrary. On the one hand there are no natural boundaries between these size classes. On the other hand all natural sources (versus laboratory sources) produce particles within a certain range of diameters (polydisperse particles). Therefore there is no sharp boundary delineating the contribution of particles from a given particle source. This argument also extends to effects produced by the particles. For example it cannot be expected that there will be much difference between 0.09 and 0.11 micrometre particles in terms of their composition and behaviour in atmospheric systems, nor in their penetration into the lung or the health effects they cause, despite the second particle being outside the defined ultrafine range.

## 4.2 SOURCES AND CHARACTERISTICS OF AMBIENT PARTICLES

Particles in ambient air are mixtures generated by a large number of sources: motor vehicles, power plants, wind blown dust, photochemical processes, cigarette smoking, nearby quarry operation, etc. A primary particle is a particle introduced from the source into the air in solid or liquid form, while a secondary particle is formed in the air by gas to particle conversion. Particles in the ultrafine and, more generally, in the submicrometre ranges are generated mainly from combustion, gas to particle conversion, nucleation processes or photochemical processes. Some of these are primary and some secondary in nature. Particles in supermicrometre size ranges result mainly from mechanical processes and are generated as primary emissions.

### **Physical properties of particles and the relationships between the properties**

The most important physical properties of aerosol particles include: number concentration, number size distribution, mass concentration, mass size distribution, surface area, shape and electrical charge. To a large extent these are the physical properties of the particles that underlie particle behaviour in the air and ultimately removal from atmospheric systems. The efficiency of various forces acting on particles and the processes to which they are subjected in the air depends strongly on the particle physical properties of which size is one of the most important. The health and environmental effect of particles is strongly linked to particle size. It is their size that is a predictor of the region in the lung where the particles will deposit and of the outdoor and indoor locations to which the particles are able to penetrate or be transported. Sampling of particles and choice of

appropriate instrumentation and methodology is primarily based on particle physical properties.

Particles suspended in the air range in size from about 0.001  $\mu\text{m}$  to about 100  $\mu\text{m}$  (Baron and Willeke, 2001): the former is a molecular size and the latter is the size above which particles sediment rapidly due to gravitational force and are thus removed from the air. Almost all of the sources generate particles with a range of sizes, (so called poly-disperse particles) rather than particles of a single size (monodisperse particles). The spread of particle size distribution is characterised by an arithmetic or geometric (logarithmic) standard deviation. The most common methods of characterisation of a particle distribution are in terms of its size: mean size - which is the average of all sizes, median size - which means equal number of particles above and below this size, or modal size - which is the size with the maximum number of particles. The terms used include: count, number or mass median diameter - which are abbreviated as CMD, NMD or MMD, respectively. MMAD is mass median aerodynamic diameter.

Particles generated by most sources have a lognormal size distribution, which means that the particle concentration versus particle size curve is “normal” (bell shaped) when the particles are plotted on a logarithmic scale. Geometric standard deviation characterises the width of the peak in the distribution. When a single pollution source is investigated and when it operates under steady conditions (for example steady parameters of the combustion process), the size distribution obtained is likely to have one distinctive peak and sometimes additional, usually much smaller peaks. Those peaks are called modes of the distribution. Different emission sources are characterised by different size distributions. However, these distributions are not unique to these particle sources alone. For such mixtures of particles of different size distributions, the measured distribution may or may not display individual peaks from the contributing sources, and thus may or may not be used for source identification (source signature). In many cases however the characteristics of size distribution can be a useful tool in source characterisation

Particle distributions are most commonly presented either in terms of number or mass distributions, or sometimes as surface distributions. The relationships between particle number, surface area and mass are presented in Figure 4.1 based on an example of a typical urban air particle size distribution measured in Brisbane (Morawska, 2000). This relationship was derived using measured particle number size distribution and calculating particle surface and mass distribution assuming their sphericity and density being equal to 1  $\text{g}/\text{cm}^3$ .

The form of presentation of particle size distributions used in the left hand side of Figure 4.1 is quite common, but is somewhat simplistic. It does not properly reflect the logarithmic nature of the distribution. A proper way for presenting particle distributions, and that which is most commonly used in the literature in representing size distributions of aerosols is by plotting in a logarithmic scale  $dN/d\log D_p$ ,  $dA/d\log D_p$ , and  $dM/d\log D_p$ , which represent particle number, surface and mass respectively, per logarithmic interval of size, as shown in the right hand side of Figure 4.1.

It can be seen from Figure 4.1 that, in terms of number, the vast majority of airborne particles are in the ultrafine range. The total mass of the ultrafine particles is, however,

often insignificant in comparison with the mass of a small number of larger particles with which most of the mass of airborne particles is associated. Therefore the peak in the number distribution spectrum appears in the area where there is almost no mass in the mass distribution spectrum and vice versa. The peak in the mass distribution spectrum is where the particle number is very low. Particle surface area, in turn, is the largest for particles somewhat above the ultrafine size range.

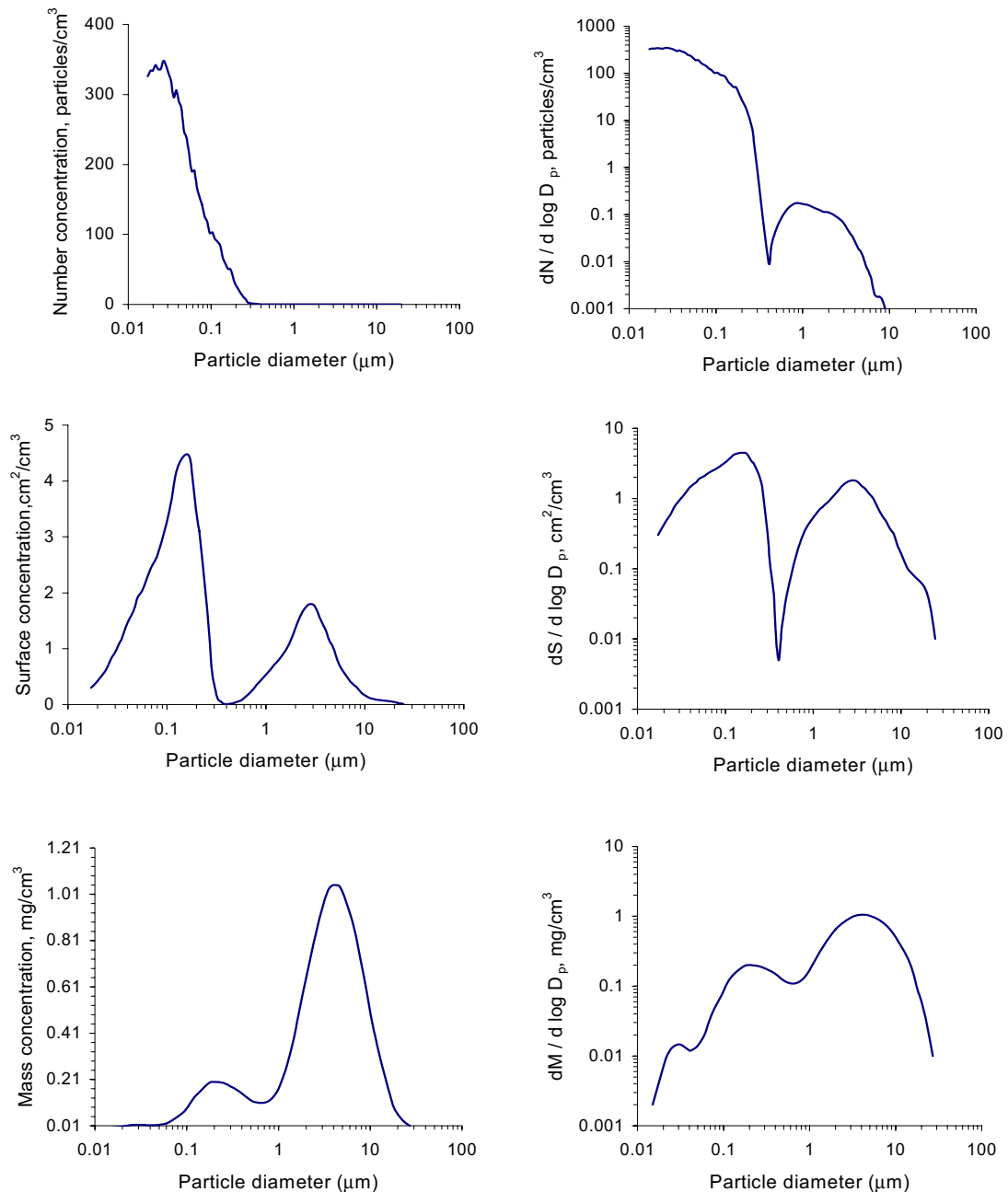


Figure 4.1 Typical - measured in Brisbane - urban air particle number size distribution (top two graphs) - calculated from the number distribution, surface (middle graphs) and mass/ size distributions (bottom graphs), respectively. Two different representations of vertical axis are used for each pair of size distributions.

Particles generated by combustion sources, including vehicle emission, are generally small. A significant proportion of diesel emission particles have diameters smaller than  $0.1\ \mu\text{m}$  (Morawska, 1998; Ristovski, 1998). Gasoline particles are mostly agglomerates ranging from  $0.01 - 0.08\ \mu\text{m}$ . Particles from CNG emissions are smaller than from diesel or even petrol emissions and range from  $0.01-0.07\ \mu\text{m}$ , with majority being between  $0.020$  and  $0.060\ \mu\text{m}$ . (Ristovski, 2000). The majority of particles emitted from biomass burning, which includes controlled burning and uncontrolled fires, are ultrafine, with only a small fraction in the larger size range, and with most of the mass present in particles less than  $2.5\ \mu\text{m}$  in aerodynamic diameter (WHO, 1999). Figure 4.2 presents examples of size distributions of particles generated from various combustion sources including vehicles operating on diesel and petrol, forest fire (vegetation burning) and environmental tobacco smoke.

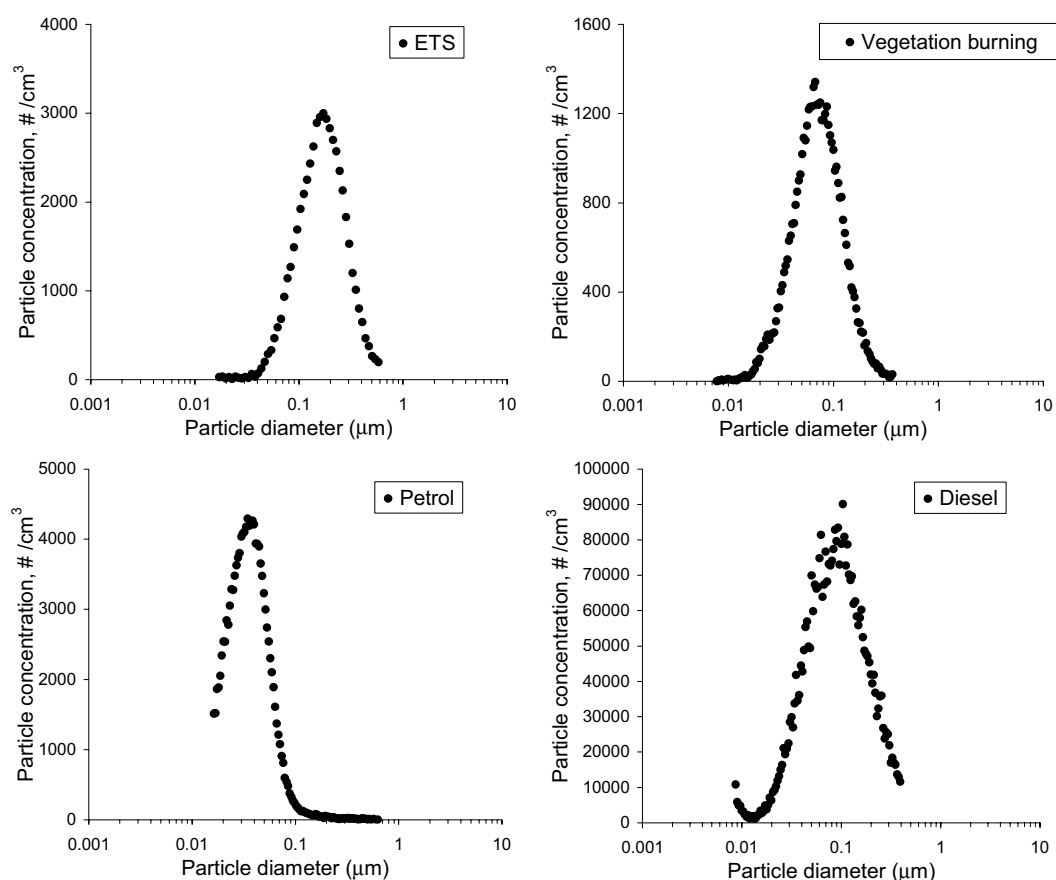


Figure 4.2 Size distribution of environmental tobacco smoke, vegetation burning, petrol smoke and diesel smoke.

As discussed above, particles in different size ranges result usually from different generation processes and only occasionally the same source generates particles with broad size distributions covering both fine and coarse ranges (for example in close proximity to forest fires there are airborne combustion products of the fire as well as large diameter particles that are entrained into the smoke column). Thus different sources contribute to generation of particles in the submicrometre range which is predominant in particle

number, and different sources contribute to larger particles, which predominate in mass. Therefore, it is only occasionally that there is a correlation between fine and coarse airborne particles, or a correlation between particle number and mass. Figure 4.3 presents a scatter-plot of particle data in terms of  $PM_{10}$  and particle number in the submicrometre size range collected over a period of two years in downtown Brisbane (Morawska, 1998). As can be seen, there is no correlation between these two particle characteristics which indicates that different sources contribute to generation of particles in the submicrometre range and to the larger particles. An example of a somewhat better correlation is shown in Figure 4.4 where the linear relationship shown in the lower part of the figure presents the number concentration values (right hand side vertical axis) plotted against simultaneously measured  $PM_1$  mass concentrations (Morawska, 1999). While the correlation appears to be better than for  $PM_{10}$ , still only less than 25 % of the variance is accounted for by assuming a linear relationship. The correlation is better because both  $PM_1$  and particle number are generated by the same sources which are mainly combustion and gas to particles conversion process, with only very little contribution to  $PM_1$  from the sources generating coarse particles. The correlation is still quite poor because the instruments measuring particle number and mass operate on different physical principles, have different averaging times, have somewhat different cut-off points, have different sensitivity to particles in different size ranges, and the TEOM (measuring particle mass) underestimates the mass due to the evaporation of some fraction of semi volatile particles (particle measurement methods are discussed in more detail below).

Various studies conducted on correlation between different particle characteristics, and in particular on correlation between mass of particles in different size ranges, often point out better correlations than those presented above. The degree of correlation depends on specific local conditions, of which the degree of contribution from different sources is of key importance. Better correlations are achieved for conditions when the majority of particles in the fine and coarse size ranges are related to the same source. In general, only limited information or no information at all can be obtained about particle number from the measurements of particle mass and vice versa.

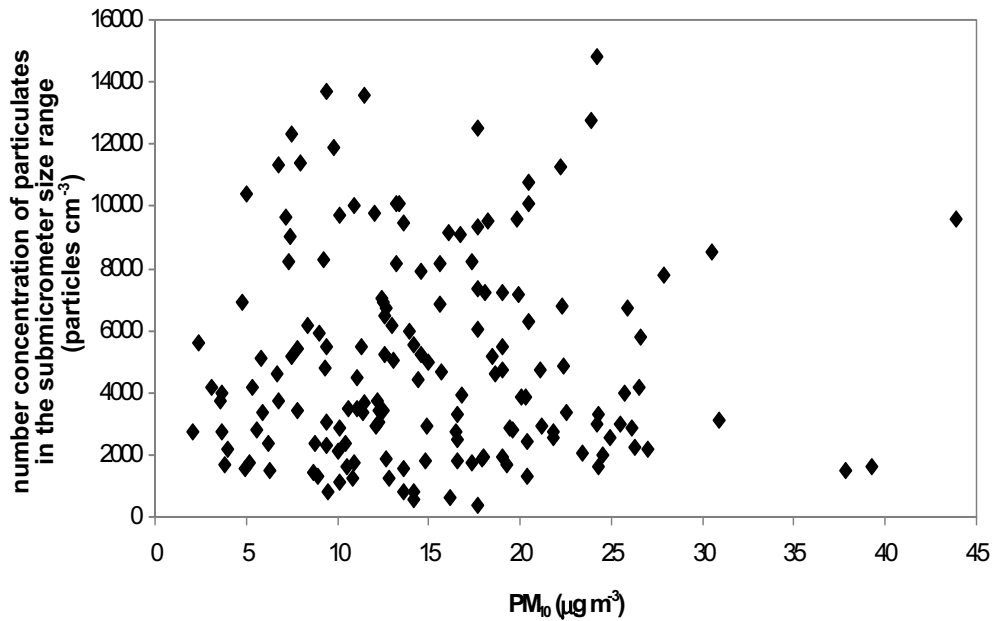


Figure 4.3 Number concentration of particles in the size range 0.016 to 0.626 μm versus PM<sub>10</sub> mass concentration (Morawska, 1998).

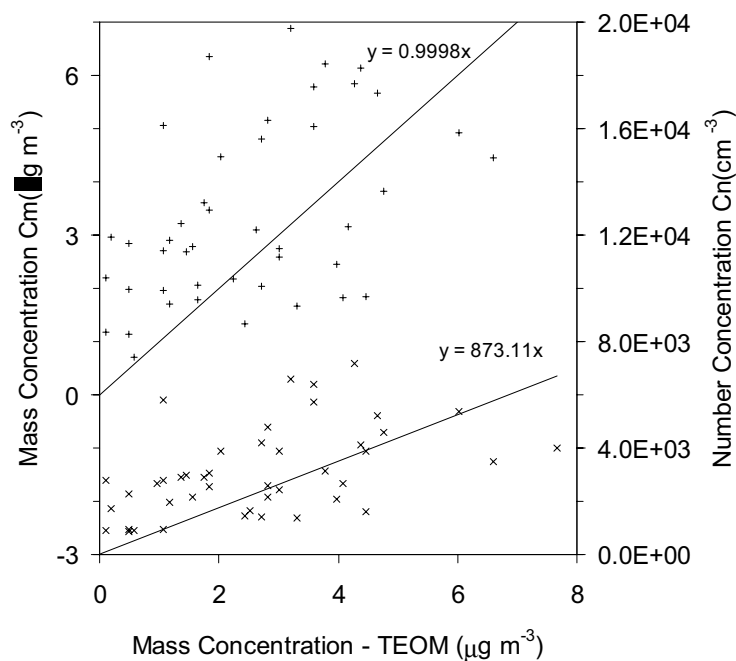


Figure 4.4 Submicrometre mass “+” (left hand side vertical axis) and number concentrations “x” (right hand side vertical axis) derived from SMPS measurement versus PM<sub>1</sub> mass concentration measured by TEOM. (Morawska, 1999)

### Summary of reported particle number concentrations

Over the last few years an increasing number of studies have reported particle number concentrations for various places and environments around the world. Again, in most cases for which particle size distributions were reported, it was also seen that ultrafine particles were the dominant fraction in the total number concentration measurement. However, in all the cases reported, the measurements covered broader windows than the ultrafine particles. Table 4.1 summarizes the reported particle number concentration levels in various places in Australia and Figure 4.5 compares background concentrations with the concentrations in the vicinity of the roads measured in Australia and in other countries in a graphical form for easier comparisons.

It can be seen from Table 4.1 and Figure 4.5 that particle concentration levels in clean environments are of the order of a few hundred of particles/cm<sup>3</sup>. However, under certain circumstances, particularly as a result of particle generation through natural biogenic activities, the concentrations can be higher, up to several thousand of particles/cm<sup>3</sup> (see also Figure 4.6 below). Clean environments for the purpose of this report mean those which are not influenced by human activities.

Particle number concentrations in urban background environments range from a few thousand to about twenty thousand particles/cm<sup>3</sup>. Background concentrations mean the concentrations measured at monitoring stations which are not influenced by local emission sources operating in their immediate proximity.

Table 4.1 Particle number concentration levels in various places in Australia

Location (Reference)	Average particle number concentrations* (particles/cm <sup>3</sup> )	Maximum particle number concentrations (particles/cm <sup>3</sup> )
Cape Moreton (Johnson, 2003)	~ 0.8 x 10 <sup>3</sup>	~4 x 10 <sup>3</sup>
Urban concentrations in six Australian cities (Ayers, 1998)	10 <sup>4</sup> – 5 x 10 <sup>4</sup>	
Immediate vicinity to busy roads (QUT, 2002)**		1.8 x 10 <sup>5</sup>
Brisbane CBD (away from emission sources) (Morawska, 1998)	7.40 x 10 <sup>3</sup>	4 x 10 <sup>4</sup>
Brisbane (150 m downwind from busy road) (Hitchins, 2000)	1.8 x 10 <sup>4</sup>	6 x 10 <sup>4</sup>

\*Particle size ranges differed between studies

\*\*This site could be classified as a road site

In proximity to roads or in tunnels where vehicle traffic constitutes the most significant source of particle numbers, particle concentrations can reach and exceed levels of 10<sup>5</sup> particles/cm<sup>3</sup>. The actual levels depend in the first instance on traffic conditions on the road (traffic flow and mode), and on meteorological conditions and the topography of the site. Concentrations are higher in the street canyons for example, and under calm

conditions with low wind speed. Dispersion of particles is lower under such conditions which results in a build up of higher concentrations.

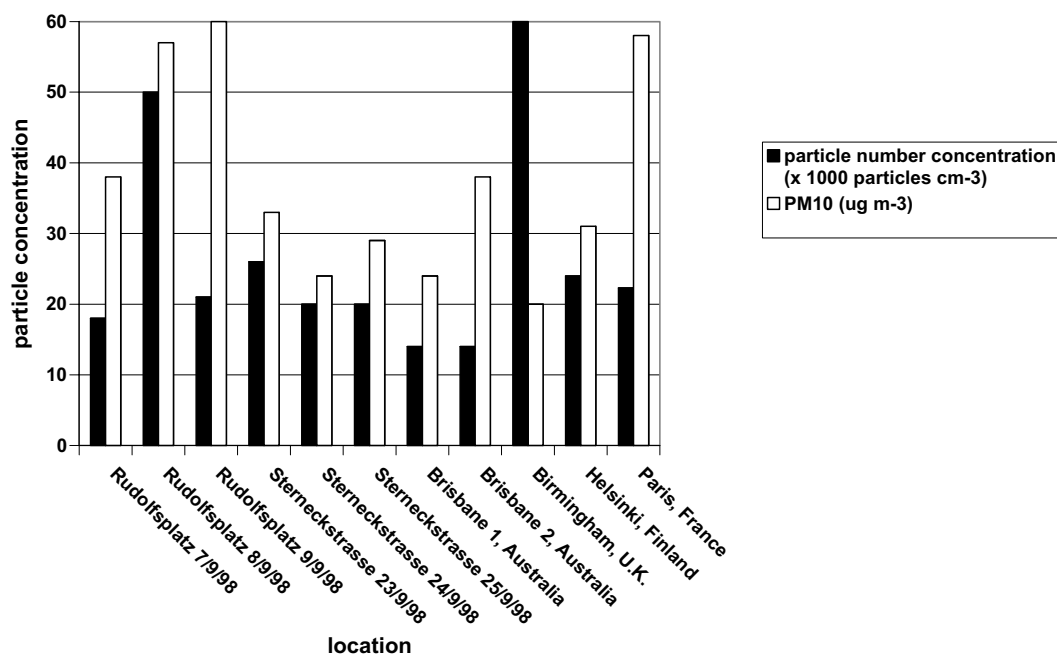


Figure 4.5 Particle number and mass (PM<sub>10</sub>) concentrations measured at the roadside locations (a) and at the non-roadside locations (b) (Morawska, 2003). In the figure: University, Rudolfspatz and Sterneckstrasse are sites in the city of Salzburg, Austria and Gaisberg Mountain and Tamsweg are sites in the Alps, outside Salzburg.

### Chemical composition and its relation to particle formation mechanisms

The chemical composition of particles is multi-factorial and depends on particle sources as well as post-formation processes. The most important chemical properties of particles include:

- Elemental composition
- Inorganic ions
- Carbonaceous compounds (organic and elemental carbon)

Interest in the elemental composition, in general, derives from the potential health effects of heavy elements like lead, arsenic, mercury and cadmium, and the possibility of using the elements as source tracers. Water-soluble ions such as potassium, sodium, calcium, phosphates, sulfates, ammonium and nitrate associate themselves with water in the indoor environments and can also be used for source apportionment. Carbonaceous compounds are composed of organic and elemental carbon. The former can contain a wide range of compounds such as polycyclic aromatic hydrocarbons, pesticides, phthalates, flame retardants and carboxylic acids some of which are tracers for certain sources while the latter is sometimes termed “soot”, “black carbon” and “graphitic carbon”.

Particles arising through different formation mechanisms display significantly different properties both physical (as discussed above) and chemical. In particular, there are substantial differences in the chemistry of primary and secondary particles.

Primary particles generated from combustion processes constitute mainly of soot, which is formed from hydrocarbons burning under fuel-rich conditions. Soot formed under such conditions appears most commonly as an ensemble of ultrafine particles, but the size of the agglomerates can extend up to a few hundred nanometres (Bockhorn, 2000). The formation of soot, which is the conversion of a hydrocarbon fuel molecule containing few carbon atoms into carbonaceous agglomerate containing some millions of carbon atoms, is an extremely complicated process. It is a gaseous-solid phase transition where the solid phase exhibits no unique chemical and physical structure. Therefore, soot formation encompasses chemically and physically different processes, including formation and growth of large aromatic hydrocarbons and their transition to particles, the coagulation of primary particles to larger aggregates, and the growth of solid particles by picking up growth components from the gas phase. The above-mentioned processes constitute the formation of the bulk of soot. In addition, numerous other processes decide on the “fine structure” of soot. More details on the mechanisms of soot formation are discussed by Bockhorn (2000).

Secondary particles are generated through the following processes (Baron and Willeke, 2001; Bockhorn, 2000): (i) gas-phase chemical reactions occur involving specific precursors - gases produce low-volatility products which are capable of homogenous nucleation to form new particles which are of molecular sizes that can then increase in size by coagulation and are captured by pre-existing ambient particles; (ii) low-volatility gas-phase reaction products condense onto pre-existing ambient particles - the so-called heterogeneous nucleation process. While homogenous nucleation may potentially increase both the number and the mass of aerosol particles per unit volume in the atmosphere, heterogenous nucleation can only increase the mass. Interest in the phenomena of secondary particles and the need to develop a good understanding of the mechanisms leading to the formation of these particles has significantly increased along with the realisation of the effect of sulfur content in diesel fuels on formation of secondary sulfuric particles of nanometre sizes (this process is described in more detail in chapter 6). What follows is a general overview on secondary particle formation.

The main chemical constituents of secondary particulate matter in urban locations commonly include sulfuric acid and ammonium sulfate, ammonium and other nitrates and organic compounds (Derwent, 2000). The sulfur and nitrogen containing secondary particle constituents are largely derived from the processes occurring during combustion of fuel containing sulfur and through photochemical oxidation of man-made  $\text{SO}_2$  and  $\text{NO}_x$  precursors. In contrast, the organic constituents appear to have been derived from natural biogenic precursors. The natural biogenic hydrocarbons play an important role in the formation of tropospheric aerosols. The sunlight driven photo-oxidation of high-molecular weight hydrocarbons has been shown to produce low vapour pressure reaction products that partition between the gaseous and aerosol phases. In the aerosol phase these reactions products are known as secondary organic aerosols. Of the natural biogenic hydrocarbons, terpenes have been shown to be effective sources of SOAs (Hoffmann, 1997), while of the man-made hydrocarbons, aromatics are the most important sources (Odum, 1996). Figure 4.6 presents changes to

ambient particle concentration and size distribution attributed to particle formation from biogenic precursors. The evolution in particle size distribution of ambient particles was measured deep inside the Brisbane Forest Park approximately 7-8 km away from any anthropogenic source on a sunny day with temperature around 20-25<sup>0</sup> C. It can be seen from the figure that there was a significant increase in particle concentration between the first and subsequent measurements, with a clear peak forming of count median diameter around 0.04  $\mu\text{m}$ . This peak was attributed to particles formed from natural biogenic hydrocarbons in the process of sunlight driven photo-oxidation (Morawska, 1999).

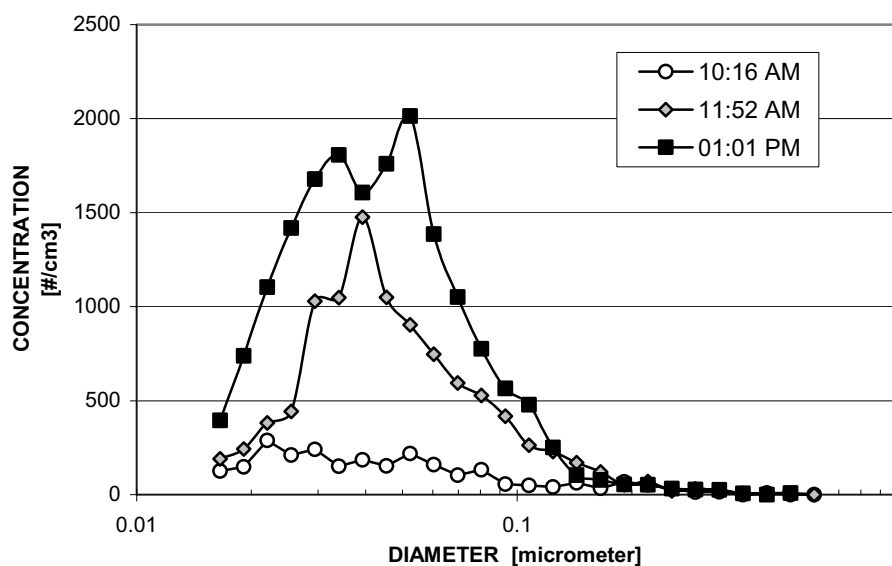


Figure 4.6 Changes to ambient particle concentration and size distribution attributed to particle formation from biogenic precursors measured in the Brisbane Forest Park.

There are still major questions existing in relation to the different mechanisms of the formation of secondary particles, the relative contributions of the different mechanisms and the absolute concentration levels of particles resulting from these processes. For example (Derwent, 2000) summarised the results of modelling of secondary emissions in the UK. A highly sophisticated Lagrangian dispersion model has been used in the UK to describe the formation of particle sulfate by the photochemical oxidation of  $\text{SO}_2$ . A comparison of model particle sulfate with observations for five rural monitoring sites showed overall good agreement. By contrast, formation of secondary organic aerosols is much less understood and the questions asked are of a much more basic nature. It was concluded that the formation of secondary organic aerosols from the photo oxidation of terpenes is likely to be several times greater in magnitude than that from aromatic hydrocarbon photo-oxidation. It was concluded that the major gaps in knowledge in relation to the ambient secondary particles in the UK include:

- Fundamental lack of knowledge as to how much of the ultrafine secondary particulate matter in the UK atmosphere arises by the homogenous or heterogenous nucleation routes.

- There are so few measurements of ultrafine particulate matter in the UK that it would be difficult to check the model performance against observations in any comprehensive manner.

An example of a comprehensive characterisation of size classified particle chemical composition was presented by (Cass, 2000). Measurements of ultrafine particle mass concentration made in seven Southern Californian cities showed that ultrafine particle concentrations in the size range 0.056-0.1  $\mu\text{m}$  aerodynamic diameter (lower stage of the cascade impactor used in the study) average 0.55-1.16  $\mu\text{g}/\text{m}^3$ . The chemical composition of the particles averages (for all the sites) 50% organic compounds (32 – 67%), 14% trace metal oxides (1-26%), 8.7% elemental carbon (3.5-17.5%), 8.2% sulfate (1-18%), 6.8% nitrate (0-19%), 3.7% ammonium (0-9%) ion, 0.6% sodium (0-2%) and 0.5% chloride (0-2%). The most abundant catalytic metals identified in the ultrafine region include: Fe, Ti, Cr, Zn, with Ce also present. The numbers in brackets present the ranges of concentrations for the individual sites, which can be quite large and depend on the local composition of the emission sources.

#### *Combustion emissions – general summary*

Of great concern in relation to health risks is the chemistry of emissions from combustion sources. Under ideal conditions, complete combustion of carbon would result only in generation of carbon dioxide ( $\text{CO}_2$ ) and water. Any products other than  $\text{CO}_2$  are often called products of incomplete combustion and include particulate matter and gases. Combustion particles are mainly of anthropogenic origin. The majority of them in terms of number are in ultrafine size range (while in terms of mass, in the submicrometre range), of complex chemistry, carrying most of the trace elements, toxins, carcinogens, etc generated by the combustion process. Therefore the discussion below focuses on the chemistry of combustion emissions. A more specific discussion on vehicle emissions is provided in the section below.

Combustion of different types of fuels results in emissions of various trace elements, which are present in the fuel material. In most cases there is not just one specific element that is related to the combustion of a particular fuel, but an entire source profile of elements. Table 4.2 presents examples of the most common source profiles of trace elements related to specific combustion sources. For comparison, the crustal elements include Mg, Ca, Al, K, Sc, Fe and Mn.

Trace elements are often co-emitted with other pollutants which can be more or less volatile, such as many hydrocarbons. Since most of the trace elements are non-volatile, associated with ultrafine particles and less prone to chemical transformations, they tend to undergo long-range atmospheric transport and remain in the form in which they were emitted. To follow the trace elements back to their potential emission sources, air parcel movements in the form of calculated backward trajectories are combined with the measured concentrations using various methods (Gao, 1996). Whether elemental signatures can provide meaningful qualitative and quantitative source apportionment will depend on how independent the regional signatures are, as well as on the variability and stability during long distance transport. Elemental concentrations could be highly variable, therefore the concentrations alone are not considered to be reliable regional tracers. Use of elemental signatures to apportion aerosols into major regional

sources requires an understanding of the behaviour of the trace element bearing aerosols during transport, and also of the seasonal variations of the signatures.

Table 4.2 Characteristic elements emitted from various combustion sources. (Morawska, 2002).

Emission Source	Characteristic Elements Emitted
Oil fired power plants	V, Ni
Motor vehicle emissions	Br, Ba, Zn, Fe, Pb (in countries where leaded petrol is used)
Refuse incineration	Zn, Sb, Cu, Cd, Hg
Coal combustion	Se, As, Cr, Co, Cu Al
Refineries	V
Nonferrous metal smelters	As, In (Ni smelting), Cu
Use of pesticides	As
Iron and steel mills	Mn
Plant producing Mn metal and Mn chemicals	Mn
Copper refinery	Cu

All of the combustion sources generate large amounts of volatile and semi-volatile organic compounds. Semi-volatile organic compounds can be present in the air either in the vapour or in particle form (solid or liquid). Exposure to many of the organic compounds emitted to the air has been associated with various types of health effects.

Polynuclear Aromatic Hydrocarbons (PAH), some of which are strongly carcinogenic, are one class of compounds contained in the organic fraction of the fine particulate matter. PAH compounds are synthesised from carbon fragments into large molecular structures in low-oxygen environments, such as occurs inside the flame envelope in the fuel-rich region of the flame structure. If the temperature is not adequate to decompose compounds upon exiting from the flame zone, then they are released into the free atmosphere and condense or are adsorbed onto the surface of particles. Many different combustion systems are known to produce PAH compounds. The most studied PAH is benzo[a]pyrene (B[a]P), which is a physiologically active substance that can contribute to the development of cancer in human cells.

A compilation of the health effects of selected non-heterocyclic PAH has been published by (World Health Organization (WHO)). The PAHs considered in the document included: acenaphthene, acenaphthylene, anthracene, benzo[a]pyrene, benzo[a]anthracene, dibenzo[a,h]anthracene, fluoranthene, naphthalene, phenanthrene, and pyrene. The US EPA introduced a list of the 16 priority PAHs that include: (acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo[a]pyrene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, pyrene (Collier et al 1998).

High concentrations of PAHs have been found in soot generated from wood burning stoves and coal burning stoves (Mumford, 1987). PAHs have also been found in gasoline and diesel soot, and the relative abundance of individual PAH species may be different for different types of soot. This makes it possible to use PAHs as source signatures of different types of fuels on one hand, but may also result in different health effects due to inhalation of emissions from different fuels.

Semi-volatile aliphatic hydrocarbons (ALIs<sub>v</sub>) present in ambient air are n-C<sub>19</sub>, n-C<sub>20</sub>, n-C<sub>24</sub>, n-C<sub>25</sub>, while particle related aliphatic hydrocarbons (ALIs<sub>p</sub>) are n-C<sub>21</sub>, n-C<sub>22</sub>, n-C<sub>29</sub>, n-C<sub>31</sub>, (Colombo, 1999). The aliphatic signal of diesel and gasoline engines consists of a narrow band of C<sub>15-27</sub> n-alkanes maximising at C<sub>20-21</sub>, a very similar pattern to lubricating oils n-C<sub>13-27</sub>, maximising at C<sub>19</sub>. The signal of diesel fuel has a broader spectrum extending to n-C<sub>33</sub>, with a higher proportion of lower molecular weight components (n-C<sub>10-22</sub>, maximising at C<sub>19</sub>) (Simoneit, 1985).

Other types of semi-volatile compounds include guaiacol and its derivatives (e.g., 4-methylguaiacol, 4-ethylguaiacol) that result solely from the pyrolysis of wood lignin. Guaiacol and most of its derivatives appear to be relatively stable in the atmosphere. Therefore, these compounds can serve as unique tracers of wood smoke (Hawthorne, 1992). Another important semi-volatile example is that of 3-nitrobenz[a]anthracene, a strongly carcinogenic compound present in diesel emissions. Organic acids, of which the major constituents are monocarboxylic (emitted from combustion of fossil fuels and biomass) and dicarboxylic acids (Limbeck, 1999), can also contribute to source apportionment and have been linked to health effects.

Table 4.3 presents a summary of the most common organic compounds emitted by a number of combustion sources. This table was compiled from the summary presented by (Cass, 1998).

From the point of view of the effect on human health, the specific physical form of the semi-volatile compounds when they are inhaled could be of significance. They could be either in vapour form, or could be associated with particles of specific sizes. There is very little information available on this aspect, which is due not only to the recency of scientific interest, but also mainly to the difficulties in investigating organic composition of small amounts of mass. The mass of particles in the fine and ultrafine range is very small and, in order to collect sufficient mass for standard organic chemistry analyses, long sampling times are required, which are logistically and financially prohibitive for most studies of exposure or health effects.

Table 4.3 Summary of the most common organic compounds emitted by a number of combustion sources (Cass, 1998).

EMISSION SOURCE	EMITTED COMPONENTS
Environmental tobacco smoke	Nicotine, iso-alkanes, anteiso-alkanes (anteiso-triacontane, anteiso-hentriacontane, anteiso-dotriacontane, iso-tritriacontane),
Road transport Motor vehicle emissions	Hopanes and steranes (present in lubricating oil for diesel and gasoline vehicles, and in diesel) black elemental carbon (present in a higher fraction in diesel emissions) high molecular PAHs: coronene and benzo[g,h,i]perylene (these are less specific)
Tyre dust	styrene/butadiene copolymer, very high molecular weight even number n-alkanes, benzothiazole
Natural gas powered motor vehicles	some PAHs and oxyPAHs, aldehydes
Vegetation burning Wood combustion	Retene, phytosterols, ligmens, phenolic compounds from lignins, diterpenoids from resins.
Small combustion Meat charbroiling Natural gas fired home appliances	Cholesterol, supplemented by fatty acids benzo[a]anthracene
Vegetative detritus	High molecular weight n-alkanes ranging from C <sub>27</sub> – C <sub>34</sub> (high concentration of odd number n-alkanes)

#### *Combustion emissions – vehicles*

Vehicle emissions, like other combustion products, are comprised of pollutants in gaseous and particle forms, which are complex in chemistry, and contain many compounds, which have been shown to affect human health. The main gaseous emissions include hydrocarbons (HC), CO, NO<sub>x</sub>, CO<sub>2</sub>, SO<sub>2</sub> and water vapour. The chemistry of particles originating from vehicle emissions varies and depends on the type of fuel on which the vehicle operates, on its specific composition and on other characteristics, as well as lubricating oil used and its composition. There are thus differences between particles originating from diesel or spark ignition vehicles, the latter including petrol, compressed natural gas (CNG), liquid petroleum gas (LPG) and ethanol fuelled vehicles.

Diesel emission particles are primarily elemental carbon, but they also contain adsorbed or condensed hydrocarbons, hydrocarbon derivatives, sulfur compounds and other materials (Kittelson, 1998). Solvent extractable organic components of diesel aerosols represent 5 – 40% of the particle mass. In general, composition of emitted particulate matter varies greatly and depends on engine technology, test conditions, fuel composition, etc. (Kittelson, 1998). Associated with particles (especially fine and

ultrafine) are many toxins, trace elements and carcinogenic compounds. An example of these is 3-nitrobenzanthrene, a nitrated polycyclic aromatic hydrocarbon (nitro-PAH), which has been shown to have high cancer-causing potential.

Particles emitted from spark ignition vehicles are mostly carbonaceous spherical submicrometre agglomerates consisting of a carbon core with various associated organic compounds. The main components of the particle phase include soot and ash which consist of trace elements such as lead, iron, chlorine and bromine, organic compounds and a low-to-medium boiling fraction of engine oil (Zinbo, 1995). Lubricating oil and other fuel hydrocarbons are the main contributors to emissions of particles of nanometre size (Kittelson, 2002). The sulfate particles present in gasoline engine emissions are mainly from catalyst-equipped vehicles utilising unleaded gasoline (Brodowicz, 1993). Common organic compounds are polycyclic aromatic hydrocarbons (PAHs) such as pyrene, chrysene, benzo[a]pyrene. The semi-volatile fraction of the emissions can be associated either with vapour or with particle phases.

#### *Combustion emissions – wood heaters/woodstoves*

Small combustion devices, such as household cooking stoves and space heaters, are counted in billions throughout the world, providing for the very basic household need for heat (see for example: Environment Australia Technical Report No 5, Emissions from domestic solid fuel burning appliances:

<http://www.ea.gov.au/atmosphere/airtoxics/publications.html>).

The types of fuels and stoves used, however, are very unevenly distributed between developed and developing countries and between rural and urban households. A number of studies characterised the emissions from residential wood burning stoves in developed countries, mainly in the USA. The studies reported that: (1) the particle mass distribution from wood (pine, oak, eucalyptus) combustion have a single mode at approximately 0.1 – 0.2  $\mu\text{m}$  (Kleeman et al., 1999). This means that particle number distribution has its mode below 0.1  $\mu\text{m}$ , thus in the ultrafine range; (2) The particles are compact structures with fractal-like dimensions and contain low mass fractions of volatile compounds (Hueglin et al., 1997); and (3) that operating conditions, such as the amount of air supply, have a strong impact on the particle size distribution and the emission of particle-bound PAHs (Hueglin et al., 1997).

The emissions from wood burning stoves were found to be acidic (pH = 2.8-4.2) (Burnet et al., 1986). Organic compounds were the dominant components of both wood smoke and meat charbroiling smoke. Noticeable elemental carbon was found in wood smoke as well as measurable quantity of Na, K, Fe, Br, Cl, nitrate, sulfate and ammonium. Statistically significant amounts of Na, Al, K, Sr, Ba, Cl, nitrate, sulfate were found in meat charbroiling emissions (Kleeman et al., 1999).

High concentrations of PAHs have been found in soot generated from wood burning stoves and coal burning stoves (Mumford et al., 1987). Although PAHs have also been found in other combustion emissions (gasoline and diesel soot), the relative abundance of individual PAH species may be different for different types of soot. This relative abundance makes it possible to use PAHs as source signatures in receptor modelling for residential wood and coal combustion (Li and Kamens, 1993). Guaiacol and its derivatives (e.g., 4-methylguaiacol, and 4-ethylguaiacol), however, result solely from

the pyrolysis of wood lignin. Guaiacol and most of its derivatives appear to be relatively stable in the atmosphere and therefore these compounds can serve as unique tracers of wood (Hawthorne et al., 1992).

### **Source inventory**

Quantification of emissions from individual pollution sources and generation of emission inventories at local, regional and national levels is important for developing appropriate management and control strategies in relation to air quality. One aim of pollution concentration and emission measurements has been to provide relevant information that would enable a complete inventory of time series to be compiled for all particle size ranges. Estimates of emission inventories and vehicle contribution to the total ambient particle concentration levels have been conducted in many countries and for various urban environments, mainly in relation to TSP or PM<sub>10</sub>, and less so for PM<sub>2.5</sub>. To date, not enough measurements have been conducted and there are very few data available to compile inventories of vehicle emissions for other particle mass size ranges or for particle number emissions.

One example of a completed inventory is the estimation conducted for source emission contribution to different particle mass size ranges in Europe in 1993 (excluding the former Soviet Union) (Holman, 1999). The following sources were identified as the main contributors to PM<sub>0.1</sub>: road transport (41%), production processes (24%) and power generation (17%). By contrast, the contributions of the first two sources to PM<sub>10</sub> were only 17 and 14 %, respectively.

Another example is the assessment conducted by the Airborne Particles Expert Group on behalf of the Department of the Environment, Transport and the Regions, the Welsh Office, the Scottish Office and the Department of the Environment (Northern Ireland) (Airborne Particles Expert Group, 1999) An approach was taken such that inventories for PM<sub>2.5</sub>, PM<sub>1</sub> and PM<sub>0.1</sub> were estimated based on the UK PM<sub>10</sub> monitoring data and from the mass fractions in these size ranges available for different emission sources and fuel types. While only 33 particle spectra were investigated, the report provides a comprehensive analysis of emission trends for the years 1970 to 1996. After analyzing the contributions of individual combustion sources to particle emission inventories, it was evident that in all size fractions motor vehicle emissions were the major contributor out of all other combustion and non-combustion sources in urban areas. With decreasing particle size, the contribution of road transport to the total emissions increased and for PM<sub>0.1</sub> it reached 60%. Contributions from other combustion sources tended to decrease with decreasing particle size. One of the conclusions from the data presented in the report is, that there has been a significant decrease in emissions in the PM<sub>10</sub> and PM<sub>2.5</sub> ranges during the period of time from 1970 to 1996, less in the PM<sub>1</sub> range and very little in the PM<sub>0.1</sub> range. This could be related to the increase in the number of vehicles used, as well as to the lack of strategies for decreasing emissions of the ultrafine fraction of particles.

A source emission inventory constructed for the South Coast Air Basin that surrounds Los Angeles (Cass *et al.*, 2000) estimated the primary ultrafine particle emission rate to be 13 tonnes per day. These emissions were attributed primarily to mobile and stationary fuel combustion sources and were estimated to consist of 65% organic compounds, 7% elemental carbon, 7% sulfate, 4% trace elements, with very small

quantities of sodium, chloride and nitrate. Sources contribution to primary ultrafine particles was also estimated and is presented in Figure 4.7. It can be seen from this Figure that the major contributors to the primary particles are on-road vehicles (43.1%) and stationary fuel use (32.2%).

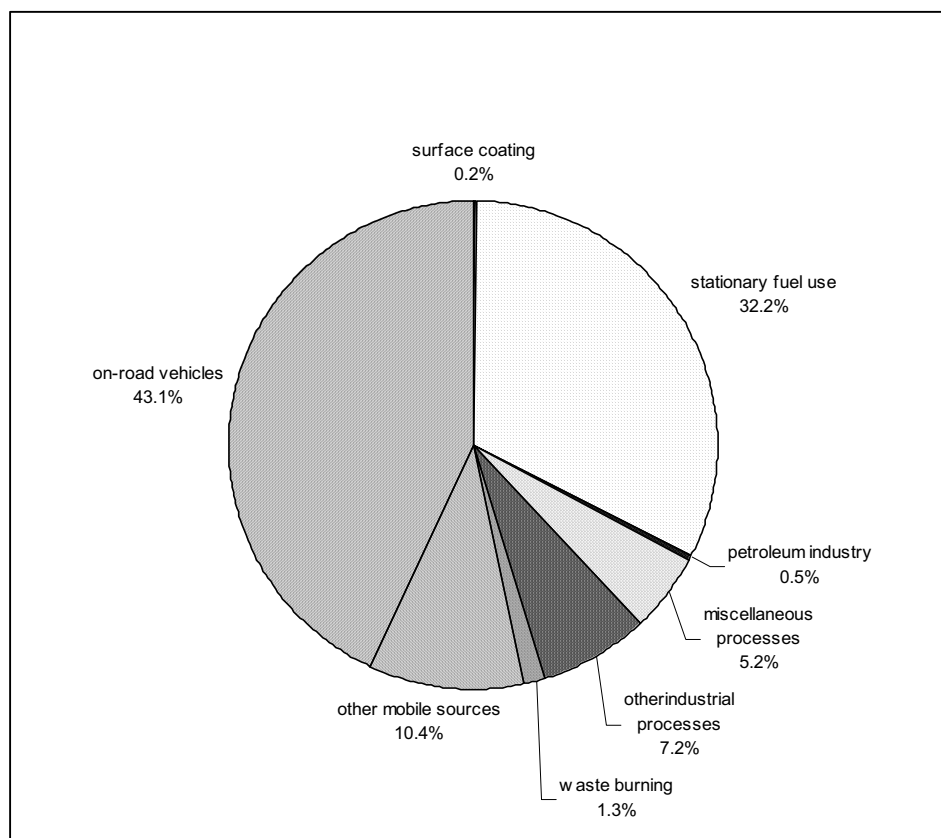


Figure 4.7 Source contributions to primary ultrafine particle emissions in California's South Coast Air Basin (1996) (Cass, 2000).

The authors concluded that the mass emission rate was sufficient to explain the  $0.8 \mu\text{g}/\text{m}^3$  ambient ultrafine particle concentration measured in the Los Angeles area and that the chemical composition distribution in the emissions was generally similar to measured ambient ultrafine particle concentrations once the trace metals in the emissions were converted to the mass of their oxides. It was further concluded that the ambient ultrafine particles in the Southern California atmosphere in the investigated fraction of the ultrafine range may be explained by primary particle emissions plus secondary aerosols nitrate formation at some places and times.

### **Residence time in the air and dispersion of particles from the emission sources**

Following emission, pollutants, including particles, undergo dilution with ambient air, and then undergo various types of changes and transformations during the transport process. Larger particles are gravitationally deposited on the ground soon after emission, while smaller particles can travel larger distances and remain suspended in the air for hours and days after emission. The residence time of larger particles in the air is short and ranges from minutes to hours. The residence time of submicrometre

particles is much longer, and in the lower troposphere is approximately 10 days – due to lack of efficient removal mechanisms (Raes, 2000). Processes such as coagulation, diffusion, and convection transport, govern the behaviour and fate of these particles in the air.

Of significant interest in recent years has been the dispersion of particles from roads, as vehicle emissions constitute the most important source of pollution in most urban environments. A number of investigations have been reported on dispersion of particle mass ( $PM_{10}$  and  $PM_{2.5}$ ), and only a few report on particle numbers. Analysis of the reported studies has shown that, despite significant differences in the designs of the individual studies, clear general trends in relation to particle mass and number concentrations as a function of a distance from the road can be identified (Morawska, 2003):

- There is very little or no gradient in TSP,  $PM_{10}$  and  $PM_{2.5}$  concentrations within the distance from the road. All the reported studies showed that the decrease in mass concentration between these at the minimum distance from the road, and the background levels ranged from 0 to about 25 – 30%. The absence of a gradient means that the road does not contribute in any measurable way to the concentrations of these mass fractions.
- Particle number concentration, like the concentration of gaseous pollutants, decreases significantly with the distance from the road. Decay in particle concentration was approximated by exponential curves in a number of studies, and it was shown that the impact of the road on particle number concentration, while significant in the immediate vicinity of the road, is not distinguishable past about 300 m from the road. It was shown that dispersion is the main factor responsible for the decrease in particle concentration with distance from the road. Modelling of particle concentration using the same approach as that used for the modelling of dispersion of gaseous pollutants (CALINE4), showed that in some cases an even better approximation of the decay could be by power law (Gramotnev, 2003). While this approach does not include coagulation, the effect of coagulation on a relatively broad particle number window was not significant, as shown by excellent agreement between the theory and the experiment.

A practical implication from these findings is that the exposure to the number concentration of airborne particles is significantly increased within the first 100 or so metres of the road, compared to average urban exposure levels, and is reduced to the urban background level at distances greater than about 300 m from the road. On this basis, it is reasonable to assume that people living and working in close proximity to an urban arterial road will be likely to be exposed to levels of ultrafine and submicrometre particles beyond what could be considered ‘normal’ ambient levels.

### **4.3 MEASUREMENT METHODS**

Characterisation of ultrafine particles includes identification of their physical and chemical properties (not discussed in this report are particle biological properties). Physical properties include mass, number, surface area, size distribution and morphology. Some of these properties can be measured in real time, including number and number size distribution, less frequently mass. Other properties, such as mass and

mass size distribution or morphology, require that samples are collected first, and then the properties are investigated under laboratory conditions using appropriate instrumentation. Particle mass of collected samples is determined using microbalances (this method also requires stringent pre- and post-sampling conditions of the filter). Information about particle size, morphology and surface properties is readily acquired using the scanning transmission electron microscope (STEM), while high resolution transmission electron microscopy (HRTEM) allows acquisition of structural information on particles and atomic clusters to sub-0.2 nm resolution.

Particle chemical composition studies are almost entirely conducted using sophisticated laboratory instrumentation which, again, requires that first a representative sample is collected eg (Maynard, 2000; Baron and Willeke, 2001). Following collection and sample preparation, chemical composition of particles is analysed. Particles down to nanometre size diameters can be analysed using electron energy loss spectroscopy (EELS) and X-ray emission in the STEM. Scanning probe microscopy offers the possibility of analysing nanometre diameter particles under ambient conditions, thus removing some of the constraints imposed by electron microscopy. Imaging methods such as atomic force microscopy and near field scanning optical microscopy enable characterisation of specific aerosols. All the above methods are very costly, complicated and not suitable for field application.

The focus of the brief review in this chapter is on methods for characterisation of ultrafine particle physical characteristics. As explained above, particles in the ultrafine size range reach high concentrations in terms of their numbers; however, mass of these particles is often very small. Therefore measurements of particles in ultrafine or broader, submicrometre ranges are most commonly based on particle number rather than mass concentrations.

Due to different physical properties, different methods need to be used for measuring very small particles which are mostly affected by diffusion, and for large particles which are mostly affected by inertia. The techniques used for characterisation of particle number concentrations in the size range up to 1 micrometre can be broadly divided into two groups:

- Measurements of total number concentrations: These include in the first instance optical particle counters and condensation particle counters.
- Measurements of number size distribution: These include a combination of techniques: in most cases the particles are first classified according to size. This classification is based on particle electrical mobility or diffusive properties, and then the size-classified particles are counted by condensation particle counters.

In general, the instrumentation used for particle number concentration and size distribution measurements are complicated and expensive, as the particles, which they investigate are very small, down to molecular sizes (in other words, they are nanoparticles). The instruments used have different properties and in particular differ in the lower size range of particles they can detect, and in general sensitivity. In addition, while there are absolute methods for calibration of the instruments in relation to the size of the measured particles (by using test calibration particles of known sizes), there are no methods for absolute calibration of the instruments for the concentration levels

measured. It is assumed that when all the operating parameters of the instruments are set according to the specifications, particularly the flow rates, the instruments read the correct concentrations. However, it is known that even the same types of properly operating instruments can yield readings differing up to an order of 20% (Rickeard, 1996). The differences between different types of instruments can be much higher due to the variation in the size ranges covered, sensitivity, etc. There is no standardisation in relation to such instruments or techniques used, and therefore it is often difficult to compare the results reported by different studies. Much more developmental work is needed to enable cheaper, reliable and repeatable measurements of particle number concentrations in the submicrometre range down to the size of a few nanometres (WHO 2002).

### **Particle number concentration**

Particle number concentration is measured in real time by optical particle counters (OPCs) based on the principle of light scattered by single particles. This is achieved by directing the aerosol flow across a light beam and by collecting a portion of the scattered light into a detector. Each particle traversing the light beam results in a detector signal at the output, and the number  $n$  of signals during a certain time  $t_p$  is proportional to the particle concentration  $N$  according to the formula:

$$N = \frac{n}{Q \cdot t_p}$$

Where  $Q$  is the air volume flow rate. This technique enables detection of only the particles large enough to deliver a measurable scattering signal. If more than two particles cross the light beam at the same time they will produce one pulse and be counted as a single particle, which results in the so called coincidence error. Occurrence of the coincidence error limits the application of the OPC's to the environments of relatively low number concentrations, usually below  $10^4$  particles/cm<sup>3</sup>. The cut-off size for most OPCs is above 0.1  $\mu\text{m}$ . In order to detect particles smaller than this, condensation particle counters (CPCs) are used. A CPC acts as a particle magnifier in which a liquid (usually an alcohol vapour) condenses on the particles, resulting in their growth to the sizes detectable by an OPC, which follows in a continuous flow arrangement (Agawal, 1980). CPCs usually detect particles down to diameters of 0.01  $\mu\text{m}$ , but frequently down to 0.003  $\mu\text{m}$ .

There is presently no alternative to CPCs for real time particle number concentration measurement. All other existing methods, such as those measuring collective extinction or scattering from an aerosol probe, require information on particle size, shape and composition to derive the true number concentration.

### **Particle size distribution**

Particle size distribution measurements are conducted in relation to particle mass or particle number. Mass distribution measurements involve either sample collection on a multistage impactor followed by gravimetric analyses of the masses collected at different impactor stages, or real time assessment if a quartz microbalance is used. Particle number distribution measurements are conducted using real time methods

based on time of flight measurements (for larger particles), electrical mobility measurements (for smaller particles) and light scattering (both smaller and larger particles).

### *Multistage impactors*

Multistage impactors are the most common instruments used for sizing of airborne particles according to their aerodynamic diameters. Particle mass size distribution is then usually obtained by gravimetric analyses of masses deposited on each impactor stage. There are also multistage impactors available, which use quartz crystal microbalances to provide real time approximation of particle mass distribution (Chuan, 1976). Each impactor stage consists of an orifice and an impaction plate. Between orifice and plate, the flow performs a 90° change of direction. Due to their larger inertia, particles above a certain size impinge on the plate, where they stick, while smaller particles (of smaller inertia) follow the flow to the next stage. The nozzle-plate geometry and the gas pressure at each particular stage define the cut-off diameter. The smallest diameters measured with commercial impactors are of the order of tens of nanometres.

A somewhat different concept is used in the Electrical Low Pressure Impactor (ELPI) (Marjamaki, 2000), in which the aerosol is charged in a diffusion charger and the electric current of the charged particles is measured at each impactor stage. This method is free from the problems associated with erroneous mass measurements due to bad contact between the particles and the surface of the quartz crystal, and has also good time resolution. Consideration, however, has to be given to a few aspects which limit the instrument application under certain conditions or for certain types of aerosols. In particular, the impactor has to be cleaned periodically to avoid modification of the impactor characteristics due to particle pile-up. This constitutes a limitation in the instrument application for strongly agglomerated particles, such as those resulting from diesel emissions, when the operation time between cleaning events is severely reduced (van Gulijk, 2001). Models suppressing this pile-up effect by using sintered impaction plates soaked with oil, have become available. However, this modification has a somewhat negative effect on the sharpness of the impactor cut-offs. Another limitation of the ELPI arises from dependence of the charging and impaction processes on different equivalent diameters. This makes the interpretation of the measured signal difficult in the case of strongly non-spherical particles. Finally, these instruments require larger than standard vacuum pumps which are noisier, and therefore it may be necessary for indoor applications to place the pump outdoors and connected to the impactor by sufficiently long tubing.

Recently, variable pressure impactors have been used as single-stage size spectrometers (Fernández de la Mora, 1996). Impactor models for laboratory applications are capable of size classification of particles with diameters of the order of a few nanometres. Such instruments, however, require very large pumps, which make them rather unsuitable for most indoor applications. Commercial variable pressure impactors are not available yet.

### *Electrical mobility measurement*

The distribution of electrical mobility equivalent diameter is measured by a differential mobility analyser (DMA) (Fissan, 1983). The aerosol enters a cylindrical chamber through an annular slit and is carried downward in laminar flow parallel to the cylinder's axis. High voltage is applied between the walls of the cylinder and a central rod and charged particles are deflected towards the centre rod by a radial electric field. At a particular applied voltage, particles of a specific mobility exit through the slit in the lower part of the centre rod. More precisely, the extracted particles have a narrow mobility distribution, the mean of which is defined by the deflecting voltage applied between the centre rod and the outer cylinder. To obtain the size distribution, the number concentration of the exiting particles is measured as a function of the applied voltage. If the charge distribution of the particles is known, the size distribution can be calculated from this function. A variety of DMA models are available on the market. The most common application of this technology is in the Differential Mobility Particle Sizers (DMPS) or Scanning Mobility Particle Sizers (SMPS), which consist of a diffusion charger, a DMA and a condensation particle counter (CPC). The deflecting voltage is automatically scanned in a programmed manner, and the CPC response is measured as a function of the voltage. This function is automatically converted to the particle size distribution by a software algorithm. The main difference between the DMPS and SMPS systems is in the manner in which the deflection voltage is scanned. The SMPS system continuously ramps the voltage while the DMPS system scans the voltage in a series of steps. To record mobility distribution takes less than a minute with an SMPS system and several minutes with a DMPS system which provides more precise size distribution data. The inlets of commercially available systems are usually equipped with impactors with a cut-off smaller than 1  $\mu\text{m}$ . This guarantees a well-defined maximum size which is required for data reduction.

Different data reduction algorithms have been applied in these systems, leading to significantly different results. The size distributions obtained with them must therefore be regarded as approximations.

#### **4.4 SUMMARY OF STATE OF KNOWLEDGE OF MEASUREMENT AND TECHNOLOGY IN RELATION TO ULTRAFINE PARTICLES**

Ultrafine particles have been defined as those which are smaller than 0.1 micrometres. It should be kept in mind, however, that the divisions between ultrafine and larger particles, similar to the other divisions between different particle size classes, are somewhat arbitrary. On the one hand there are no naturally - occurring boundaries between these size classes, and, on the other hand, all natural sources (versus laboratory generators) generate particles with a certain range of diameters - polydisperse particles - therefore there is no sharp boundary delineating contribution of particles from particle source.

##### *What is known?*

1. Particles in the ultrafine, and more generally submicrometre ranges, are generated mainly from combustion, gas to particle conversion, nucleation processes or photochemical processes, with some being primary (emitted

directly by the source) and some secondary in nature (formed in the air from the precursors emitted by the sources).

2. In terms of number, the vast majority of airborne particles are in the ultrafine range. The total mass of the ultrafine particles is, however, often insignificant in comparison with the mass of a small number of larger particles, with which most of the mass of airborne particles is associated. Particle surface area, in turn, is largest for particles somewhat above the ultrafine size range.
3. Chemical composition of particles is multi-factorial and depends on particle source as well as post-formation processes. The most important chemical properties of particles include elemental composition, inorganic ions and carbonaceous compounds (organic and elemental carbon). Primary particles generated from combustion processes constitute mainly of soot, which is formed from hydrocarbons burning under fuel-rich conditions. The main chemical constituents of secondary particulate matter in urban locations commonly include sulfuric acid and ammonium sulfate, ammonium and other nitrates and organic compounds. There is also a whole suite of trace metals associated with ultrafine particles. Chemical composition of particles differs significantly from place to place and depends on the type of the local sources, relative contributions from the sources and the fuels on which the sources operate (in relation to combustion sources).
4. Since ultrafine particles reach high concentrations in terms of their numbers although their mass is often very small, measurements of particles in ultrafine or broader, submicrometre ranges are more commonly based on particle number rather than mass concentrations. Ultrafine particle number and number size distribution are usually measured in real time, while mass, mass size distribution or morphology require that samples are first collected and then the properties investigated under laboratory conditions using appropriate instrumentation. In general, the instrumentation used for particle number concentration and size distribution measurements are complicated and expensive, as the particles which they investigate are very small, down to molecular sizes. Particle chemical composition is almost entirely conducted using sophisticated laboratory instrumentation which, again, requires that a representative sample is collected first.
5. Since different sources contribute to the generation of particles in the ultrafine range (more generally, submicrometre range) which predominate particle number, and different sources contribute to larger particles which predominate mass, it is only occasionally that there is a correlation between fine and coarse airborne particles, or a correlation between particle number and mass. The degree of correlation depends on specific local conditions, of which the relative contribution from different sources is of key importance. In general, only limited information, or no information at all can be obtained about particle number from the measurements of particle mass and vice versa.
6. Particle concentration levels in clean environments are usually of the order of a few hundred particles/cm<sup>3</sup>. Clean environments for the purpose of this report mean those which are not influenced by human activities. In urban

environments background particle number concentrations range from a few thousand to about  $2 \times 10^4$  particles/cm<sup>3</sup>. Background concentrations mean the concentrations measured at monitoring stations which are not influenced by a local emission source operating in their immediate proximity. In proximity to roads or in tunnels, where vehicle traffic constitutes the most significant urban sources of particle numbers, particle concentrations can be ten times higher or more, and can reach and exceed levels of  $10^5$  particles/cm<sup>3</sup>. This is in contrast to PM<sub>10</sub> and PM<sub>2.5</sub> concentrations, which have been shown to be no more than 25 – 30% above background level at roads (calculated as the difference between the maximum at the road and the background levels). Therefore people living and working in close proximity to an urban arterial road are likely to be exposed to levels of ultrafine particles well above ‘normal’ ambient levels and only to somewhat elevated PM<sub>10</sub> and PM<sub>2.5</sub> levels.

7. Particle number concentration, like the concentration of gaseous pollutants and other surrogates for very small particles, decreases significantly with the distance from the road, and this decrease is usually approximated by exponential (or power law) decay. The concentration decreases to urban background levels at a distance usually not greater than about 300 m from the road.

#### *Recommendations for future work*

While there is a general understanding of sources generating ultrafine particles, the ranges of the particle concentration levels encountered in different environments, the general nature of their chemical composition and the dispersion in atmospheric systems, the two main areas, which require further work include:

**Developing national and local databases and knowledge of ultrafine particles.** This encompasses local and national:

- Concentration levels of ultrafine particles and time series of the concentrations;
- Chemistry of ultrafine particles;
- Source contribution and inventory of primary and secondary ultrafine particles; and
- Relationships between different particle metrics (for example particle number and PM<sub>2.5</sub> concentrations). While most commonly there is only limited relationship or no relationship, in some local environments such relationships may exist and could be utilised.

Since all the above ultrafine particle characteristics vary from place to place and depend on the myriad of local conditions, this local and national knowledge is essential to conduct local risk assessment and for identifying local control and management strategies.

**Standardisation of measurement techniques and study designs.** There is no standardisation in relationship to the instruments or techniques used for investigations of ultrafine particles, and therefore it is often difficult to compare the results reported by different studies. Much more developmental work is needed, to enable cheaper,

reliable and repeatable measurements of particle number concentrations in submicrometre range, down to the size of a few nanometres.

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