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CHARACTERISATION OF PARTICULATE MATTER EMISSIONS FROM MOTOR VEHICLES

By

COLIN T. WELBURN, B. ENG.

A thesis submitted to the Faculty of
Graduate Studies and Research in partial
fulfilment of the requirements for the
degree of

Master of Engineering

**Ottawa-Carleton Institute of Civil Engineering
Carleton University
Ottawa, Ontario
October 2, 2000
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**"CHARACTERISATION OF
PARTICULATE MATTER
EMISSIONS FROM MOTOR
VEHICLES"**

submitted by **Colin T. Welburn, B. Eng.**
in partial fulfillment of the requirements for
the degree of Master of Engineering

Chair

CIVIL AND ENVIRONMENTAL ENGINEERING
Department

Thesis Supervisor

CARLETON UNIVERSITY
July 3, 2001

ABSTRACT

Fine particulate matter ($PM_{2.5}$) in motor vehicle exhaust is a significant contributor to ambient $PM_{2.5}$ concentrations, which have been linked to human health effects. Characterisation of motor vehicle PM emissions is particularly challenging due to the effects of dilution patterns on the collected PM samples.

Exhaust from gasoline-fuelled motorcycles and one diesel-fuelled bus were studied using a chassis dynamometer and dilution tunnel for different combinations of driving cycle, fuel, ambient temperature, and after-treatment. $PM_{2.5}$ mass emission rates and compositions expressed as elemental and organic carbon (EC/OC) and ionic species were determined from samples collected on filters. A dilution model was developed to assess and compare on-road dilution processes with laboratory conditions.

The current testing methodology for gaseous emissions from light duty gasoline vehicles and PM emissions from heavy-duty diesel vehicles was inadequate for quantitative characterisation of $PM_{2.5}$ emissions from the motorcycles.

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This report is dedicated to my late father Sandy and to my daughter Anna, who taught me that one is never too young to teach nor too old to learn.

Ours the Task Eternal

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LIST OF ABBREVIATIONS

4-Phase FTP: Two sets of the LA4 with a ten-minute soak in between LA4s

ANOVA	Analysis of Variance
APS	Aerodynamic Particle Sizer
bhp.hr:	Brake horse power-hour (Unit of energy)
CBD	Central Business District Driving Cycle
CFV	Critical Flow Venturi
CI	Compression ignition engine (i.e. diesel)
CO:	Carbon Monoxide
CPC	Condensation Particle Counters
CPC:	Condensation Particle Counter
CSS	Catalytic stripper system
CVS:	Constant Volume Sampling
DME	Dimethyl Ether
DMPS:	Differential Mobility Particle Sizer
EC	Elemental Carbon
EDXRF	Energy Dispersive X-ray Fluorescence
EGR	Exhaust Gas Recirculation. Emission Control Device
ELPI	Electrical Low-Pressure Impactor
ERMD:	Emissions Research and Measurement Division (Environment Canada)
FID	Flame Ionisation Detection
FTP:	Federal Test Procedure for testing vehicle emissions
GC	Gas chromatography
GPM:	Emission rate for FTP 75 driving cycle, g/mile
GPP:	Mass of pollutant emitted in each phase, g
HDTC	Heavy Duty Transient Cycle
HDV	Heavy Duty Vehicle
HDV:	Heavy duty vehicle
HEPA	High Efficiency Particulate Air – Standard for PM removal for clean air

HMSA:	Hydroxymethane sulphonic acid
HPLC	High Performance Liquid Chromatography
LA4:	First two phases of light duty FTP.
LDV	Light Duty Vehicle
LII	LASER Induced Incandescence
MMAD	Mass median aerodynamic diameter
MMT	Methylcyclopentadienyl manganese tricarbonyl
MOUDI	Micro-Orifice Uniform Deposit Impactor
NIOSH	National Institute for Occupational Health and Safety
NMHC:	Non-methane hydrocarbons
NO _x :	Collection of nitrogen oxides (NO, NO ₂)
NYCC:	New York City Cycle
OC	Organic Carbon
OEM	Original Equipment Manufacturer
PAH	Polynuclear aromatic hydrocarbons
PART5:	Particulate Matter Emissions inventory model for vehicles developed by the U.S. EPA
PC	Pyrolised carbon
PCV	Positive Crankcase Ventilation System. Emission Control Device
PIXE	Proton Induced X-Ray Emission
PM _x :	Particulate Matter smaller than x diameter in μm (generally 10 or 2.5 μm).
RCP	Remaining Carbon portion
RSD	Relative standard deviation
SFE	Supercritical Fluid Extraction
SFTP	Supplemental FTP Procedures (i.e. US06 cycle)
SGC	Summer Grade Commercial Gasoline
SI	Spark ignition engine (i.e. gasoline)
SMPS:	Scanning Mobility Particle Sizer
SOF	Soluble organic fraction of particulate matter

SVOC:	Semivolatile organic compound. Compounds generally between C_{13} to C_{26} that partition between the gas and particle phase
TB	Tracheobronchial region of respiratory system
THC:	Total Hydrocarbons
TOR	Thermal optical reflectance
TOT	Thermal optical transmittance
TSP:	Total Suspended Particulate Matter
U.S. EPA:	United States Environmental Protection Agency
UDDS:	Urban Dynamometer Driving Schedule
US06:	Supplemental driving schedule to simulate aggressive driving
VOC:	Volatile Organic Compounds. Compounds generally smaller than C_{12} that do not partition to the particle phase

LIST OF SYMBOLS

α	Significance level for identifying statistical significance
ϕ	Equivalence ratio. Ratio of stoichiometric air:fuel ratio to actual air:fuel Ratio
η_{inlet}	Aspiration efficiency of inlet
λ	Ratio of ambient (relative airflow conditions to exhaust flow conditions). Defined as
	1) Mass flux $\left(\frac{\rho_s u_s}{\rho_j u_j} \right)$ for coaxial conditions and
	2) Energy flux $\lambda = \left(\frac{\rho_s}{\rho_j} \right)^{0.5} \frac{u_s}{u_j}$ for cross flow conditions
μ	Viscosity of fluid.
ρ_p	Particle density
A_N	Negative artefact from filtering
A_P	Positive artefact from filtering
C	Cunningham correction factor – accounts for diversions from continuum interactions due to mean free path.
C_0	Initial concentration of component in raw exhaust
C_m	Centreline concentration downstream of jet exit
C_∞	Concentration of exhaust at pipe exit
c_p	Heat capacity (Joules/kg °C)
D_f	Diameter of Fibre
DF	Dilution Factor. Ratio of the concentration of carbon components following stoichiometric combustion to the concentration of carbon components in dilute exhaust stream.
D_j	Diameter of jet
D_p	Diameter of particle

$DR(x)$	Dilution ratio as a function of x. Measure of the mixing from raw exhaust to dilute exhaust. Calculated by mixing relationships or by mass balance of exhaust flow.
D_x	particle diffusion coefficient
E_D	Efficiency of particle collection by Diffusion
GPM_{FTP-75}	Emission rate for FTP 75 driving cycle
$GPP_{(CT, HT, CS)}$	Mass of pollutant emitted in each phase
h_i	Convective heat transfer coefficient
L_p	Length of pipe (m)
L_{pc}	Length of Potential Core
l	Mean free path
m	Mass flow rate (kg/s)
m_{RAW}	Standardized flow rate of raw exhaust in transfer pipe (scfm)
MSE	Mean Sum of Squares for Error
m_V	Standardized flow rate of dilution tunnel venturi (scfm)
n	Sample size
$P_{C,V,T}$	Exponential decay coefficients for temperature (P_T), momentum (P_V) and concentration (P_C).
Pe	Peclet number. The ratio of bulk flow to diffusion flow
$Q_{1,2,3}$	Ident of Quartz filter for OC correction
S	Saturation Ratio. Ratio of vapour pressure to saturated vapour pressure for a condensable species
$srappf$	Studentized range percent point function.
Stk	Stokes Number
T_i	Ident of upstream Teflon filter for OC correction
T_a	Gas temperature at the beginning of the pipe
T_b	Gas temperature at the end of the pipe
T_D	Temperature of dilution air
T_{Raw}, T_0	Temperature of raw exhaust

T_w	Temperature of the wall
T_x	Temperature after mixing
T_∞	Temperature of air flow into which exhaust is mixing
U	Velocity of exhaust at x
U_p	Velocity of exhaust at pipe exit
U_s	Velocity of surrounding flow
V_α	Velocity of tunnel
V_E	Volume of dilute exhaust
V_o	Face velocity
V_{rel}	Relative velocity of between channel and sampling inlet
V_{sam}	Velocity of sampler
x	Distance downstream of exhaust pipe
$X_{(CT, HT, CSI)}$	Distance traveled in each phase
x_{Stk}	Stokes stopping distance

Chapter 1 **Introduction**

Airborne PM is defined as the suspension in air of solid or liquid droplets with diameters in the range of 0.005 to 100 micrometers (μm). At high concentrations, PM can induce such health effects as asthma symptoms, inducing chronic bronchitis, and increasing cardiac and respiratory hospital admissions. Exhaust-generated PM is of particular concern due to its chemical reactivity and its fine size range, which can penetrate deep into the lungs and potentially pass into the blood stream.

Recent health research indicates that PM smaller than 10 μm (PM_{10}) in diameter is potentially toxic at sufficiently high concentrations (Schwartz *et al.*, 1996). The particles that are the most toxic are those in the smallest size range. Recent policy by the Canadian government to declare PM_{10} as a toxic pollutant to be monitored by the National Air Pollution Survey (Government of Canada, 2000) is proof positive that PM_{10} is a health concern that deserves study.

In addition to the concern over the health impacts associated with high PM concentrations, other impacts from high ambient PM concentrations include enhancing climate change, decreasing visibility, soiling of buildings, and contributing to photochemical smog and acid rain. The presence of high concentrations of PM in the exhaust of internal combustion engines leads to degraded engine performance due to fouling of exhaust gas recirculation (EGR) systems and positive crankcase ventilation (PCV) systems.

Both physical and chemical characteristics are used to describe the matrix of suspended particles in the air. Size distribution is a fundamentally important characteristic in PM description. Much of the health impacts and the visibility reduction potential of PM are attributed to the size of the particle. The terminology of particle size has yet to be

standardised. In this paper, particles are categorised into three modes or size ranges. A summary of these modes can be found in Figure 1. Note that there are two distributions: the solid line represents the number-weighted distribution while the dashed line represents the mass-weighted distribution. The distributions in this figure highlight the fact that most of the population of particles are very small in size while most of the mass of a sample collected on a filter is due to fewer large particles.

Figure 1. Particle size distribution by weight and volume. (Kittelson, 1998).

Nuclei mode ($D_p < 50$ nm). These particles can be emitted from processes involving condensation of hot vapours, through soot formation processes in combustion or formed in the atmosphere by gas-to-particle conversion. This range accounts for almost all of the total number concentration of airborne particles, but little of the total mass.

Accumulation mode ($0.05 < D_p < 2.5$ μm). This range is formed by the coagulation of nuclei-mode particles or the condensation of vapours. Particles in this range generally account for most of the aerosol surface area and a substantial part of aerosol mass.

Coarse mode ($D_p > 2.5 \mu\text{m}$). This range of particles is formed mainly by mechanical attrition processes. Coarse PM is composed of soil dust, inorganic and organic carbon compounds and metals.

Three major particle distributions are quoted in the assessment of air quality and emissions. Total Suspended Particles (TSP) include particles up to about $75 \mu\text{m}$. The PM of greatest concern from an environmental perspective is the component smaller than $10 \mu\text{m}$ in diameter (PM_{10}). There is increasing tendency in the literature towards also reporting PM smaller than 2.5 microns in diameter ($\text{PM}_{2.5}$) for reasons discussed below. This paper will concentrate on the accumulation and nuclei modes, collectively referred to as the fine particle fraction.

The concentration of particles in an atmosphere can be reported in different ways, the most common being mass-based or number-based, although surface area has also been used for a basis. The varying measures have come about for two fundamental reasons. The first is that particle measurement devices rely on different methods for detecting particles. Concentrations that have been calculated using filtration techniques (See Section 3.3.1) will report mass concentrations. By contrast, devices such as condensation particle counters or electrical low-pressure impactors (See Section 3.3.3) will count the particles as they pass the detector, resulting in a number concentration.

The second source of division in particle concentration reporting methods rises from the various interests of researchers as they evaluate the gamut of impacts associated with PM. A meteorologist, for example, may be more interested in the aerosol surface area that is available in an urban atmosphere to catalyse photochemical reactions while the occupational health scientist may want to know the number of particles depositing on a miner's lung per hour of exposure.

The preceding discussion of size distributions assumed that the unequivocal measure of size is the particle diameter, which isn't necessarily true. Liquid particles are always spherical due to the surface tension of the droplet. For these particles, diameter is an unequivocal measure of size. Solid particles, however, show a variety of shapes, including, crystalline solids, straight

and curved fibres, flakes and irregular particles (Malissa, 1978). Since much of the particulate matter in ambient air is not spherical, the size is usually designated by its equivalent diameter as determined by its inertial or electrical mobility, which is a function of particle surface area, shape and density.

The residence time of particles in the atmosphere will vary significantly for each size range. The particles with the longest residence times (on the order of about one week) are those in the range from 0.1 to 10 μm in diameter. Particles larger than this are quickly removed by settling while smaller particles are removed by diffusion and coagulation. The typical residence time for 10 nm particles in the atmosphere is approximately 15 min (Kittelson, 1998), with the main mechanism for removal being coagulation, which shifts the particles into the accumulation mode.

1.1 Impacts of Aerosols

Concerns over ambient concentrations of PM have been triggered by studies that have identified a link between mortality and high concentrations of PM_{10} and $\text{PM}_{2.5}$ (Schwartz *et al.*, 1996). Incidentally, the PM portion of vehicle exhaust is considered the one that poses the greatest health concern. Although there have been other concerns associated with particles, including light extinction, acid deposition and contributions to global climate change, this discussion shall focus primarily on health effects associated with PM, followed by an overview of the other possible impacts.

1.1.1 Health Effects

The health effects associated with PM are largely the result of deposition of PM onto lung tissue. The mechanisms that govern deposition of particles onto lung tissue are similar to those that govern filtration (See Section 3.3.1), although there are some fundamental differences. There are two major differences between the nature of the airflow through a filter and the exchange of air in the lung. The first is that while the flow in a filter is unidirectional and can be held constant, the flow of air into the lungs decreases as the air reaches deeper portions of the lungs. In addition, air flow in the lung is *tidal*, with air that is inhaled at the beginning of the breath reaching deeper in to the lungs than air inhaled at the end. Because of

the slow flow of air in the alveolar region, sedimentation (a mechanism that is not a factor in filtration) becomes a dominant deposition mechanism.

Before considering deposition mechanisms, it is necessary to establish a working knowledge of lung terminology. The respiratory system is divided into three regions. The *head* region comprises the portion from the nose/mouth to the larynx. The *tracheobronchial* (TB) region represents the pathways from the larynx down to the terminal bronchioles. The *alveolar* region is the deepest and most sensitive region of the lungs, which extends from the terminal bronchioles to the alveolar sacs.

Particles are deposited onto lung tissue primarily by inertial impaction, sedimentation or diffusion. Each of these mechanisms targets a particular particle range, depending on the effective diameter of the particle, its density, airflow velocity and breathing pattern.

As the air enters the head region by the nose or mouth, it is humidified and passes through a tortuous route past the pharynx and epiglottis to the larynx. The dominant deposition mechanism in this region is inertial impaction. Inertial impaction is the phenomenon of particles continuing in their original direction despite a change of flow and is proportional to the air velocity and particle diameter. For mouth breathing, 20% of 5 μm particles and 70% of the 10 μm particles are removed. For nose breathing, 70% of the 5 μm particles and 100% of 10 μm particles are deposited in the head region (Hinds, 1982). If inhalation rate is increased, the deposition in the head region also increases.

As the air enters the tracheobronchial region, the remaining particles larger than 3 μm are removed by inertial impaction as a result of the airflow splitting into progressive generations of the bronchial system. Particles of 5 and 10 μm aerodynamic diameter are removed at efficiencies of 50% and 90%, respectively (Hinds, 1982, p. 219). Particles smaller than 0.1 μm will also become deposited in this region as a result of diffusion.

Inhaled air enters the alveolar region of the lung through a combination of very slow air flow and diffusion, with the last millimetre of the journey to the alveolar sacs occurring exclusively

by diffusion. The low flow rates in this region result in very long residence times. Particles that deposit in the alveolar region do so by sedimentation and diffusion. Sedimentation occurs when gravitational forces acting on the inhaled particles exceed the forces of flow and buoyancy and as a result, benefits particles with larger diameters. Diffusion is the result of particles moving down a concentration gradient and is increasingly effective at smaller particle sizes.

Figure 2. Human respiratory tract deposition versus particle mass-median aerodynamic diameter (MMAD), including PM_{10} and $\text{PM}_{2.5}$ sampler data (U.S. EPA, 1999a).

A summary of deposition efficiencies versus particle size is shown in Figure 2. This figure shows the predicted deposition fractions of particles in the alveolar region, the tracheobronchial region and the thoracic region (the sum of alveolar and TB deposition) versus the mass median aerodynamic diameter (MMAD). The total deposition line represents thoracic deposition plus deposition in the head region. Generally, health effects may be triggered by particle deposition occurs in the thoracic region. One can see in this figure that

maximum thoracic deposition occurs in two size ranges. The regions peak at 3 μm and 0.01 μm , with maximum deposition rates occurring at 0.01 μm .

The fate of deposited particles in each region varies greatly. Deposited particles in the head region are removed by coughing or sneezing. Particles that deposit in the tracheobronchial region are removed through coughing and movement of the mucous membrane to the epiglottis by cilia (minuscule follicles that line the bronchial walls). Particles deposited in the alveolar region (and to some extent in the TB region) may also be consumed by epithelial cells or macrophages that line the walls of the airway, or be dissolved and absorbed into the bloodstream. These last clearance mechanisms are much slower than the mucociliary mechanisms, which increase the residence times of deposited particles. In addition, ultrafine particles are taken up poorly by microphages, which results in higher probability of penetration through the epithelial cells to the highly sensitive interstitial cells, as well as longer residence times, further increasing their toxicity.

High particle concentrations result in an overloading of these removal mechanisms. Typical conditions associated with over-exposure to particles include bronchitis (restricted air flow in the bronchial due to mucous build-up); asthma (blockage of air to alveolar region or inability of air to transfer to blood); emphysema (thinning and destruction of alveolar walls); and lung cancer (mutation of cells lining the lung passages leading to uncontrolled growth).

There appears to be evidence that deposition isn't the only factor in ultrafine particle toxicity. Other factors that have been suggested are the number of particles and particle surface area per unit mass. The chemical and structural composition of particulate matter may also play a significant role in the potential health impact of particles. Ultrafine particles have a very high surface-to-volume ratio, so that those that are chemically, biologically or catalytically reactive will exert a near maximum effect. Rats exposed to high concentrations of particulate matter were the most likely to develop tumours with fine or ultrafine particles ($<3.5 \mu\text{m}$) and with transition metals bonded to the particulate matter (Health Effects Institute, 1997). It has also been noted that the pulmonary defence against solid particulate matter is weaker than against liquid condensates Mayer *et al.*, 1998).

It also appears that certain substances that are non-toxic as particles in the μm range may be toxic in the nm range. Rats exposed to the same mass of 0.25 μm and 0.02 μm diameter TiO_2 retained more of the smaller particles in the interstitial tissue of the lung and developed marked inflammatory response. Similar results were observed when Teflon was administered in the form of nanoparticles. Modest concentrations of 0.03 μm Teflon fume particles caused acute pulmonary toxicity in rats. Both Teflon and TiO_2 are considered to be biologically inert at larger particle sizes (Kittelson, 1998).

Epidemiological studies have shown that the correlation between health effects and atmospheric particle concentration is increased when fine particle concentration ($\text{PM}_{2.5}$) is used rather than PM_{10} (Schwartz *et al.*, 1996). These health effects may be synergistic with other effects, such as cigarette smoking or industrial exposure. The segments of the population that are most at risk when exposed to high PM concentrations are those with pre-existing diseases, those of with a predisposition to sensitivity, and certain age groups, particularly the very young or very old. These groups are likely to produce responses (acute or chronic) earlier, in a more prominent way or at lower concentrations than would be expected in healthy adults.

1.1.2 Other Effects of PM

Other impacts of PM include visibility attenuation in ecologically sensitive areas such as the Grand Canyon, increased acidic deposition onto heritage structures, and contribution to global climate change. While the impacts of these effects may be substantial, they are very difficult to quantify and relate to specific PM concentrations or emission rates of PM. In addition, the perceived impacts of these effects are not as universal as what is expected from health impacts.

The optical properties of particles influence atmospheric visibility and aesthetic damage. These properties depend on particle size, shape and composition. Particles interact with light by absorption and scattering. Light absorption is due to the carbon content of the particles while light scattering is largely a function of particles that are a similar size to the wavelength of the visible spectrum (0.4 to 0.8 μm). The effects of this scattering of light include haze and reduced visibility.

It has also been noted that PM may have a positive or negative contribution to the greenhouse effect, which may exacerbate climate change. The mechanisms identified, which may reduce the greenhouse effect, include the light scattering phenomena mentioned above and the enhancement of cloud formation by PM acting as a condensation nuclei, thus increasing the albedo of the Earth. Conversely, PM may also contribute to global warming through the increased absorption of solar radiation of soot particles in the atmosphere.

The mechanisms that convert emissions to ambient concentrations of smog components and greenhouse gases are extremely complicated. Assessing the impact of particles on climate change is a very new science and although the monetary impact may be large, it is very difficult to establish a definite link between the cause and effect. Similarly, applying a dollar value to reductions in visibility is controversial. The damages associated with limited visibility and acid deposition are also very difficult to quantify. By contrast, health effects of PM are easy to quantify in terms of hospital admissions and death certificates. Dollar values associated with health effects are abundant and the interest is clearly universal. Thus, the driver for the interest in studying PM and for determining how it can be reduced is the effect of PM on health.

1.2 PM Emission Inventories

Before any effort is made to try to manage PM concentrations in the atmosphere, it is necessary to determine the source of particles and what their relative contributions are to the observed ambient concentrations. In Canada, natural sources were estimated to account for 98% of the total mass of PM_{10} and 94% of the total mass of $PM_{2.5}$ emitted in 1990 at the national level (Government of Canada, 1997). Natural forms of PM are atmospheric dust (composed of entrained earth aggregate – 0.01 to 10 μm), sea salt nuclei (0.05 to 5 μm), and condensed organic compounds emitted from vegetation. Given the contribution of natural sources to the national PM load, efforts to reduce anthropogenic sources would appear to be barking up the wrong tree. What should be noted, however, is that the short residence time of PM in the atmosphere dictates that concentrations are strongly dependent on the proximity to the source. It has been shown that fine PM can occur at very high concentrations in urban microenvironments (Turner, 1997) and that PM from anthropogenic sources, particularly

combustion, is generally smaller in particle size and thus potentially more lethal than PM from natural sources.

Anthropogenic $PM_{2.5}$ is formed from primary emissions of diesel and gasoline engines, fuel combustion in power plants and industrial processes or from secondary atmospheric reactions. These secondary chemical reactions create compounds such as sulphates (from SO_2), nitrates (from NO_x), which then react with gaseous ammonia to form ammonium sulphate, ammonium bisulphate, and ammonium nitrate particles. Volatile organic compounds (VOC) from either natural or anthropogenic sources also react with free radicals to produce nuclei-mode particles.

Presently, emission inventories suggest that engines and vehicles are the principal contributors of fine particles to the atmosphere in urban areas. For example, Schauer *et al.* (1996) estimate that 51 to 69% of fine particles in downtown Los Angeles in 1982 were vehicle related. Because of the propensity of PM_{10} to change in size distribution as a result of particle conversion mechanisms such as coagulation and deposition, and for new PM to form as a result of photochemical reactions, it is necessary that elaborate air-shed models be used to predict their persistence and mutation in the urban atmosphere. Emission inventories are a fundamental component of these air quality models. The development of transportation emission inventories consists of calculating a weighted average of emissions factors (generally expressed in g/mile) for all vehicle classes. The development of emission factors for each vehicle class involves averaging the results of emission testing for a particular class then applying adjustment factors to account for the vehicle age distribution and the presence of high-emitters.

The development of emission inventories for vehicles presents a number of challenges. The first is that the variety of vehicles on the road dictates that emissions data be available for all vehicle types. In addition, the distribution of vehicle types on the road may vary not only from region to region but also between zones in the region. An additional challenge is that emission rates for a particular vehicle are dependent on the fuel type, driving behaviour, emissions

control and ambient conditions, to mention but a few factors. Thus, determining the effect of these factors and which factors are most relevant to the local modelling area is no easy task.

Presently, the model used to predict particle emission rates is a program called PART 5. In spite of the complex mechanisms that drive particulate matter emission, PART 5 is a much simpler model than MOBILE 5, the model for the estimation of the emission of criteria pollutants (CO, NO_x and THC). In particular, the emission factors in PART 5 exhibit no dependence on temperature, altitude or vehicle deterioration (Turner, 1997).

A particular area that requires revision in PART 5 is the data for gasoline engines. According to the model, the carbon portion of PM from all gasoline-powered vehicles is too small to warrant its characterisation into soluble organic fraction and remaining carbon portion. While the emission rates of these components are smaller for gasoline engines, the majority of trips on the road are from gasoline vehicles. In addition, the proportion of particles in the nuclei mode is higher emissions from gasoline vehicles. These factors certainly indicate a need for improved emissions inventories and particulate matter emission models

One of the few sources of data for emissions inventories is laboratory emission testing. In laboratory testing, the vehicle exhaust is mixed with dilution air and drawn through a constant volume sampling system (CVS). The dilution of the exhaust cools and dries the sample to facilitate chemical analysis and allows for the determination of total pollutant mass emitted from the vehicle using a relatively small sample. Unfortunately, PM differs from other pollutants in the fact that its size distribution and chemical composition are linked to the exhaust dilution process. Thus, the study of exhaust-generated PM demands a review of the laboratory dilution system and a comparison of its parameters to the conditions that describe the dilution of exhaust into ambient air.

1.3 Summary of Study

In this study, the effect of driving cycle and fuel-sulphur content on the PM_{2.5} emissions from two motorcycles and the effect of ambient temperature and an oxidative catalytic converter on PM_{2.5} emissions from an urban bus were evaluated. In addition, the exhaust dilution path in

sampling system was compared to the best available estimate of how vehicle exhaust dilutes in the atmosphere to evaluate the performance of the sampling system in measuring PM emission rates.

The interest in motorcycle emissions might seem odd at first, given that motorcycles as a class do not account for a significant share of driving activity in Canada, particularly in the winter. The drive to test the emissions from motorcycles stems from a limited amount of PM emissions data on motorcycles and the unique nature of motorcycle engines compared to more commonly tested vehicles. Motorcycles have only recently come under emissions regulations in Canada and the U.S. Present emissions regulations for motorcycles are limited to HC and CO emission rates. Developing an emission inventory will help to guide future regulation requirements. Motorcycles have simplified emissions controls, if there are any at all, due to physical limitations on where to put them as well as the previous lack of regulation. As a result, motorcycles may provide a baseline by which to compare what effect emissions controls have on the PM emission rates. In addition, the small size of motorcycle engines results in very high dilution ratios, which will reduce the amount of material on the sample and test the limits of detection for the analytical techniques used.

There were two key objectives in evaluating the effect of temperature on bus emission rates. The first was to evaluate the performance of an oxidative catalyst in cold temperatures. The second objective was to produce PM_{2.5} and VOC emissions source characterisation profiles for buses that were representative of an in-service bus in the Ottawa region during both summer and winter. These profiles could then be applied in local source apportionment studies.

This report continues in Chapter 2 with a review of the physical and chemical characteristics of exhaust-generated PM, as well its formation mechanisms and control parameters. Chapter 3 summarises the PM sampling and analysis procedures that are currently used in the vehicle emissions testing environment. The particular procedures for the vehicle emissions testing in this study are outlined in Chapter 4 and the results are presented and discussed in Chapter 5.

Chapter 6 assesses the difference between the dilution path of vehicle exhaust with the atmosphere in the on-road scenario and that of the vehicle exhaust in the laboratory. From these differences, potential differences in the PM emission rate and composition are inferred. The two mixing scenarios were compared through the development of a simple dilution model and the application of heat transfer relationships to estimate exhaust cooling during laboratory testing.

Chapter 2 **Vehicle Exhaust PM**

This chapter will outline the properties of exhaust PM, discuss the mechanisms that form PM, review the factors that affect its formation rate and chemical structure, and conclude with a summary of options for reducing PM emissions. Although there are numerous sources of PM from vehicles, this discussion will focus on exhaust PM exclusively. Other sources of PM (road dust, brake wear, etc...) are largely derived from mechanical processes. Because very little of the PM generated from mechanical processes is in the inhalable range, exhaust PM is of greater importance and interest than the other sources of transportation PM.

2.1 Physical and Chemical Properties of Vehicle Exhaust PM

2.1.1 Size Distribution

Exhaust PM from compression-ignition (diesel) engines and spark-ignition (gasoline) engines share common characteristics. The PM from exhaust is found almost exclusively in the fine range ($<2.5\text{ }\mu\text{m}$), with a bimodal (two peaks) size distribution. These two peaks are considered the nuclei mode nanoparticles ($<50\text{ nm}$) and the larger accumulation mode particles (up to approximately $1.0\text{ }\mu\text{m}$). The relative influence of these two modes depends on the type of engine and operating condition. In general, the mass distribution of PM from diesel engines appears to be lognormal with a single peak (unimodal), with at least 99% of the mass being found in the accumulation mode. The number distribution of diesel PM is more balanced, with 50% up to 99% of particles present in the nuclei mode (Kittelson, 1998). A sample number distribution for a diesel engine is shown in Figure 3.

Figure 3. Number weighted size distribution for 1995 engine (Kittelson, 1998).

The differences between the PM from gasoline and diesel engines are elaborated upon in Section 2.3.1. In general, the PM emissions from gasoline vehicles have an increased proportion of nuclei-mode particles and lower mass emission rates. Mass-weighted size distributions determined from emissions testing of catalyst and non-catalyst gasoline vehicles (Hildemann, 1991) are shown in Figure 4. Note in this diagram that there is a single peak between 0.1 and 0.2 μm in particle diameter with an evident shoulder between 0.03 and 0.05 μm . The peak and the shoulder coincide roughly with the two peaks observed in the number-weighted distribution for diesel PM shown in Figure 3.

Figure 4. Mass distribution of particulate matter from catalyst and non-catalyst gasoline vehicles (Hildemann, 1991).

2.1.2 Particle Composition

In general, exhaust PM consists of a solid core, composed mainly of carbon, sulphates and trace elements. This core is sheathed in liquid material that is composed of condensed organic gases. The carbon core, also known as soot, consists of aggregates of nearly spherical primary particles of diameters in the range of 5-30 nm. Photomicrographs show that diesel soot particles have a very light, fluffy structure, with a bulk density of about 0.07 g/m³ (U.S. EPA, 1993) and range in size from 10 to 1000 nm. The carbon core is formed via processes

discussed in Section 2.2.1. Most of the sulphur in the fuel is oxidised to SO_2 , but a small fraction is oxidised to SO_3 , which leads to sulphuric acid and thence to sulphate aerosol. Metal compounds in the fuel and oil are oxidised in combustion and lead to a small amount of inorganic ash. A small fraction of the fuel and evaporated oil escape oxidation during the combustion process. As the exhaust cools, these species may condense onto the particles generated during combustion or nucleate to form nanoparticles. Figure 5 shows typical relative amounts of these components for PM sampled from a diesel engine.

Figure 5. Typical particle composition for heavy-duty engine exhaust tested in a transient cycle (Kittelson, 1998).

A convenient distinction between material from the solid core and condensed species is the soluble organic fraction or (SOF). The SOF is the fraction of the PM collected on filters that can be extracted through solvents such as benzene or hexane. This fraction is associated with unburned fuel and lubrication oil and it can range from less than 5% to more than 90% by mass (Kittelson, 1998). The factors that affect SOF include engine design, engine condition, operating condition, and ambient conditions.

The next section will discuss the processes that form PM. It is divided between the PM that is formed directly in the combustion chamber (soot formation) and the PM that results from the mixing and cooling of exhaust with the atmosphere (gas-to-particle conversion).

2.2 Particle Formation Processes

2.2.1 Soot Formation

Soot is formed by the conversion of hydrocarbon molecules with carbon chains between 8 and 15 links long into agglomerates of millions of carbon atoms. This process occurs in a time frame of a few milliseconds through an extremely complex series of reactions. It occurs in up to three stages. The first is the *inception* stage, where hydrocarbons are partially oxidised during combustion, forming small radicals that react with one another to form polycyclic aromatic hydrocarbons (PAHs) of molecular weight 500 to 2000. In the *growth* stage, these particles pick up gas phase material or coagulate further to form larger particles in the 50 nm size range. A third stage that may occur, the *oxidation* stage, is discussed later in this section. A schematic of the first two stages of soot formation process is shown in Figure 6.

Because soot is formed during the combustion process, the nature of the combustion will significantly affect the amount of soot produced. In diesel engines, liquid fuel is injected into the combustion chamber during the compression stroke and ignites as the piston reaches maximum compression. This results in two-stage combustion. The first is the almost instantaneous premixed stage, where the fuel that is already vaporised mixes with the air and ignites. The diffusion stage of combustion, where fuel and air diffuse into the flame zone from essentially pure bulk regions, is much slower. In gasoline engines, fuel is vaporised and mixed with the air in the intake manifold so that it is fully mixed before entering the cylinder.

Soot formation occurs in fuel-rich zones, where there is insufficient oxygen to completely oxidise the fuel. It can occur in either a premixed or a diffusion flame. In most premixed combustion conditions, however, the operating fuel-air ratio is much leaner than the critical fuel-air ratio to form soot so little particle formation is expected (although in non-homogeneous pockets, the local fuel air ratio may be rich enough to form soot). In diffusion

flame combustion, the fuel-air ratio runs the gamut from excessively rich to excessively lean. Thus, there is consistently a zone in diffusion flame that produces soot.

Figure 6. Schematic representation of soot formation under premixed combustion mechanisms. (Gülde, 1998)

An additional stage, soot oxidation, also becomes apparent in diffusion flames. This stage occurs at the "top" of the diffusion flame zone, where hot combustion products are rising and leaving the flame. In this stage, the soot agglomerates are attacked by oxygen or combustion radicals, resulting in the decay of particle size. These formation processes are shown in Figure

Figure 7. Schematic representation of soot evolution in laminar diffusion flame (Gülder, 1998).

2.2.2 Gas-to-Particle Conversion

At temperatures above 500 °C PM consists of soot particles alone. Below 500 °C, the particles become coated with adsorbed and condensed high molecular weight organic compounds. In certain conditions, these organic compounds may condense homogeneously into liquid particles with no solid core. These condensed species form the soluble organic fraction (SOF) of PM. As engine exhaust is diluted and cooled, SOF will form by two paths: adsorption onto existing particles or nucleation to form new particles. This section will review the processes that result in the gas-to-particle conversion and will discuss the key factors that decide what form the SOF will take.

The type of gas-to-particle conversion that occurs has a significant effect on the spectra of particle sizes and the chemistry of the PM. Adsorption of SOF onto existing particles increases the size and mass of the PM while nucleation results in a dramatic increase in the number of nanoparticles in the nuclei mode. It is therefore important to determine what factors decide the dominant process that will occur.

The key factors that affect the condensation of material are the saturation ratio of the condensing species; the amount of aerosol surface area available for adsorption; and time spent at condensation-favourable conditions. The saturation ratio (S) is defined as the partial pressure of the gaseous organic species divided by the saturation pressure for that species. If a vapour is in a supersaturated state ($S > 1.0$), condensation should occur. Condensation may also take place at $S < 1$ for droplets in the presence of condensation nuclei and the presence of the right mixing conditions. Conversely, the supersaturated state may increase to values much higher than 1 in the absence of these nuclei and the presence of rapid mixing conditions. Because the condensation of material is not an instantaneous process, time in the highly saturated state will play a significant role in the amount of material condensed.

Adsorption is the process of gaseous material adhering to the surface of the particles. While condensation requires a supersaturated state to occur, adsorption can occur at vapour pressures well below saturation. As adsorption of organics in the exhaust begins, vapour molecules form a single molecular layer by physically binding to surface sites available for attachment. If adsorption continues after the initial layer is formed, more layers of semivolatile OC (SVOC) will adhere to the particle in a process that increasingly resembles condensation.

If saturation ratios are sufficiently high, new particles may form by nucleation. This is even more likely if there is insufficient particle surface available in the exhaust for adsorption to occur. Nucleation is responsible for the formation of the nuclei-mode nanoparticles measured in diesel aerosol. The nuclei mode is frequently observed when exhaust is rapidly diluted under either atmospheric or dilution tunnel conditions (Kittelson *et al.*, 1998b, p. 15).

Nucleation of SVOCs in exhaust may occur either by homogeneous or heterogeneous nucleation. In homogeneous nucleation, vapour molecules form molecular clusters. If the vapour is sufficiently supersaturated, the clusters will become large enough to allow condensation. The cluster will then grow into a particle and continue to increase in size as long as supersaturation continues. Homogeneous nucleation is an "all or nothing" phenomenon that requires saturation ratios in the range of 3 to 4. Below the critical saturation ratio, homogeneous nucleation will not occur. Above the critical ratio, homogeneous nucleation rates will in fact dominate adsorption and condensation phenomena (Kittelson *et al.*, 1998b).

Heterogeneous nucleation, also called nucleated condensation, occurs when there are nuclei already available in the exhaust. In combustion gases, the nuclei around which condensation will occur consist of sulphuric acid and metallic ash. Heterogeneous nucleation can occur at supersaturation values of just a few percent, much lower than the values required for the formation of the homogeneous nuclei. Calculations of saturation ratios associated with hydrocarbons comprising the SOF, suggest that they rarely approach 1.0, and never reach values of 3 - 4 necessary for homogeneous nucleation (Friedlander, 1977). Thus, it is likely that the nuclei-mode particles observed in exhaust are the result of heterogeneous nucleation.

To evaluate the conditions that can result in condensation of semivolatile species during exhaust dilution, let us consider a simple exhaust jet with a single condensable component mixing with cooler air. From the condensation perspective, two conflicting mechanisms are at work in the mixing process. First, the mixing results in a temperature drop, reducing the saturation pressure and favouring condensation. At the same time, the dilution reduces the partial pressure, discouraging condensation.

The path the saturation ratio follows can be determined by comparing the vapour-pressure curve to the dilution path. Provided that the Lewis number (ratio of thermal diffusivity to mass diffusivity) is unity (which is essentially the case for most gas mixtures - Friedlander, 1977, p. 215), it can be shown that the concentration of condensable component (c) and temperature (T) are related by:

$$\frac{c - c_{\infty}}{c_0 - c_{\infty}} = \frac{T - T_{\infty}}{T_0 - T_{\infty}}$$

, where

$c = c_0, T = T_0$ in the exhaust

$c = c_{\infty}, T = T_{\infty}$ in ambient air

This relationship can be plotted as a straight line on a mass fraction versus temperature diagram, as in Figure 8. The vapour pressure curve for the condensable component can be superimposed on the same diagram since partial pressure is proportional to concentration. In this figure, three different source outlet temperatures have been considered. For the condition with the high exhaust temperature, no condensation will occur during the dilution to ambient conditions. For the leftmost initial condition, the dilution line intersects the vapour pressure curve, indicating that condensation may occur, depending on availability of nuclei and mixing rates. The middle line shows the limiting condition.

Figure 8. Air-vapour mixtures at three different source conditions (c_0, T_0) mixing with air.

The processes discussed above have been reviewed through experimental analysis of simple jets exiting into cooler air (Friedlander, 1977). It was found in these experiments that condensation does not occur until some distance downstream and that the region from the end of the nozzle to condensation point is in fact supersaturated. It was also found that the distance from exit to condensation point could be extended by increasing the exhaust temperature or decreasing the concentration of the condensable species. It was also found that the distance could be shortened by inserting fine wires into the mixing region, which accelerated mixing through increased turbulence; or introducing sulphuric acid nuclei, which facilitated heterogeneous nucleation.

It should be noted that this form of analysis does not help to estimate the time that the vapour spends in a supersaturated condition, which is a critical factor in determining the type and degree of condensation that will occur. In addition, tracking the saturation ratios for the matrix of condensable species would be very difficult. Thus, it is important to ascertain what range of dilution conditions will result in condensation.

A common measure of the extent of mixing between a jet and ambient air is the dilution ratio (DR). The DR at a particular distance downstream of an exit pipe is defined as the concentration of an exhaust component at the pipe exit to its diluted concentration. As exhaust dilutes, dilution ratio increases gradually from unity towards infinity. Figure 9 is a plot of the saturation ratio versus dilution ratio for two condensable species in a vehicle exhaust. In this diagram, two hydrocarbons (with boiling points of 610 and 720 K) exiting at two temperatures (480 and 600 K) mix with dilution air at 27 °C.

Figure 9. Effect of saturation ratio for two condensable species at two exhaust temperatures (Kittelson and Dolan, 1980).

It can be seen that the saturation ratio reaches a maximum for dilution ratios from 5 to 50 over this relatively wide range of temperature conditions. This range of dilution ratios will be termed the Critical DR Range as it represents the most favourable conditions for PM formation by condensation. Determining the time that exhaust spends in this critical DR range will help to determine what type and degree of condensation will occur. It should be

noted that this range is arbitrary. Low exhaust temperatures or low ambient temperatures result in increasing the peak saturation ratio, thus widening the range of dilution ratios that can cause condensation.

2.2.3 *Secondary Particulate Matter*

A large fraction of particulate matter emitted from vehicles is not actually emitted as particles but is the result of gas-to-particle conversions or due to gas-phase compounds attaching to existing particles. Particles formed from atmospheric reaction of emitted NO_x , SO_2 and NH_3 produce inorganic PM composed of ammonium nitrates and sulphates. This PM and the PM formed through the conversion of low-volatility organic compounds are considered secondary PM. They are distinguished from the PM formed immediately following exhaust mixing with cool air because their formation can occur hours after emission.

Homogeneous production of the inorganic secondary PM starts with the compound being formed and emitted in the gas phase, then being converted to the aerosol phase by condensation or dissolution. Heterogeneous production requires aerosol precursors such as SO_2 , NO_x , and volatile organic compounds (VOC) first to be dissolved in a liquid aerosol phase, such as water droplets, where they react to produce secondary aerosols. The formation mechanisms are very complex and beyond the scope of this research. Nevertheless, the presence of sulphate in the PM and the potential for these gaseous precursors to form PM after exposure to the atmosphere dictates that their measurement be included in a PM emission survey. Furthermore, the formation of sulphates in exhaust (a key component of exhaust PM) does warrant some discussion.

During combustion, the sulphur in fuel (and a small amount of sulphur from engine oil) is converted almost completely to sulphur dioxide. With exposure to the atmosphere, the sulphur dioxide will react either photochemically or catalytically to form sulphate. However, some of the sulphur in the fuel will be converted directly to SO_3 , which leads to sulphuric acid and sulphate aerosol. Typically, 1.2% to 2.4% of fuel sulphur is converted to SO_3 in combustion (Wark, Warner, Davis, 1998, p. 401). In the PART5 model, it is predicted that 2%

of sulphur in fuel is converted to sulphate immediately and that 12% of sulphur dioxide is converted to "indirect" sulphate in the atmosphere (U.S. EPA, 1995).

Sulphate formation is also enhanced through the presence of certain catalytically active species in the exhaust. Metal oxides in the exhaust, such as those of manganese, vanadium, and iron, have been found to catalytically oxidise SO_2 (Chughthai *et al.*, 1993). Of course, these observations are from experiments that were performed over periods of days with exposure to high catalyst concentrations and are unlikely to account for much sulphate production in the short time frame available in an internal combustion engine. It would be expected that the presence of an oxidative or a 3-way catalytic converter may also enhance the oxidation of SO_2 . SO_2 will also oxidise in the presence of molecular oxygen and steel (Glassman, 1996, p. 397).

2.3 Control Factors in Particulate Matter Emissions

2.3.1 *Compression Ignition versus Spark Ignition*

The proportion of PM that is soot in exhaust from a compression ignition (CI) engine is much greater than that in a spark ignition (SI) engine, owing to the larger fuel rich zone in a diffusion flame (see Section 2.2.1). By contrast, there are significantly higher concentrations of volatile and semivolatile OCs observed in exhaust produced from a spark-ignition engine (due largely to the quenching of the premixed flame near cylinder walls). High concentrations of SVOCs result in higher concentrations of adsorbed or condensed species formed during the exhaust dilution process. If condensation occurs by nucleation, then a high proportion of nanoparticles will be observed. Thus, we expect to see lower mean diameters, higher SOF values, and lower mass and number emission rates for gasoline vehicles compared to diesel vehicles.

These inferences have been confirmed in a number of studies. In general, it has been found that PM emission rates are much higher in both mass and number for diesel engines compared to gasoline vehicles (Moon & Donald, 1997; Norbeck *et al.* 1998). In fact, light-duty diesel engines have been found to emit up to two orders of magnitude more particles than comparable catalyst-equipped gasoline vehicles (U.S. EPA, 1993, Moon & Donald, 1997). Many of these studies have found, however, that number emission rates of gasoline engines

match those of diesel engines at speeds of 120 km/hr (Moon & Donald, 1997). Typical total particle number emission rates for gasoline vehicles are 1×10^{13} to 4×10^{15} particles per mile and 1×10^{14} to 3×10^{15} particles per mile for diesel vehicles. A survey of mass emission rates for vehicles built after 1997 have found they emit PM at a rate of approximately 2.5 - 3 mg/mile while light-duty diesel vehicles had PM mass emission rates of 500 - 800 mg/mile (Norbeck, 1998).

Studies that have calculated the particle mean diameters have also shown that PM from gasoline vehicles is smaller in size than that from diesel vehicles, although there can be quite a large range. It has been found that the volume distributed mean particle size for PM from gasoline vehicles range between 60 nm - 430 nm, while the range for diesel vehicles is 100 - 190 nm (Graskow *et al.*, 1998, Kittelson, 1998). Number weighted size distributions indicate an increased dominance of nanoparticles in gasoline vehicles, with average number-weighted mean diameters between 45 and 60 nm for gasoline vehicles and 90 nm for diesel vehicles (Moon & Donald, 1997)

It should be noted that when comparing PM emissions from diesel engines to those from gasoline engines, it is best if the comparisons are performed on tests that use the same sampling system and analysis procedures. This minimises differences between results that arise from using different dilution ratios, tunnel residence times, ambient conditions and PM collection equipment, all of which will affect the results as shall be explained later in Section 2.4.3.

2.3.2 Engine Design

The design of an engine is a significant factor in the nature of particulate matter emitted. Due to the increasingly strict emission standards imposed on diesel vehicles, mass emission rates of soot have been reduced through improved engine efficiency. The SOF resulting from unburned fuel has been reduced through improved fuel injector nozzle design, increased fuel injection pressure to improve mixing, and optimised injection timing. PM from lubricating oil can be controlled through improved piston ring design and incorporating valve-stem seals. Reductions in lubricating oil consumption also help to reduce hydrocarbon and PM emissions.

The result is that diesel engines today emit little more than 10% of the particle mass observed in engines built 15 to 20 ago (Mayer, 1998).

Although these modifications have been extremely effective in reducing the mass emission rate of soot in diesel engines, they have been less effective at reducing the emission of SVOCs. In other words, the portion of the SVOCs emitted that will condense at the mixing point has not changed while the abundance of condensation nuclei has decreased. Because of the reduced surface area available, these SVOCs will form nuclei-mode particles rather than adhering to accumulation-mode particles. The end result is that the size distribution of particles from new engines will be low in mass and high in number of nuclei-mode particles. The shift to lower mass emission rates and smaller average particle sizes in new engine designs has been observed by many laboratories (Health Effects Institute, 1997). The size distribution of vehicle emissions for three different diesel engines is shown in Figure 10.

Figure 10. Comparison of particle size ranges from three different diesel engines operated at rated speed mode 9. (Data for 1988 and 1991 engines from Bagley et al., 1996 and Baumgard and Johnson) (Health Effects Institute, 1997).

The results show that newer engines produce much higher numbers of nuclei mode particles. Testing conducted as part of the joint European VERT program has noted emission rates of nanoparticles ($D_p < 50\text{nm}$) were six times higher when comparing the PM emissions from a new-technology engine to those an older engine from the same family (Mayer *et al.*, 1998). It should be recalled that these smaller particles are able to penetrate deeper into the respiratory system, which may have an impact of the toxicity of the PM (see Section 1.1.1).

Another problem with the design of low soot engines is that the reduction in PM formation often results in an increase NO_x formation. The design features for low soot engines help to promote the premixed stage of combustion, which is hotter and produces less PM.

Unfortunately, the premixed stage is also more conducive to NO_x production. Thus, low-soot engines do not necessarily present an ideal emission reduction strategy.

New-technology gasoline engines also have lower PM emissions rates, in spite of LDV PM emissions only recently coming under regulation in Tier 1 emissions standards. The standard for PM_{10} emissions for a Tier 1 light duty vehicle is 80 mg/mile. Given that this standard is intended to apply to light-duty diesel vehicles, it is not surprising that most new gasoline vehicles have PM_{10} emission rates that are well below this mark. A sample of PM mass emission rates from a study of 111 in-use vehicles in Denver found that gasoline vehicles built before 1981 have been found to be as high as 95.5 mg/mile compared to gasoline vehicles built after 1996, which were 2.82 mg/mile (Graham, 2000, p. 17). The design factors that have been identified as being the instrumental in lowering PM emission rates are fuel injection, spark timing and improved air-fuel ratio control during acceleration. Although it has not been shown unequivocally in the research, it is expected that new-technology gasoline vehicles are also emitting smaller particles overall compared to their older counterparts.

2.3.3 *Operating Condition*

The three key factors of engine operation that affect PM emissions are the fuel/air (equivalence) ratio, engine load, and the cold start phenomenon. The state of repair of the engine also plays a large part in PM emissions. The effects of these factors shall be discussed in turn.

Equivalence ratio (ϕ) is defined as the ratio of the measured fuel-air ratio to the chemically correct fuel-air ratio. If the mixture is rich ($\phi > 1.0$), there is insufficient air for combustion, leading to incomplete oxidation of hydrocarbons and more soot. In CI engines, the engine is generally run on the lean side ($\phi \approx 0.2-0.5$) of stoichiometric air-fuel ratio, although there will be a region in the diffusion flame zone that is rich enough to form soot. This zone expands with load as more fuel is injected into the cylinder at high loads. By contrast, the equivalence ratio is approximately 1.0 in SI engines for most operations. Transient operations such as

starts, warm-up and high loads are associated with high equivalence ratios. In fact, equivalence ratios may exceed two in cold start conditions (Kittelsohn, 1998)

It has been found that in addition to increased number and mass emission rates at high equivalence ratios, particle diameter also increases (Kittelsohn, 1998). This is attributed to higher emission rates of soot particles and SVOCs. The soot particles act as adsorption sites for the condensed species. Because there are more adsorption sites, there is less likelihood that nucleation will occur. SVOC emissions also increase at high equivalence ratios because there is less oxidation of the fuel in these conditions, thus increasing the amount of material that adsorbs onto PM.

In CI engines, fuel-air ratio is proportional to engine load. In SI engines, equivalence ratios also increase at high loads to ensure sufficient power. Thus, it is expected that high loads and high accelerations will also be associated with higher number and mass emission rates and larger particles. This has been shown in numerous studies (Graskow, 1998, Health Effects Institute, 1997). The higher emission rates with load also result in higher mass emission rates measured over a transient cycle. It was observed by Hildemann (1991) that in fact, transient test mass emission rates were as much as ten times higher than steady state mass emission rates for gasoline-fuelled vehicles.

The composition of PM will also change with engine load. It has been observed that SOF values are highest at light engine loads when exhaust temperatures are low (Kittelsohn *et al.*, 1998b). At low exhaust temperatures, the saturation pressure for condensable species approaches the vapour pressures.

It should be expected that steady state emissions would be more stable. There is some evidence, however, that this is not the case for SI engines. During real-time steady state testing, sudden spikes in number emission rates with lifetimes of 10-30 seconds were observed when testing a 1993 4-cylinder engine (Graskow, *et al.*, 1998). These spikes occurred at random intervals, regardless of load or fuel used. The spikes were found to be composed of approximately 100% volatile material. These spikes in hydrocarbon emission rate were

believed to be associated with the occasional break-up of intake valve and combustion chamber deposits. In spite of these spikes in emissions, overall emission rates were repeatable from test to test. It should be noted that this particular test was the only one reviewed that used a different dilution system from the traditional constant volume sampling system discussed later in Section 3.1.1)

When testing some of the catalyst equipped gasoline vehicles in their test fleet, Hildemann *et al.* (1991) also noted that, in the later part of the high speed steady state testing, mass emission rates would drop. Concurrent with this reduction in PM emissions was a shift in mass distribution from unimodal distribution to a bimodal distribution. This change in emission rate was attributed to greater efficiency at the higher cylinder temperature and less oil used with expanded piston rings.

PM Emission rates for both SI and CI engines peak during the start sequence. This is due to the fuel enrichment needed to start. During cold starts, where the engine is at ambient temperature, emission rates of the products of incomplete combustion (HC, CO, PM) will be higher than hot-start (less than one hour after shut-down) emission rates. This is due to longer start sequences and increased quenching of combustion due to cold cylinder walls. It has been observed that cold start mass emissions of PM may be up to three times higher than hot start emissions (Maricq *et al.*, 1999).

Vehicle maintenance also plays a large part in PM emissions. "Smoking" vehicles are those that emit visible smoke during operation. This is generally the result of oil consumption or overly rich operation. Smoking vehicles may have PM mass emission rates that are two orders of magnitude higher than a new technology gasoline vehicle (Hildemann, 1991). From an emissions inventory perspective, it is critical to identify the proportion of vehicles that are high emitters due to poor maintenance in order to properly account for their contribution to the regional emission inventory.

2.3.4 *Ambient Conditions*

The key factors to be considered in ambient conditions are temperature and residence time from exhaust exit to receptor. Colder temperatures result in higher PM emission rates by exaggerating the effect of cold starts and extending the time required for oxidation catalysts to become effective. Once stabilised, it is anticipated that changes in density and temperature of air entering the combustion chamber will have a negligible effect on soot formation. Changes in the density and temperature of the air that mixes with exhaust can also have significant impacts on the gas-to-particle conversion processes outlined previously. If the exhaust is mixing with colder ambient air during dilution, the supersaturated region will be extended, resulting in higher proportions of condensed species.

If allowed to diffuse naturally in ambient air for sufficient time, the nuclei-mode particles will eventually coagulate and develop into accumulation mode particles. This has been shown through the study of ambient PM concentrations adjacent to a roadway with various meteorological conditions (Kittelson *et al.*, 1998b). The study found that the volume-distributed mean diameter of ambient PM shifted from larger to smaller as prevailing winds shifted from parallel to perpendicular relative to the roadway. It was concluded that lower crosswind components resulted in longer residence times and thus more opportunity for nuclei mode particles to coagulate prior to reaching the receptor.

Another point worth noting is that exhaust pipe position also has an effect on PM exhaust concentrations at receptor level. For example, it has been found that in urban hotspot areas such as street corners, urban buses with low exhaust pipes generate higher concentrations of roadside fine PM than buses with elevated exhausts (Balogh *et al.*, 1993). This has been attributed to the longer time between exhaust exit and receptor inhalation, thus increasing dilution.

2.3.5 *Correlation with other pollutants*

As mentioned above, PM is a product of incomplete combustion. As a result, it may be expected that there is a link between PM and the gaseous products of incomplete combustion (e.g., CO and THC). For example, The U.S. EPA's Air Toxics report refers to Hammerle

(1992), which estimated that particulate matter mass emission rates are 1.1% the mass of total HC emitted for FTP tests. The results from emissions testing remain inconclusive.

It has been shown (Mulawa *et al.*, 1997) that in some cases there is a good correlation between HC and PM while other studies have had less promising results (Cadle *et al.* 1997, Sagebiel *et al.* 1997, Norbeck *et al.*, 1998). The general consensus is that if a strong correlation is evident, the dominant source of PM is from incomplete combustion of the fuel. If no trend is apparent or if the correlation ratio is poor, then other sources, such as the excessive evaporation of lubrication oil are the major source of PM. It has also been noted in LDV emissions testing that the relationship between PM and the incomplete combustion is less apparent after the catalyst lights off and becomes active. It has been suggested that this is due to reduced the catalyst efficiency for particulate removal compared to that for gas-phase hydrocarbons (Maricq *et al.*, 1999).

2.4 Particulate Matter Control Measures

The reduction in PM mass emission rates in recent model vehicles has been the result of major efforts to improve combustion efficiency. In this study, efforts to reduce PM emissions have been catalogued into three approaches: engine design, fuel formulation and exhaust after-treatment. The impacts of engine design were discussed earlier in Section 2.3.2. Because PM has been a target pollutant for diesel engines for 30 years and only recently regulated in light duty vehicles, the measures discussed here are limited to diesel emissions controls.

2.4.1 Fuel Formulation

Numerous methods have been put forward to reduce the toxicity of vehicle emissions through varying degrees of fuel reformulation. A range of alternatives have been considered, from adjusting the relative contribution of functional groups to experimenting with non-petroleum based fuels. These methods have met with varying degrees of success and all have hurdles to overcome before they will be considered viable options for reducing PM emissions. In the field of SI engines, the options are limited to fuel reformulation and alternative fuels such as alcohols, natural gas and hydrogen. In diesel engines, the most promising fuel options are water emulsification of diesel, biodiesel and Dimethyl Ether (DME).

Fuel reformulation consists of optimising the mixture of hydrocarbons in the fuel to a particular end, such as improved performance or reduced emissions. The desired characteristics of reformulated diesel are low aromatic compound content, low sulphur composition and a high cetane number. It appears that fuel reformulation has little effect (10% reduction, Mayer, 1998) on the number or mass emission rate of particles. In gasoline engines, the use of oxygenated fuel, such as a 10% ethanol mix, reduces PM emissions by a similar factor when compared to conventional gasoline (Mulawa *et al.*, 1997).

A factor in reformulated gasoline that deserves more elaboration is the fuel sulphur content. Sulphur is naturally present in petroleum fuels. The national average sulphur content is 360 ppm for gasoline, 300 ppm for on-road diesel and 2400 ppm for diesel used in off-road applications. The reduction of sulphur is recommended for numerous reasons. The most elementary of these is that reductions in fuel sulphur will reduce sulphur dioxide emission rates, as well as direct and indirect sulphates. Studies have also shown that reduced fuel sulphur levels also reduce the emission rate of nuclei mode particles by several orders of magnitude (Baumgard & Johnson, 1996). This is likely the result of reduced sulphuric acid concentrations in the exhaust, which would have limited heterogeneous nucleation processes (see Section 2.2.2).

In addition to being the key source of sulphur dioxide emissions, current sulphur levels limit the effectiveness of emissions controls on newer-technology gasoline fuels. For example, sulphur dioxide poisons many oxidative catalytic converters by sticking to catalyst sites. The continuously regenerating particle filter, described later in this section, requires very low sulphur fuel in order to operate.

The development of biodiesel fuels and water-emulsified diesel fuels are two of the newest contenders for fuel reformulation solutions. Biodiesel is a mixture of mono alkyl esters of long chain fatty acids derived from renewable lipid sources. These lipids are generally vegetable oils, often soy-derived. Biodiesel contains no sulphur compounds, which virtually eliminates contributions to secondary aerosol. It either can be mixed with traditional diesel or be used exclusively. Preliminary tests of these fuels indicate that PM emissions are significantly

lower (55.4% for pure biodiesel - B100 and 18% reduction for 20% mixture - B20) and are significantly less toxic than the emissions from traditional diesel fuel (60-90% reduction for B100 and 12-20% reduction for B20). It should be noted that while emissions appear to be less toxic for all toxic components based on testing reported at the National Renewable Energy Laboratory (Peterson and Reece, 1994), testing at ERMD has observed substantial increases in carbonyl emissions for biodiesels compared to petrodiesels (Graham L., personal communication 30/10/2000).

The limiting factor to the use of biodiesel is its cost, which is presently \$1.50 - \$2.25 U.S. per gallon. It is expected that the price difference between conventional diesel and biodiesel will reduce with time, as the production costs for biodiesel reduce through optimisation and the cost of conventional diesel increases with dwindling reserves and stricter emissions standards (U.S. Department of Energy, 2000).

Treating diesel with water was originally designed to reduce the peak temperature of combustion and thus reduce NO_x emissions. What has since been found is that the mixing of water with diesel also significantly reduces PM emissions. The cause of this reduction has been linked to the explosive evaporation of water droplets during combustion, which in turn atomises the diesel particles adhered to the water droplet and facilitate faster and more complete combustion (Windsor Workshop, 2000)

It is much easier to optimise a combustion system if the fuel is a single compound, rather than a mixture of 300-400 compounds, as diesel is. Dimethyl ether (DME) is the most likely candidate for a single-component fuel. It is a very simple compound and has a sufficiently high cetane number to be used in compression ignition engines. The effect of DME use over traditional diesel is a reduction PM emissions by 75%, which has been attributed to low lubricating oil consumption (Gray *et al*, 2000). It should be noted, however, that emissions of other toxic components, particularly formaldehyde, are significantly increased with the use of DME.

2.4.2 Exhaust Aftertreatment Devices

There are a number of exhaust aftertreatment devices that are used to reduce exhaust emissions from the engine prior to exiting into the environment. On light duty vehicles, the most common is the 3-way catalytic converter, so named because of its ability to oxidise both hydrocarbons and carbon monoxide while reducing NO_x to nitrogen. It has also been found to effectively reduce PM mass emissions, largely due to the reduction of the SOF component. Although this may be a function of engine design, it has been found that mass emission rates can be up 10-30 times higher for non-catalyst vehicles compared to catalyst vehicles (Hildemann, 1991). It also appears that catalysts are ineffective at reducing PM number emission rates at speeds of 120 km/h (Graskow *et al.*, 1998).

The two most common end-of-pipe solutions being used for diesel engines are ceramic particle traps and oxidative catalytic converters. Particle traps are constructed in numerous forms; the two most common forms are ceramic monolith and fibrous mesh designs. Ceramic monolith traps consist of a honeycomb of long channels with porous walls. The open channels of the honeycomb are alternately blocked with high temperature cement at the ends so that all the exhaust entering the open channels must pass through the porous ceramic walls to exit the trap. Particulate matter is filtered by interception. In fibrous mesh traps, larger particle sizes are filtered through interception of the particles with the mesh elements. Smaller particles are filtered through diffusion to the mesh surface.

A shortcoming of particle traps is that the regeneration of traps consists of passing hot air through the trap, which will burn off the deposited particle layer. The problem with this method is that the burn-off could result in emissions of particulate matter or other combustion products. The counter argument to this concern is that the light-off will occur more gradually and the emissions will be less toxic.

One of the methods to promote light-off of trapped PM is to introduce additives to the fuel that will promote oxidation of particles once they are fixed to the trap. During combustion, these additives oxidise, the oxides of which are catalytically active. These oxides adhere to soot, where they catalyse the carbon oxidation during the combustion and also after deposition

in the trap. This method has met with limited success. In the absence of a trap, these fuel additives will actually increase PM mass emission rates. Thus, either all engines use particle traps or the additive has to be injected separately. A further limitation of this method is that the oxides that form are a smaller size than soot particles and thus are more likely to be able to penetrate the trap. In addition, these oxides are catalytically active, which makes them potentially more toxic (Mayer *et al.*, 1998).

Another form of regenerating trap is a combination oxidation catalyst and a ceramic particle filter known as the continuously regenerating trap. In addition to converting VOC and CO, the catalyst oxidises NO to NO₂, which in turn oxidises the PM that has been collected on the filter down stream. Because the oxidation catalyst is highly reactive, the system requires a fuel with a very low sulphur content. It is possible that the catalyst could increase sulphate emissions but fuel sulphur levels are required to be very low so the amount sulphate produced will likely be small. In addition, NO₂ emission rates are higher with this arrangement compared to untreated exhaust.

Unlike particle traps, which are virtually ineffective at reducing emissions of other pollutants, catalytic converters (oxicats) have been found to be up to 70% more effective in lowering emissions of total hydrocarbons (Health Effects Institute, 1997). This is not to say that catalytic converters are uniformly better performers than particle traps. In general, the reduction efficiencies of PM traps are much higher than the efficiencies for oxidative catalysts. In addition, oxicats reduce the SOF, but do little to reduce the number of particles. In fact, they may produce more soot through the partial oxidation of the SOF. Oxicats have also been found to increase emission rates of nuclei-mode particles by two orders of magnitude (Abdul-Khalek, 1998). This has been attributed to the oxidation of SO₂ to SO₃, which leads to sulphuric acid formation as the exhaust dilutes and cools (Mayer *et al.*, 1998).

2.4.3 *Effect of Sampling Conditions on PM Emissions*

It was established in Section 2.2.2 that condensation and adsorption of semivolatile species in ambient dilution will be a function of the path that is taken as the exhaust dilutes from temperature and concentration conditions of the exhaust to the conditions for ambient air.

We shall find later in Section 3.1 that, unlike the continuous dilution process in the atmosphere, the dilution process in the laboratory is a one- or two-step process where the exhaust is mixed with ambient air to a particular dilution ratio where it remains until it is sampled. In this section, we will review the results of studies that have evaluated the effect of sampling at various dilute exhaust conditions on the nature of the collected sample. The key conditions that will be considered here are dilution ratio (DR), temperature of dilute exhaust and residence time.

It is expected that lower dilution ratios (i.e. less mixing) will result in higher PM emission rates because the concentration of semivolatile species will remain high, favouring more condensation. Reichel *et al.* (1983) investigated the effect of changing the dilution ratio by changing either the exhaust flow rate or the dilution air rate. Reducing the dilution ratio from 40 to 15 by increasing exhaust flow rate resulted in a 28% increase in calculated PM emission. Conversely, reducing the airflow to change DR by the same amount resulted in a 13% increase in PM mass emission rates. Dilute exhaust temperature was kept constant (40°C) by increasing the temperature of the dilution air. The difference between these two methods was attributed to the fact that changing exhaust flow was inherently associated with increasing the dilute exhaust temperature. This in turn resulted in a larger spread of temperatures between dilution air and the exhaust.

Plee and MacDonald (1980) also investigated the effect of dilution ratio on the PM mass emission rate from an automotive diesel engine. They found that increasing the dilution ratio from 5:1 to 100:1 at a constant filter temperature of 52°C decreased particle mass emission rates by approximately 26%. Thermogravimetric analysis revealed that the increase in emission rates were the result of condensed semivolatile species. It is not known whether Plee and MacDonald changed dilution ratio by varying engine exhaust flow or dilution airflow.

Another important factor to determine is the nature of the gas-to particle conversion that is occurring. In Section 2.2.2, three formation processes, adsorption, condensation, and nucleation were identified. Particles formed by these processes have significantly different size

distributions. Hence, the dominant process will have a significant effect on the size distribution of the particles collected.

Reichel *et al.* (1983) developed a theoretical model of particle formation in dilution tunnels. The results of this analysis showed that adsorption is the main source of mass increase when using low dilution ratios. Adsorption would result in increased size of particles and larger mass emission rates. An important caveat that must be included in the dominance of adsorption in gas-to-particle conversion is the requirement for there to be sufficient particle surface available for adsorption to occur. New technology vehicles may have such low soot concentrations in the exhaust that adsorption rates are restricted.

A number of studies have shown that at sufficiently low dilution ratios, nucleation is more likely to occur, particularly in the absence of solid soot particles. Figure 11 shows the effect of dilution ratio on particle size distribution. In this study, the engine was tested first with no exhaust after-treatment at a DR of 12. When the particulate filter was included, a spike in nanoparticles was observed. When the dilution ratio was increased to 19 or 32, this spike disappeared. This spike in nanoparticles was attributed to the low dilution ratio and the presence of the PM trap, which removed much of the solid PM but did not remove the condensable species, which resulted in homogeneous nucleation at the low dilution ratio.

Figure 11. Effect of dilution ratio on particle size distribution from a heavy duty diesel engine (Luders, 1998).

Another interesting observation is that modifying dilution ratio can result in increased sulphate conversion. It has been observed that increasing the dilution from 10:1 to 50:1 reduced sulphate conversion from 5% down to almost 2% (Ahlvik *et al.*, 1998).

The reduction of diluted exhaust temperature may be expected to result in higher condensation rates, since lower temperatures will increase saturation ratio of semivolatile species. This has been shown in Luders (1998 - illustrated in Figure 12), where the dilution air temperature was increased from 20°C to 35°C. At 20°C, condensation of nanoparticles was observed at a dilution ratio of 12. When the dilution air temperature was increased to 35°C, the dilution ratio had to be reduced to 4 before condensation of nanoparticles was observed again. Similar results were observed by Reichel *et al.* (1983), which found that particle mass emission rates increased by 50% by lowering the mixing temperature from 50 °C to 20 °C through cooling dilution air.

Figure 12. Effect of dilution air temperature on particle size distribution from a heavy-duty diesel engine at rated power. (Luders *et al.*, 1998).

Extending the residence time in the dilution tunnel may be expected to give higher mass emission rates and larger particle diameters. Keeping in mind that gas-to-particle conversion mechanisms are rate functions, the longer the exhaust spends at a low dilution ratio, the more material would condense, resulting in higher mass emission rates. In addition, the longer residence time will allow more time for coagulation to occur at the unnaturally high concentrations associated with low dilution ratios. The result of coagulation would be an increase in particle size with no significant increase in mass concentrations.

Ulfvarson *et al.* (1997) sampled exhaust from old and new diesel engines for PM using a dilution tunnel with a residence time of 2 seconds followed by an exposure chamber with a total residence time of 40 seconds. It was found that particle mass emission rates calculated from samples taken in the exposure chamber were significantly higher than those using

samples from the dilution tunnel, particularly with the new engine. Although the dilution ratio was not specified, estimates based on the temperature information provided give DRs that range from 24 to 80.

This chapter has demonstrated the great deal of variability observed in PM emissions in terms of rate, composition, and size distribution. This variability manifests itself between vehicles, geographical regions and road types. To develop an emissions inventory for a region that accounts for such factors as the age distribution of vehicles, the driving behaviour on the road network and the ambient conditions is already an arduous task. We have also observed that variability in sampling procedures can also affect the nature of the PM collected. The next section will present the methods for sampling vehicle exhaust and for isolating and characterising the PM suspended in the sample.

Chapter 3 **Particulate Matter Sampling and Characterisation**

This chapter summarises the procedures used to determine vehicle exhaust PM emission rate and its physical and chemical characteristics. There are two fundamental goals in the measurement of vehicular PM emissions in the laboratory. The first is to ensure that the hot exhaust gases are diluted and cooled in a way that is similar to actual dilution processes that occur on the road. The second goal is to ensure that sufficient sample is collected to facilitate quantification without causing changes in the physical and chemical composition of the PM emissions. This chapter will discuss the methods by which these goals are achieved. It begins with a review the methods for collecting and conditioning vehicle exhaust. This is followed by a summary of the equipment used to take a representative sample of the exhaust, isolating the PM from that sample, and analysing the characteristics of the collected PM.

3.1 Exhaust Sampling

3.1.1 Laboratory Test Procedures

The regulatory vehicle emissions test procedure, known as the Federal Test Procedure (FTP), is described in the U.S. Code of Federal Regulations (Title 40, Part 86). The test procedure consists of first preconditioning the vehicle prior to testing, followed by mounting the vehicle onto a chassis dynamometer, connecting the exhaust to a constant volume sampling system (CVS - See Figure 13), and operating the vehicle over a given test cycle. When testing heavy-duty vehicles, it may be necessary to remove the engine and test it on a shaft dynamometer. Emission rates are traditionally reported as g/mile in chassis dynamometer testing and g/bhp.hr for shaft dynamometer testing.

In chassis dynamometer tests, the driver of the vehicle follows a Driver's Aid, which is a computer monitor that shows both the speed of the vehicle measured from the dynamometer

and the speed required to follow the driving cycle. The various driving cycles that are commonly used in emissions testing are described in Section 3.1.2.

Figure 13. Schematic of Critical Flow Venturi Constant Volume Sampling System.

It has also been argued that vehicle operation prior to emissions testing can affect the repeatability of emissions testing. For example, excessive idling could lead to build-up of material on sparkplugs and other equipment, which would hinder combustion efficiency and increase THC and CO emission rates. To ensure that effects of operations prior to testing are consistent, a preconditioning procedure is also included in the FTP. The preconditioning procedure consists of mileage accumulation on a predetermined route operating on the fuel to be used for testing. In regulatory gasoline vehicle testing, the standard test fuel is Indolene. The vehicle is operated for 12 hours, followed by a “soak” time of 12 – 36 hours where the vehicle is not operating.

A chassis dynamometer can consist of a single- or double-roller assembly. The driving wheels are placed on the rollers, which simulate the surface of the road. The dynamometer applies resistive torque to the rollers to simulate the road load. The simulated forces are inertial forces associated with acceleration and aerodynamic drag. Other resistive forces such as friction

between the tire and the surface and friction losses to the axle are accounted for in the operation of the vehicle. For heavy-duty vehicles, the higher loads and vehicle sizes may be too large for many chassis dynamometers. As a result, heavy-duty vehicle tests often consist of first removing the engine from the vehicle and connecting the drive-shaft to a dynamometer. In both cases, a signal is sent from the dynamometer to a computer that manages the test so that the Driver's Aid can track the speed of the vehicle and ensure it complies with the driving cycle.

During engine operation, exhaust from the vehicle is routed to the dilution tunnel by a heated transfer pipe. There, it is mixed with clean air and drawn through the dilution tunnel. A constant mass flow rate of dilute exhaust is ensured through the attachment of a Critical Flow Venturi (CFV) to the end of the dilution tunnel. The pressure drop across the CFV is sufficiently large to maintain choked flow, ensuring a constant mass flow rate. In this system, the varying exhaust volume produced over a transient driving cycle is diluted by whatever make-up air is required to maintain the constant flow rate. Thus, the time-averaged concentration of a pollutant in the dilution tunnel over the duration of a test is directly proportional to the mass of that pollutant emitted by the vehicle.

Gaseous emissions are collected in Tedlar bags and analysed for carbon monoxide, carbon dioxide, nitrogen oxides and hydrocarbons. Sampling for PM emissions consists of drawing diluted exhaust through an isokinetic inlet, isolating PM smaller than a desired size, and analysing it through methods described in 3.2. A summary of the method for calculating emission rates of both gaseous pollutants and particulate matter is presented in Appendix. A.

3.1.2 Driving Cycles

The current light-duty driving cycle used for FTP emissions testing is the US-75 cycle or the Urban Dynamometer Driving Schedule (UDDS). It consists of three phases, shown in Figure 14. The US-75 cycle evolved from the LA4 cycle (the first two phases of the UDDS), designed by the U.S. EPA in 1965 to simulate a typical morning trip to work in rush-hour traffic in Los Angeles. The UDDS cycle consists of three phases: Cold Transient (CT), Cold Stabilised (CSt) and Hot Transient (HT). There is a ten-minute soak period between the

second and third phase. The HT phase, which is identical in speed profile to the CT phase, is included to account for the effects of starting with warm engine and emission controls. Originally, two complete LA4s were completed for the US-75 test. However, it was found that the emission rates in the second stabilised phase were the same as the first stabilised phase. Thus, to save time and money, it was decided to remove the second stabilised phase and weight emissions from the stabilised phase accordingly.

Figure 14. Speed profile for Urban Dynamometer Driving Schedule (U.S. EPA, 2000).

Emission rates are calculated through a weighted average of the three phases.

$$GPM_{FTP-75} = 0.43 \left(\frac{GPP_{CT} + GPP_{CSi}}{X_{CT} + X_{CSi}} \right) + 0.57 \left(\frac{GPP_{HT} + GPP_{CSi}}{X_{HT} + X_{CSi}} \right) \quad \text{Equation 1}$$

Where: GPM_{FTP-75} = Emission rate for FTP 75 driving cycle, g/mile

$GPP_{(CT, HT, CSi)}$ = Mass of pollutant emitted in each phase, g

$X_{(CT, HT, CSi)}$ = Distance traveled in each phase, mile

Research has found that the UDDS cycle does not cover a significant portion (only 15%) of driving conditions and types of driving behaviour (Faiz *et al.*, 1997). In 1996, the US EPA

issued a supplemental test procedure (SFTP), which includes two new driving cycles: the US06 and the SC03. The US06 represents aggressive driving while the SC03 simulates driving immediately following vehicle start-up with the onboard air conditioner engaged. Only the US06 was evaluated in this study. Thus, only the speed profile for the US06 is shown in Figure 15. It should be noted that this is a modified US-06 cycle. Due to limitations of the dynamometer, the speed for the trace was clipped and set to 60 mph. The original US06 cycle has a maximum speed of 80 mph.

Figure 15. Speed profile for modified Supplementary FTP (US06) driving cycle (Graham, 30/10/2000).

Another supplemental test frequently performed is the FTP Non-Freeway Cycle or New York City Cycle (NYCC). This cycle simulates driving in congested conditions with much of the time spent idling. The speed profile for the NYCC is shown in Figure 16.

Figure 16. Speed profile for NYCC driving cycle (U.S. EPA, 2000).

Unlike light-duty emissions testing, the original heavy-duty driving cycle was a steady-state cycle known as the 13-mode test. In this test, the vehicle/engine was operated at 13 combinations of engine speed and load (mode). The emissions rate at each mode was weighted and the sum of the emissions from each mode was reported. This method was replaced in 1985 by the Heavy Duty Chassis Transient Cycle (HDTC) transient test to better simulate on-highway conditions and improve repeatability. Where facilities exist and where it is appropriate, chassis emissions tests can be performed using the speed profile for the HDTC is shown in Figure 17. Elsewhere, the engine may have to be removed and tested on a shaft dynamometer following a cycle that dictates both engine speed and torque.

Figure 17. Speed profile for HDTC cycle (U.S. EPA, 2000).

A criticism of the HDTC is that it is not representative of certain heavy-duty operations, particularly urban buses. To better simulate these conditions, other driving cycles used for heavy duty testing include synthesised cycles such as the CBD (shown in Figure 18), which was used in this study. Synthetic cycles are often criticised for consisting of accelerations that cannot be met by all vehicles and as being biased towards a single steady state speed (Brown *et al.*, 1997).

Figure 18. Speed Profile for CBD cycle (ERMD, 2000).

3.1.3 ERMD's Dilution Tunnel

In this section, we will outline and evaluate design elements of the dilution tunnel. In particular, we will consider efforts that have been made to minimise artefacts in the PM sample; review potential issues that arise with the geometry of the tunnel and lastly discuss the methods used to transport dilute exhaust to the filters.

The dilution tunnel used in this study is shown in Figure 19. A summary of the dimensions and flow rates for the dilution tunnel is discussed later in Section 6.2.

Figure 19. ERMD's Dilution Tunnel

The sampling system consists of a transfer pipe (which is heated when possible), a HEPA filter system for cleaning dilution air, a U-shaped dilution tunnel and a sampling train. The exhaust feeds into the top end of the dilution tunnel and PM samples are drawn from bottom end of the tunnel. After the PM sampling station, the diluted exhaust goes through two 90° bends, passes another five meters of tunnel where gaseous pollutants are sampled, followed by the critical flow venturi then the blower which draws the dilute exhaust through the tunnel.

The dilution air was drawn from the ambient air in the test facility and conditioned by removal of PM and volatile organics using the HEPA filter arrangement shown in Table 1.

Table 1. Summary of Ambient Air Preconditioning Filters.

Stage	Depth	Type	Purpose	Removal Efficiency	Resistance	
					Initial Pressure drop ("H ₂ O)	Changeout Pressure Drop ("H ₂ O)
1	2 "	Pleated	Pre-Filter	45-55 %	0.16	0.9
2	22"	Envopac bag filter	1 st Stage Particle Removal	90-95 %	0.4	0.74
3	24.5"	Activated carbon	Hydrocarbon, VOC Removal	Not Available	0.35	0.35
4	2"	Pleated	Pre-Filter for HEPA	45-55 %	0.16	0.9
5	11.5"	Astrocel HCX HEPA Filter	2 nd Stage Particle Removal	99.99 %	1.4	1.4
Total Pressure Drop ("H ₂ O):					2.47	4.29

To minimise the possibility of reentrainment of particles during testing, the dilution tunnel has been sectioned into seven portions that can be taken apart and cleaned between tests. The portions are flanged with O-rings to eliminate leaks. The cleaning process consisted of spraying the tunnel with methanol, followed by wiping away the residue and polishing the surface with low-lint paper towels. The inside of the transfer pipe was cleaned by spraying degreaser into the pipe, scrubbing with a telescopic brush, followed by rinsing with tap water.

During the emissions testing (See Chapter 4), the tunnel was taken apart and cleaned between changes in either fuel or vehicle for motorcycle testing. For bus testing, the tunnel was cleaned once prior to the start of testing. An additional advantage of using a demountable dilution tunnel is that it affords an opportunity to inspect the tunnel for particle deposition between testing.

The dilution tunnel was designed to ensure that the raw exhaust was introduced to the dilution tunnel at a point where the dilution airflow was fully established. A schematic of the T-section where the mixing point is located is shown in Figure 20. The raw exhaust inlet is located approximately six inches past the edge of the duct that introduces the dilution air. This arrangement ensures that dilution airflow is fully established in the horizontal direction before the exhaust is introduced to the dilution tunnel.

Figure 20. Schematic of mixing point in dilution tunnel.

Some complications could arise with this arrangement. One is that the dilution air passing over the last 2.5 feet of exhaust inlet could be cooling it down to such an extent that mechanisms such as thermophoresis and gas-to-particle conversion are enhanced. This would be most apparent for small engines where the flow rate through the exhaust inlet would be low. In the case of the light duty and heavy-duty vehicles, the maximum residence time in this

section of pipe is 0.9 seconds and 0.04 seconds respectively. Scaling the engine size down by a third for motorcycles, we find that idling motorcycle exhaust can remain in the last section of the exhaust inlet for up to 3 seconds. If we consider that these conditions would also be associated with the coolest exhaust gas, the potential for condensation and thermophoresis becomes considerable.

Another potential complication is that there may be separated flow immediately downstream of the dilution air inlet. This could result in partially deflected flow of the exhaust at its inlet. Deflected exhaust could mean that the exhaust is not diluting instantaneously across the cross section as had been assumed in the tunnel dilution modelling. This in turn can result in regions of large temperature gradients between the exhaust and the walls, leading to non-uniform heat transfer. It is highly recommended that the possibility of a recirculation region in the exhaust be more carefully considered in future studies. One of the possible solutions for minimising the degree of flow recirculation would be to install flow straighteners into the dilution tunnel. The arrangement could be as simple as a honeycomb type structure, with vanes as short as two inches, which would be installed between the T-junction and the mixing point.

3.1.4 Artefacts in the Dilution Tunnel

This section will consider whether the geometry of the dilution and sampling system will have an effect on the particle emission rates or particle distribution. The term "artefact" refers to changes in PM content in the sampling stream by loss or addition of material. Negative artefacts, or loss of PM in the sampling system, are the result of deposition to the walls of the system plumbing (i.e. exhaust pipe, transfer pipe, dilution tunnel and sampling lines). Positive artefacts, addition of PM, can result from reentrainment of previously deposited material into the exhaust. Some deposition of particles naturally occurs in the vehicle combustion and exhaust system. This deposition is not of interest in this report because they do not contribute to on-road emissions, although the reentrainment of these deposits may be of concern.

The mechanisms that result in particle deposition are similar to those for lung deposition, discussed in Section 1.1.1. These mechanisms are inertial impaction, sedimentation, and

diffusion. Inertial impaction results from eddies that propel the particles into the laminar sub-layer of pipe walls and through flow deflection at bends in the sampling system. Sedimentation occurs along the horizontal distance of the sampling system. Both of these mechanisms will be dominant on particles larger than $1\text{ }\mu\text{m}$ but they have little effect on typical exhaust particles, which have a mass mean diameter between 0.1 and $0.3\text{ }\mu\text{m}$ (See Section 2.1.1). Diffusion is the dominant deposition mechanism for particles smaller than $0.05\text{ }\mu\text{m}$ in diameter.

From the above estimates, it appears that the size range of exhaust PM will pass through dilution tunnel with little or no deposition. However, another mechanism, thermophoresis is a major source of particle deposition in exhaust sampling systems. Thermophoresis describes the phenomenon of particles moving down a temperature gradient from hot to cold. Like diffusion, the effect of this mechanism is greater for smaller particles. Because of its dependence on temperature gradient, its effect is greatest in the exhaust lines and in the transfer pipe where the temperature difference between the exhaust and the walls is greatest.

Kittelson and Johnson (1991) developed a deposition model for a two-stage dilution system. It was determined that in a single stage dilution tunnel, total thermophoretic deposition losses could exceed 3.5%. This is significantly higher than the fraction estimated by the model for mechanical deposition, which was 0.14% for an estimated mean particle diameter of $0.3\text{ }\mu\text{m}$.

A possible manifestation of thermophoretic deposition was observed during the cleaning of the dilution tunnel between testing runs. A black film, patchy in distribution, was observed on the section immediately downstream of the mixing point on a limited cross-section of the tunnel. This film faded with increasing distance downstream from the mixing point, which could have been deposited PM due to flow-separation phenomena at the mixing point.

There are numerous methods available for reducing thermophoretic losses. The simplest is to increase the inside temperature of the pipe walls. This can be performed by heating the walls, using insulation and reducing the pipe wall thickness. Another method is to pre-dilute the

exhaust with air prior to the transfer pipe. In Kittelson and Johnson's deposition model, a combination of insulation, preheating transfer pipe to 150°C and adding dilution air to the tailpipe to limit the exhaust temperature to 150 °C resulted in reducing thermophoretic deposition to 0.25%.

What may be a more critical issue is the entrainment of deposited particles from previous tests into the air stream. These particles will be larger than the particles originally deposited because of agglomeration upon deposit. In this particular study, we are considering PM_{2.5}, which is separated with a cyclone (described earlier in Section 3.1.6). Thus, it is unlikely that these positive artefacts will be of concern, since they will be separated from the sample stream in the cyclone rather than collecting on the filter. Another issue worth considering, however, is the outgassing of volatile material from the deposited PM, which can later condense to form new PM.

3.1.5 Inlet considerations

An integral part of any PM sampling system is an inlet to draw the sample from the dilute exhaust. It is important that this inlet draw the gas isokinetically (i.e. at the same speed at which the gas is moving in the dilution tunnel). This characteristic is particularly important for sampling particles larger than a few micrometers, since the trajectories of the particles may deviate substantially from the streamlines of the gas due to inertia and gravity. Regardless of the size of particles considered, efforts should be made to ensure isokinetic sampling and a properly aligned inlet so that there is a minimum deviation of streamlines at the sampling inlet.

Inlet efficiencies have been determined using the following expression (Hinds, 1982):

$$\eta_{inlet} = 1 + \left(\frac{v_{ae}}{v_{sam}} - 1 \right) \left(1 - \frac{1}{1 + Stk \left(2 + 0.62 \frac{v_{sam}}{v_{ae}} \right)} \right) \quad \text{Equation 2}$$

Where:

η_{inlet} = aspiration efficiency of inlet
 v_{at} = velocity of tunnel
 v_{sam} = velocity of sampler
 Stk = Stokes Number

Stokes number is considered the ratio between the stopping distance and a sampling tube dimension (often the radius). The stopping distance can be calculated using the following expression:

$$x_{Stk} = \frac{V_{rel} D_p \rho_p C}{18\mu} \quad \text{Equation 3}$$

Where

V_{rel} = relative velocity of between channel and sampling inlet
 D = particle diameter
 ρ_{part} = particle density
 C = Cunningham correction factor ($\approx 1 + 1.728/l$)
 l = Mean free path; and
 μ = Viscosity of fluid.

Based on these relationships, it can be seen that when the sampling velocity is faster than the dilution tunnel velocity, the efficiency will be less than one. If the sampling velocity is slower than the dilution tunnel, the sampling efficiency will be greater than one, which means that particle concentrations in the sampling line will be greater than those in the dilution tunnel. Using sampling conditions for the PM dilution tunnel an inlet diameter of 1 cm, and the sampling flow rate of 91 lpm, the sample air travels into the inlet at 19.7 m/s. Figure 21 and Figure 22 plots the aspiration efficiency of the inlet for dilution tunnel configured for light-duty and heavy-duty vehicles as shown in Table 33.

Figure 21. Aspiration efficiencies for light duty emissions sampling.

Figure 22. Aspiration efficiencies for heavy-duty emissions sampling.

It can be seen that while the aspiration efficiency is very good for heavy-duty vehicles, the aspiration efficiency for particles at $2.5\mu\text{m}$ diameter is only 82%, which is rather poor. Given that the average diameter of PM vehicle exhaust is around $0.2\mu\text{m}$ and the maximum diameter is $1\mu\text{m}$, however, there is little risk of errors due to loss or addition of material during light duty testing.

3.1.6 Cyclone considerations

There is still a potential for particle losses downstream of the sampling inlet but these losses become intentional, to a certain extent. In this study, we are concerned with $\text{PM}_{2.5}$. Particles larger than $2.5\mu\text{m}$ are removed from the air stream using a cyclone. Cyclones rely on centrifugal flow to remove particles through inertial impaction. By increasing the flow rate, the centripetal acceleration also increases, resulting in progressively smaller particles colliding with the cyclone walls. The plot of particle cut-diameter (diameter of particles that will be removed at 50% efficiency) versus flow rate as provided by cyclone manufacturer is shown in Figure 23. This cyclone has a cut diameter of $10\mu\text{m}$ at 16.7 lpm and $2.5\mu\text{m}$ when operated at 91 lpm .

Figure 23: Cut diameters for cyclone used in study.

Yet another important factor that needs to be considered to ensure the adequate performance of the cyclone is its alignment. It has been found at ERMD that the alignment of the cyclone will affect the flow distribution of air leaving the cyclone. If the cyclones are not aligned vertically, the PM collected on 90-mm filters is preferentially deposited onto the lower half of the filter. This uneven distribution of filter material can result in flow restrictions or short-circuiting of air - either condition is undesirable.

This concludes the discussion of sampling issues. We have seen that there while emissions testing equipment and procedures are required to meet certain regulatory standards, there are still numerous parameters that can effect the PM in the exhaust sample that are not under regulatory control. What is also apparent is that the sampling equipment should be optimized for the flow of the dilution tunnel to ensure that excess material is not lost. While the sampling equipment is well configured for heavy-duty emissions testing, the set-up for light duty testing should have been optimised to prevent the low aspiration efficiencies that have been calculated here.

3.2 Particulate Matter Characterisation

This section focuses on the procedures used to isolate the PM from the sample collected above and characterise the collected material. We will first consider methods used to evaluate the physical characteristics of a particle sample then review methods for chemically characterising the particulate matter sample, with particular emphasis on chemical analysis of PM collected on filters.

PM as a pollutant is unique in its variety of physical and chemical characteristics. The source of the PM and its residence time in the atmosphere will have a significant effect on its chemical composition and size distribution, which will subsequently determine its impact on health and the environment. Because of its capacity for mutation and conversion, the nature of PM measured at the receptor can be significantly different from what is observed at the source. For these reasons, any survey of PM source emissions should include a detailed characterisation of the nature of these emissions. The characterisation of PM will help determine the impact of the PM at the emission point, facilitate a better estimate how these

emissions may change with time, and provide information regarding the presence of stable marker compounds, which will help identify PM emissions at a receptor that is far from the emission point.

There is some dispute as to what the most appropriate measure of PM concentrations is. From a health perspective, nuclei and accumulation mode particles appear to be the most hazardous and as a result, they should be targeted in any measure of PM. The U.S. Environmental Protection Agency has recently included $PM_{2.5}$ as a criteria pollutant in its National Ambient Air Quality Standards. In addition, the EPA has recently approved the establishment of 50 chemical speciation stations for $PM_{2.5}$ (U.S. EPA, 1999). These sampling stations will be measuring a number of chemical characteristics of $PM_{2.5}$. The characteristics of interest are ionic species, trace elements, organic and elemental carbon and particulate mass. (U.S. EPA, 1999).

From an emissions measurement perspective, particularly when considering the transient nature of vehicle emissions, there are conflicting issues to consider. Ideally, real-time measurement of PM emissions should be conducted to evaluate the events that lead to fluctuations in emission rates. The resolution of particles into discrete size ranges is also of critical importance. At the same time, sufficient sample should be collected to facilitate mass measurements and chemical analysis. In addition, chemical analysis dictates that PM should be collected onto a medium that does not contaminate the sample. Unfortunately, there is no single instrument capable of meeting all of these objectives. Thus, it becomes necessary to prioritise the measurement of these characteristics according to the study and determine which instruments will facilitate the characteristics commensurate with the study's budget.

3.3 Physical Characterisation

For the purposes of this discussion, physical characterisation shall be considered to include all methods that a) quantify the mass / number/ surface area of PM in a sample of gas and/or b) measure the size distribution of particles in a gas sample. Section 3.3.1 reviews filtration and discusses efficiency issues. Section 3.3.2 discusses the various methods for determining the

mass of material collected on filters. The methods for evaluating size distribution are much more varied and are discussed in Sections 3.3.3 - 3.3.5.

3.3.1 Filtration

Filtration is one of the most common methods for mass determination and collection for chemical characterisation. This section will review the general structure of filters, review factors that affect the collection efficiency of filters, and summarise considerations for sampling with filters.

The filters used for the collection of aerosols consist of a network of small openings formed from one of the following structures:

1. Overlap of fibres as in fibre glass or cellulose filters;
2. Controlled size pores in an organic medium as in membrane filters;
3. Random pores with a fixed medium as in sintered glass filters; and
4. Random pathways through a granular medium.

The most common methods used in aerosol collection are the first two listed above. A common misconception is that filters remove particles like a sieve, collecting only particles that cannot pass through the empty space. In fact, filters for PM collection are mostly pore space. In general, fibrous filters have porosities from 70% to greater than 99%; porous membrane filters have much lower porosities, ranging from 50 to 90% (Hinds, 1982). Instead of blocking the particles, particle removal occurs by collision and attachment of particles to the surface of the filters.

The forces at work to separate the particles from the air in filters are similar to the particle deposition mechanisms discussed in Sections 1.1.1 and 3.1.4. The mechanisms at work in filtration include direct interception, impaction, diffusion and electric and gravitational forces. The first three of these mechanisms are the most dominant and shall be discussed in detail.

The efficiency of each of these mechanisms can be estimated by assessing the probability of a particle colliding with a single theoretical fibre. Although these estimates may not be applicable to micropore filters given the different geometry, the mechanisms at work and the relationships between collection efficiency and flow rate or particle number size will be similar.

The relative importance of the individual collection mechanisms is governed by a combination of face velocity, porosity and fibre diameter and particle diameter. The filter face velocity will vary depending on the sampling flow rate and the area of the filter. The porosity of the filter medium chosen for sample collection will have an effect on the interstitial air velocity and head loss, which will in turn affect the collection of semivolatile material due to its partitioning between the particle and gas phases, discussed later in Section 3.4.1. The diameter of the fibres will dictate the volume of gas affected by diverting around the fibre, which will in turn have an impact on the efficiency of each mechanism.

Inertial impaction of a particle with a fibre, shown in Figure 24, occurs when a particle diverts from the streamline due to changes in flow direction in the vicinity of a fibre and collides with the fibre. Impaction is governed by the Stokes number, discussed in Section 3.1.5. Inertial impaction efficiencies improve with increased flow velocity and particles larger than $1\text{ }\mu\text{m}$.

Figure 24. Particle collection by impaction. (Hinds, 1982).

Diffusion by Brownian motion (Figure 25) will result in the collection of ultrafine particles. Brownian motion is the random movement of particles due to collisions with other molecules and particles. The single-fibre efficiency due to diffusion is a function of the Peclet (Pe) number, which is the ratio of the product of fibre cross section and flow velocity to the diffusivity. The single fibre efficiency for diffusion is defined by Hinds (1982) as:

$$E_D = 2Pe^{-2/3}, \quad \text{Where} \quad \text{Equation 4}$$

$$Pe = \frac{d_f V_0}{D_x}$$

E_D = Efficiency of collection by Diffusion
 Pe = Peclet Number (Ratio of bulk flow to diffusivity)
 d_f = fibre diameter
 V_0 = Face velocity
 D_x = particle diffusion coefficient

The particle diffusion coefficient is a measure of the mobility of a particle due to a concentration gradient. For spheres with a unit density, typical values for diffusion coefficient are $5.2 \times 10^{-4} \text{ cm}^2/\text{s}$ at a diameter of $0.01 \text{ }\mu\text{m}$ and $2.7 \times 10^{-7} \text{ cm}^2/\text{s}$ at $1.0 \text{ }\mu\text{m}$ diameter. Thus, the collection efficiency for diffusion mechanisms is maximised by low velocity and small particles.

Figure 9.7 Single-fiber collection by diffusion.

Figure 25. Particle collection by diffusion (Hinds, 1982).

Interception (Figure 26) occurs when a particle follows a gas streamline and nonetheless impacts with the fibre. It is the only mechanism that applies to particles in the size range that are too small to be affected by impaction and too large to be deflected from streamlines by Brownian motion. The collection efficiency by interception is dependent only on the ratio of particle diameter and fibre diameter and the porosity of the filter. Collection efficiencies by interception are quite small, given the limited proportion of particles that are exposed to this mechanism.

Figure 26. Particle collection by interception (Hinds, 1982).

When these mechanisms are considered together to determine the overall filter efficiency, we find that collection efficiencies are high at either small particle diameters (less than approximately $0.1\mu\text{m}$) or very large diameters ($> 1.0\mu\text{m}$). Between these sizes, efficiencies tend to drop. This can be seen in Figure 27, which is a plot of collection efficiencies versus particle size for two face velocities (1.0 cm/s and 10 cm/s). One observes in this figure that the minimum efficiency is a much lower value for high face velocities and that the critical diameter (diameter associated with minimum efficiency) decreases with increased speed. A similar phenomenon is observed for fibre diameter, although with larger fibre diameter, the critical diameter shifts to larger particle sizes, rather than smaller, as in the case of higher face velocities. The reduction in efficiency at these higher flow rates is due to the reduced effectiveness of diffusion as a collection mechanism. The figure also shows that diffusion is much more sensitive to velocity changes than is impaction.

Figure 27. Efficiency versus particle size for face velocities of 1 and 10 cm/s (Thickness=1mm, porosity = 0.95, and average fibre diameter = 2μm) (Hinds, 1982).

Unlike cartridges or filters that are used for adsorbing gases, breakthrough is not an issue when considering PM filtration. If the sampling period is exceedingly long, however, clogging may occur. Clogging will result in restricted flow and increased pressure drops across the filter. Not only will the sampling flow rate be inconsistent but also the pressure drop may affect the partitioning of semivolatile species. Thus, care should be taken to ensure that sampling times are appropriate for the expected filter loading and that there is an accurate method of measuring the airflow through the instrument. Pressure differential methods of estimating and calibrating sampling flow rates should also be avoided where possible, since a clogged filter may not be recognised.

3.3.2 Mass determination

The mass concentration of PM in the gas that passed through the filter is determined by dividing the mass collected by the product of the gas volumetric flow rate and sampling time

interval. There are numerous methods for determining mass, including direct gravimetric determination of collected particles, measurement of the soiling of filter paper by the diminution of light reflectance or transmittance and measurement of transmittance of β -radiation. The most common mass-determination method for emissions testing is gravimetric.

Gravimetric methods consist of calculating the difference between the weight of the filters before and after sampling. Errors associated with this method include sensitivity to large particles, the necessity for large sampling times in order to collect sufficient sample and sensitivity to humidity. Because the amount of adsorbed water can significantly change the mass of the filter, the temperature and relative humidity must be controlled during equilibration prior to weighing. Static electricity is also a source of uncertainty but can be easily controlled using ionisers during weighing procedures. Teflon micropore filters are good filters to be used for gravimetric analysis because they have low tare weight, low sensitivity to humidity and do not adsorb chemical species with exposure to the atmosphere.

Measurement of the diminution of light reflectance consists of assessing the darkness of stained filters by a reflectometer. The instrument consists of a light source and a photosensitive element mounted together. The results may be converted to concentrations of 'standard smoke' by calibration curves. While this is an acceptable method for routine monitoring, its accuracy leaves much to be desired in the realm of research and regulatory testing. Uncertainties arise due to the presence of crystalline particles, which may increase the reflectance of the filter, and, in some cases, the colour of the PM collected.

Mass determination through β -radiation transmittance is performed by measuring and comparing the attenuation of β -radiation through a clean filter to the attenuation of a filter that has been used for sampling. The β -radiation is produced by a radioactive source and measured by ionisation chambers. The additional attenuation by the PM on the loaded filter is proportional to the mass collected. This method is particularly effective for long-term automatic sampling of short time periods. Sources of uncertainty include deviations that occur when there is a high proportion of heavier elements in the PM and sensitivity of the meter to

moisture (Harrison and Perry, 1986). This method is generally reserved for continuous atmospheric measurements at automated stations.

Filtration is the most common method for determining mass of PM and is the only reliable method for determining the chemical composition of PM. Generally, only particles larger than a certain “cut” diameter are removed upstream of the filter, yielding the mass concentration of particles smaller in size than the cut diameter (e.g. PM₁₀, PM_{2.5}, PM_{1.0}). This is because filtration conducted on higher resolutions, with individual filters collecting particles in a discrete size ranges, would collect very small amounts of material. Such discretized particle ranges result in net masses that are closer to detection limits. If a complete size distribution is desired, then other options need to be considered. The next section will review instruments designed to accurately determine the particle size distribution.

3.3.3 *Particle Size Distribution Instruments*

This section reviews methods that calculate the distribution of mass, surface area, or number of PM in a sample by particle diameter. The discussion shall limit itself to a brief outline of methods because the testing conducted for this report consisted of mass determination and chemical characterisation of PM collected on filters and did not use size instrumentation.

Aerosol sizing instruments may be divided into categories based on the measurement principle. Each instrument measures some property of the aerosol that relates to size, including but not limited to electrical mobility, inertial mobility, optical behaviour, and photoelectric emission. Given the sizes across which exhaust PM exists (0.001 - 1 μ m), no single instrument is capable of accurate size measurement across the whole spectrum. As a result, it may be necessary to either select the instrument that is best for the size range of interest or, if the aerosols of interest span across a large enough size range, consider using two different types of instruments.

Because PM is an agglomeration of particles that are not all necessarily spherical, results are quoted in terms of equivalent diameters. The unit quoted will be a function of the technique

used to determine the distribution. This means that a particle is assigned the diameter of a spherical particle that would have the same properties for a particular technique.

The two most common characteristics used to isolate particles of a particular diameter range are inertial mobility and electrical mobility. Equipment that relies on inertial mobility will draw the air through a tortuous path to deflect the airflow and use the inertia of particles for collection. Electrical mobility equipment relies on first charging the particles then using electric fields for separation. It is important to note that these two measures of diameter are not necessarily equivalent.

3.3.3.1 Inertial Mobility Equipment

Most instruments that rely on inertial mobility are variations on a cascade impactor. Cascade impactors consist of a series of impactor stages. Each stage consists of a nozzle to accelerate the flow of gas and a plate that forces the gas to deflect around it. Particles with sufficient inertia are deflected from the sample stream and onto the plate. Each successive impactor stage has a narrower jet to accelerate the gas to a higher speed and a shorter distance between nozzle and the plate. These two features ensure that sequentially smaller particles are collected on each successive stage. To facilitate collection of particle diameters smaller than approximately 50 nm, some cascade impactors include a filter as a final stage to collect PM that is smaller than the last impaction stage. A schematic of a cascade impactor is shown in Figure 28.

A limitation of impactors is that some particles (solid particles in particular) can bounce off the plates and become reentrained in the airflow. This effect can be reduced through coating the plate in grease that prevents particle bounce. However, this method eliminates the potential for future chemical analysis.

Figure 28. Schematic of cascade impactor (Hinds, 1982).

Another limitation of cascade impaction is that the smallest cut-off size is quite high (200 - 300 nm - Hinds, 1982). This cut-off size can be lowered to approximately 50 nm by operating the impactor at very low absolute pressures. This increases the mean free path between collisions and improves the collection efficiency of smaller particles. Unfortunately, evaporative losses for these smaller particles are expected to be high, since exhaust PM within this range is composed primarily of nucleated SVOCs.

The most common cascade impactors used today are the Electrical Low-Pressure Impactor (ELPI), and the Micro-Orifice Uniform Deposit Impactor (MOUDI). The ELPI is capable of measuring particle mass distributions on twelve stages from 30 nm to 10 μm diameter. It can be operated in either mass mode or number mode. In mass mode, the individual stages are

weighed before and after collection. In number mode, the ELPI charges the particles prior to entering the impaction stage. Each impaction stage is connected to an electrometer that detects the current produced by the impacting particles. This current is converted into a particle concentration in the corresponding size range. This approach allows the instrument to make essentially real time size distribution measurements with a time resolution of about 2 seconds. The instrument is very sensitive and can measure ambient aerosol concentrations. It can also be used to measure size distributions during transient laboratory tests of motor vehicle emissions (Kittelson, 1998a).

The key problem with the ELPI is the relatively high lower size cut-off of 30 nm. This is too large to detect the bulk of nanoparticles produced by new technology engines. Despite this, ELPI has been used for diesel particulate measurements because it is a versatile instrument, capable of spanning a wide range of particle size and concentration, in real-time, producing both number- and mass- size distributions.

The MOUDI is an 8- or 10-stage impactor with the four lower stages having micro-orifice impaction plates that rotate to provide near-uniform particle deposits over a circular impaction area. The cut points range from 10 μm to 56 nm in aerodynamic diameter with particles less than 56 nm being collected on a final filter. Although the lower size cut-off is less impressive than an ELPI, the MOUDI is a useful instrument for determining the mass size distribution of PM because it covers the entire size range, including the fraction less than 0.056 μm . Unfortunately, there is no capacity for determining number concentrations.

A variation of the MOUDI is the nano-MOUDI, which has 13 cut-sizes ranging from 10 nm to 18 μm . The improved lower size cut-off is made possible through micro-orifice technology combined with low-pressure operation in the stages collecting particles smaller than 50 nm. Gravimetric analysis determines the mass collected on aluminium foil substrates and a final stage filter. As long as they are not greased, these substrates may be analysed to determine the chemical composition of the mass collected on each stage (Kittelson, 1998a).

The aerodynamic particle sizer (APS) is another instrument that relies on inertial mobility. The operation of an APS involves measuring the acceleration of aerosol particles in response to the accelerating flow field created by the inlet nozzle. The particle response is a function of its inertia and particle size. The time-of flight is measured by scattered light that appears as it crosses laser beams. The detectable range for this instrument is 0.5 to 10 μm , which is outside the range in which most exhaust PM is found in (Kittelson, 1998a).

Generally, inertial mobility measurement equipment has a lower particle diameter limit that is too high for performing size distributions on exhaust PM. We shall find in the next section that electrical mobility equipment is much more efficient at collecting particles in the smaller size range. However, electrical mobility equipment has its own share of limitations.

3.3.3.2 Electrical Mobility Instruments

Electrical mobility instruments consist of two elements: a sorter and a detector. The purpose of the sorter is to produce an output stream with a narrow particle distribution from a sample gas with a relatively wide particle size distribution. This is achieved by passing the sample through a neutraliser that imparts a high level of positive and negative ions to the aerosols. The charged particles then pass through a variable electric field in the mobility analyser. Particles with the a positive charge and the proper electrical mobility exit through slits at the end of the classifier. A schematic of TSI Inc.'s Differential Mobility Analyser is shown in Figure 29.

Figure 29. Differential Mobility Analyser (TSI, 1998)

The detectors used to count the particles exiting from the sorter consist of either electrometers or condensation nucleus counters. Electrometers count the charges of the particles impacting on the detector. Limitations of electrometers are that they are only efficient with very low particle concentrations and the sensitivity of these detectors drops off dramatically below 10 nm due to diffusional particle losses and incomplete particle charging.

Condensation Particle Counters (CPCs) measure particles by exaggerating the size of each particle and detecting the enlarged particle. The sample stream passes through a warm region where there is a high concentration of butanol vapour. The sample then passes into a condenser tube, which is maintained at a temperature well below the butanol dew point. The supersaturated alcohol then begins to condense on the particles, causing them to grow in size from their various initial diameters to a relatively uniform final diameter of approximately 12 μm . These relatively large particles are then passed through an illuminated viewing volume.

The light scattered by these particles is measured by a photodetector and converted into a number concentration measurement. A schematic of a CPC is shown in Figure 30.

Figure 30. Condensation Particle Counter schematic (TSI, 1998).

Another particle detector is the quartz crystal substrate impactor. In this case, the sample gas is passed through a chamber that contains a small electrostatic precipitator, which deposits the particles onto one of a sequence of oscillating crystals. As the crystals collect mass, the oscillation frequency changes. The difference between its frequency and the frequency reference crystal provides an indication of the concentration of PM in the airflow. Limitations of this system include its sensitivity to moisture and the fact that the crystal has to be cleaned periodically. Another disadvantage is that because the crystal surface is greased to prevent loss of PM during sampling, the material collected cannot be used for chemical analysis later. Also, tests at the U.S. Bureau of Mines and by the AEA in the United Kingdom have shown that diesel PM is not compatible with the vibrating surfaces (Kittelson *et al*, 1998a).

A major limitation to the applicability of electrical mobility equipment in the measurement of exhaust emissions is that, although they can measure particle emissions in real time, they can only do so over a limited size range. The time to capture the concentration of particles in all size ranges is too long for transient emissions testing (Kittelson *et al.*, 1998a). Another limitation is that chemical characterisation is limited and no sample can be collected for later chemical analysis. What little chemical analysis that can be performed is discussed later in Section 3.4.1.

3.3.4 *Diffusion Batteries*

The fractionation of particles in a sample stream can also be achieved with the aid of a diffusion battery, which is an assembly of equally spaced circular tubes or holes, through which the sample gas passes. In this arrangement, the particles diffuse to the walls through Brownian motion. The sample at the end of the battery is then drawn through a CPC, or through filters. Because diffusion forces are stronger for smaller particles, the effective range is approximately 5 nm to 0.5 μm , a range ideally suited for exhaust PM.

A diffusion battery following a cascade impactor is a particularly good combination of particle collection. The key advantages of this arrangement include the large range of particle sizes measured and similarity to the deposition mechanisms for fine particles in lung tissue. If real time emissions are desired, however, a CPC would have to be fitted to each diffusion tube, which can become expensive.

3.3.5 *Particle Measurement with Photoemission and Spectrometry*

Photoemission techniques are attractive options for measuring particles because the sample is not altered during analysis. Light extinction is a commonly used diagnostic technique for measuring soot volume fraction. Unfortunately, this method measures a line-of-sight average, which is a drawback. Elastic scattering of light has also been considered but the signal from light scattering is proportional to the square of the particle diameter. Given that soot particles are agglomerated masses and thus not necessarily spherical, the application of light scattering for particle sizing is associated with large errors (Gülder, 1998). Generally, these photoemission and spectroscopy instruments are only capable of performing analysis of

particles larger than approximately 0.3 to 0.4 μm , which is not an acceptable range for exhaust PM.

Laser induced incandescence (LII) is a promising technique for measuring soot volume fraction in flames. In LII, the soot is heated by a short duration laser pulse to produce incandescence. The particles are heated to approximately 4000 - 4500 K. The soot particles radiate light as they cool back to the ambient temperature of 1500 to 2000K in the flames. The light signal is proportional to the particle volume fraction. LII is advantageous because it can be used in any environment, including flames and exhaust gas streams. The use of LII in measuring exhaust PM is limited because it can only measure soot and does not capture condensed species. In fact, the LII system presently used at NRC cannot resolve the results into soot agglomerates – it can only identify the nuclei that form the agglomerates.

In the next section, we will return to filtration issues, with particular emphasis on determining the chemical composition of the particles collected.

3.4 Chemical Characterisation

The determination of the chemical composition of PM is of critical importance for air quality modelling studies. From a health perspective, the physical and chemical characteristics of a pollutant at the receptor level are of more interest than the characteristics directly out of the pipe. In receptor oriented studies, for example, the chemical composition of an ambient sample is apportioned to potential sources of the chemical species. Although size distributions are important for exposures very close to the pipe exit, these distributions will change with time as the particles interact with the atmosphere. It is expected that any changes to size distribution will result from coagulation, rather than deposition, given the size range of exhaust PM. If this is true, we can also expect that the chemical components of the PM, particularly trace elements and other unique chemical characteristics, will remain in the air long after the exhaust exits the vehicle. Thus, knowledge of the chemical composition of PM emitted from sources can help us identify contributors to the chemical components observed in ambient PM.

The most common method of collecting PM for chemical analysis is by filtration. When selecting filters for future chemical analysis, the filter should not contain trace amounts of chemicals that may also be found in the PM. Otherwise, the detectable limits for analysing the collected sample will be excessively high. It is also critical that the medium selected does not react with the collected material, particularly during analysis. An example of poorly matched collection media and analysis method is the use of Pallflex Emfab™ (Teflon coated borosilicate glass fibre) filters for thermal optical carbon analysis. Emfab filters can be used for solvent extraction for detailed organic carbon analysis but neither the Teflon nor the glass fibres are thermally stable at the upper temperature range required for organic/elemental analysis (Graham, 2000).

The following discussion will outline the methods that are used to determine the chemical constituents of collected PM.

3.4.1 Organic / Elemental Carbon

The analysis of organic and elemental carbon consists of classifying the carbon collected on a filter into that carbon which is in the form of soot (elemental carbon - EC) and the carbon that is present as condensed organic compounds (organic carbon - OC). This analysis is useful in source apportionment studies, since there are few natural sources of elemental carbon and any elemental carbon present in an ambient sample is likely due to a combustion source.

The carbon collected on a filter can differ from the actual carbon in gas phase particles due to positive and negative "artefacts" associated with the collection method. A schematic of the artefacts associated with carbonaceous PM sampling is shown in Figure 31. The negative artefact is due to semivolatile material in the PM partitioning to the gas phase and escaping the medium after the particles have adhered to the filter. Positive artefacts result from volatile organic material in the gas phase adsorbing onto the filter medium during sampling due to the fact that, in addition to collecting PM, quartz filters have an affinity for volatile organic compounds.

Figure 31. Artefacts associated with collecting carbonaceous material of PM (A_N = Negative artefact, A_P = positive artefact) (Adapted from U.S. EPA, 1999).

There are numerous methods available to account for the positive artefact. The most common is to sample for carbon using two quartz filters in series. The upstream filter (termed Q_1 in Figure 32) collects carbonaceous PM and adsorbs some volatile organic carbon. The downstream filter (Q_2) is intended to replicate the adsorption of the organic carbon to the filter medium as it occurred on the upstream filter. The PM-bound organic carbon is calculated by subtracting from the organic carbon observed on the upstream filter, the organic carbon that has been collected on the downstream filter. Of course, the amount of positive artefact that adsorbs onto the quartz media will be a function of the concentration of gaseous organic material in the sample gas. Given that the volatile organic material that adsorbs onto the primary filter is clearly not available to adsorb onto the downstream filter, there could be potentially different adsorption amounts on the downstream filter compared to the upstream filter. This results in an under-correction of the adsorbed organic carbon, in turn resulting in an overestimate of the PM-bound organic carbon.

Another method for correcting the positive sampling artefact for organic carbon is to use a third quartz filter (Q_3), placed downstream of a Teflon filter (T_1). Because Teflon has a much lower affinity for VOC, the Teflon filter collects the particle-bound organic carbon but leaves

nearly all the VOC material in the sample so that it is available for adsorption onto the supplemental quartz filter. In addition, less of the VOC that desorbs from the PM on the filter will become readsorbed onto the Teflon filter compared to the quartz arrangement. The traditional filter set-up and the supplemental filter set-up used in this study for collection and analysis of organic and elemental carbon is shown in Figure 32.

Figure 32. Schematic of organic carbon artefact correction methods.

With this arrangement, the PM-bound OC on Q_1 is calculated by subtracting the OC observed on Q_1 by the OC observed on Q_3 (filter media- adsorbed OC). Using the terminology from Figure 32, the corrected OC can be expressed as $OC = OC_{PM} \cdot A_N + (A_{P1} - A_{P3})$. In essence, it is assumed that A_{P3} is a better estimate of $(A_{P1} - A_{N(Q)})$ than A_{P2} is.

These methods have been analysed in combustion exhaust testing (Hildemann, 1991). When testing an oil-fired boiler, it was found that the OC on the downstream filter averaged 18% of the OC mass collected on the upstream filter. Vehicle testing found that the OC collected on a quartz filter placed downstream of a Teflon filter was between 21 and 34% of an upstream quartz filter in a separate channel.

Although the correction using a third quartz filter is a better approximation of the positive sampling artefact, neither of these methods can properly account for the possibility of negative sampling artefacts, such as the desorption of organic material from the particles collected on the filter medium. It appears that this negative artefact may be of greater import than the positive artefact. Estimates of this negative artefact are that as much as 20-80% of the particle-phase organic material can be lost during sampling (Eatough, 1993).

A good method for the removal of gas-phase VOC without affecting PM-bound OC is to use a diffusion denuder upstream of the quartz filters. Denuders are similar to diffusion batteries in that they are hollow glass or metallic tubes but they are coated with an appropriate material to selectively collect gases while allowing particles to penetrate. Placing a denuder upstream of the filter packs can remove VOCs from the sample while denuders or cartridges placed downstream can also help to determine the negative artefact. Denuders have also been used to remove ammonia from the gas phase so that acidic particles can be measured on filters without neutralisation. The planned filter set-up for U.S. EPA PM_{2.5} monitoring stations is to have a denuder (for VOC cleanup) placed upstream of a single quartz filter with a post-filter sorbent to capture the negative sampling artefact (U.S. EPA, 1999). Care should be taken in selection of denuder design for exhaust sampling to ensure that the denuder does not also remove ultrafine particles.

The degree to which positive and negative artefacts will influence collected carbonaceous PM will be a function of numerous sample gas flow characteristics, such as flow velocity and temperature. The temperature of the sampling gas will affect the partitioning of the semivolatile organic compounds between the gas and particle phases upstream of the filter. In addition, filter face velocity and temperature, sampling time and absolute pressure at the filter face will affect the adsorption and desorption of organic compounds on the collected PM as well as the filter medium.

Given the sensitivity of the collected carbonaceous PM to the above factors, it becomes apparent that efforts should be made to keep sampling conditions constant over multiple tests to ensure repeatability of results. Variations in ambient temperature and atmospheric pressure

result in variability in the nature of the air used to dilute the exhaust for sampling. As we shall see later in Chapter 6, variability in these parameters can in turn result in variability in the organic fraction. Some dilution tunnels can adjust a particular parameter, such as exhaust flow rate or dilution air temperature so as to ensure some consistency in sampling conditions. Unfortunately, these arrangements generally allow for the adjustment of either dilution ratio or exhaust temperature but not both.

With these systems, it must then be decided which parameters should be kept constant at the expense of the other. This question has been evaluated by Waldenmaier *et al.* (1990) by observing the variability in organic fraction of diesel PM. Their study was conducted using a muffler/exhaust splitter system that facilitated the adjustment of dilution ratio so as to maintain a constant filter face temperature of 40° C. It was found that variability in organic fraction measurements decreased by 60% by maintaining a constant filter temperature compared to maintaining a constant dilution ratio.

In general, thermal optical methods have been the methods of choice for determining the relative quantities between organic carbon (OC) and elemental carbon (EC), also known as the OC/EC split. In fact, the definitions of OC and EC are currently based on these analytical methods. Thermal optical methods consist of exposing a section of the filter to a ramped temperature program that ranges from 20 °C up to approximately 940 °C while adjusting the oxygen content. Because of the extreme temperatures, the medium that is generally used is a quartz fibre filter.

In the search for an operationally standard method for organic/elemental carbon analysis, two methods have been key contenders - thermal optical reflectance (TOR) and thermal optical transmittance (TOT). These methods are similar in the sense that they subject a section of the filter to a ramped temperature profile while observing the optical characteristics of the section. In this study, the method used by the National Institute for Occupational Safety and Health (NIOSH), TOT was used. This method has also been recommended by the U.S. EPA for use in their Air Monitoring Stations (U.S. EPA, 1999). The procedure is illustrated in Figure 33. In this figure, three characteristics (temperature in the analysis cell; transmittance of a laser

through the filter and the response of the flame ionisation detector) are plotted qualitatively. When discussing exhaust PM, carbonate carbon concentrations are negligible and can be ignored.

Figure 33. Thermogram for filter sample containing organic carbon (OC), carbonate (CC), and elemental carbon (EC) (NIOSH, 1998).

The method consists of taking a 1.5 cm² cut-out from the loaded filter and placing it in an analysis cell. The cell is then sealed and an atmosphere of 100% helium is established in the cell. At the beginning of the analysis procedure, the temperature in the analysis cell is increased to approximately 850 °C in three or four steps. The steps are intended to spread out the evolution process and ensure that the flame ionisation detector (FID) does not become overloaded with converted CH₄. During this temperature increase, carbon begins to evaporate off the filter. This evolved carbon is first converted to CO₂ then to CH₄ and quantified by FID. At each temperature step, organic compounds with sequentially lower vapour pressures

are evolved and detected by FID. As the temperature increases and more OC is evolved, some of the OC may pyrolyse to produce char or pyrolytic carbon (PC) on the filter.

The carbon remaining on the sample after the 850°C step is a combination of PC and elemental carbon (EC). To evolve these components from the filter, a 2% oxygen/ 98% helium atmosphere is introduced to the sample and the temperature first reduced to 600 °C then stepped to approximately 940°C. The oxygen in the atmosphere oxidises the carbon to form CO₂, which is then converted to CH₄ to be detected and quantified by FID.

Throughout the analysis procedure, light transmittance of the filter sample is simultaneously monitored. The transmittance of light through the filter is inversely related to the concentration of elemental carbon on the filter and may decrease as PC forms on the filter. The conversion of PC and EC to gas results in a concurrent increase in transmittance. The shift from measuring OC to measuring elemental carbon occurs when the filter transmittance increases to its initial value at the beginning of analysis. After the EC peak as measured by FID has completely subsided, the temperature is decreased and a known measure of methane is introduced to the FID for calibration purposes.

The use of a filter transmittance as a measure of the split between organic and elemental carbon means that these methods produce results that are operationally based and do not necessarily reflect an absolute measure of carbon-as-soot or carbon-as-hydrocarbons. The results of a particular test using an operational method can only be properly compared to other data produced using similar analytical methods. Otherwise, it is necessary to include caveats in the discussion regarding the limited applicability of the comparison.

Other methods used for estimating relative proportions of soot and condensed species include measuring the soluble organic fraction (SOF) and the use of a catalytic stripper system (CSS). The SOF is considered the fraction of PM collected on the filter that could be extracted from the filter using organic solvents such as dichloromethane or benzene. A CSS can be used to determine the non-volatile portion of PM in a dilute exhaust stream. A CSS operates by passing the dilute exhaust sample over an electrically heated exhaust catalyst. The catalyst

strips 100% of the volatile components from the particulate sample without removing significant amounts of the non-volatile portion. By alternating between sample that has passed through the stripper to sample that bypassed the stripper and comparing the concentrations of the two streams, the total, volatile and non-volatile fractions can be determined.

3.4.2 Organics Analysis

The organic fraction of combustion aerosols contains hundreds to thousands of chemical components. These components include long chain n-alkanes, polycyclic aromatic hydrocarbons (PAHs) and their derivatives, most of which are semivolatile. Much of the concern regarding the health effects of PM from exhaust emissions is due to potential mutagenic and genotoxic effects of certain organic compound classes present in PM. There is also interest in the opportunities for identifying stable biomarkers, which could be used in source apportionment modelling. Generally, organics analysis includes the following steps: sample collection, solvent extraction, and concentration, clean up, and chromatographic separation. Depending on the nature of the sample, some of these steps may be avoided.

The filter of choice to collect PM for organic analysis is a Teflon-coated borosilicate glass fibre filter. Keeping in mind the volatility issues discussed in Section 3.4.1, measures need to be taken to limit the presence of positive or negative artefacts on the filter. The standard practice is to use a two-stage filter system, such as the one described earlier for organic-elemental carbon analysis.

The extraction of the organic compounds from the PM on the filter paper is typically performed by placing the filters in a Soxhlet apparatus, using organic solvents of low to medium polarity such as cyclohexane, toluene, and methylene chloride. Extraction times vary between 1 and 48 hours. Given that some compounds may decompose during the extraction procedure, alternative methods, which have shorter extraction times, are very attractive and worth consideration. Methods that have been considered are ultrasonic vibration, supercritical fluid extraction (SFE) and direct thermal desorption to a gas chromatograph (GC) (Kouimtzis and Samara, 1995).

After the organic matter has been extracted from the particulate sample, the complex array of organics is often separated into simplified mixtures for more accurate analysis. Clean up and fractionation of the extracted material is usually done by column chromatography using a variety of solvents. In the case of detailed organics analysis for engine exhaust, the organics collected are separated into the following fractions: alkanes, naphthenes, hopanes and steranes, polynuclear aromatics and polar compounds. These fractions are then sent to separate laboratories for analysis.

Organics have been traditionally analysed by gas chromatography (GC) with mass spectrometric detection. There are limitations associated with the use of GC, particularly because of the thermal instability of some species and the low volatility of the higher molecular weight species. High-pressure liquid chromatography (HPLC) is emerging as a promising method because of its improved selectivity of compounds that are often difficult to separate by GC. Furthermore, the fact that compounds can be separated at ambient temperatures also reduces the risks of the material decomposing at high temperature. However, the resolution can be lower when dealing with complex samples as can be expected with diesel PM.

3.4.3 Trace Metals and Ions

The identification of elements in the PM sample provides valuable information for PM source apportionment. Certain trace elements, such as rare earth metals in the case of gasoline vehicles with 3-way catalysts, are unique to automobile emissions. The semivolatile issues associated with organic compounds are less applicable to elemental analysis or ions, particularly for the short sampling times that are experienced during emissions testing. As a result, the use of a backup filter for determination of these characteristics is generally not considered necessary.

The determination of trace elements is generally conducted by Energy Dispersive X-ray Fluorescence (EDXRF) or Proton Induced X-Ray Emission (PIXE). These methods consist of exciting the sample and measuring the response in the X-Ray spectrum. EDXRF relies on the elements on the sample emitting characteristic radiation following excitation by electromagnetic radiation. PIXE differs from EDXRF in that the former relies on heavily

charged particles for excitation (Kouimtzis and Samara, 1995). These methods have been used extensively in the analysis of ambient aerosols because they are non-destructive, have multi-element capabilities, and are relatively inexpensive. One of the limitations of XRF analysis is that it is conducted in a vacuum to obtain the greatest efficiency and sensitivity. This procedure may result in the evaporation of volatile compounds, which may affect the results of subsequent tests.

Aerosol ions refer to chemical compounds that are soluble in water. They are of interest because of their ability to pass into the blood stream and their potential reactivity. In ambient samples, aerosol acidity is the result of ionic species present in PM. Ion analysis is generally conducted on Teflon filters. The standard analysis practice for PM analysis is to first conduct gravimetric analysis followed by submitting the same filter for XRF analysis, then after it returns, submitting it for ion analysis.

Ions analysis is similar to detailed organics analysis, in that the process consists of first extraction the ions from the sample, followed by separation and detection. The extraction process consists of first wetting the filters with isopropanol and then extracting the ions into deionised water by ultrasonification. Analysis of the extract is often performed by ion chromatography or capillary electrophoresis.

3.4.4 PM Precursors

PM precursors, particularly SO_2 , NH_3 , and gaseous organic acids, are often measured in source assessment studies to estimate the PM forming potential of exhaust gas. The conversion of these gases to PM is difficult to predict and the methods for these estimations will not be discussed here. However, since this information is valuable data for air quality modellers and collection equipment is commonly part of the sampling system, the collection of these gaseous precursors to PM shall be reviewed, with particular emphasis on SO_2 collection.

SO_2 and NH_3 samples are commonly collected on cellulose filters coated with a carbonate salt and a weak acid respectively. Gaseous organic acids are collected on quartz filters coated with

potassium hydroxide. Prior to passing the sample through these filters, PM is removed through filtration to eliminate confounding factors such as PM-bound sulphate ions.

Sulphur dioxide is oxidised to sulphate ion in the chain of reactions shown below and adheres to the filter. Note that some water is necessary on the filter to facilitate the collection.

The ammonia is converted to ammonium citrate during the reaction with the citric acid that is impregnated on the filter through the reaction shown below.

Organic acids bond to the impregnated potassium through an acid-base neutralisation reaction. After sampling, the material is extracted from the filters and the extracts are then analysed by ion chromatography.

The collection of gases by coated filters is certainly one of the simplest and most cost-effective method for sulphur dioxide sampling. It may not be the most efficient method, however. Schorran and Keislar (1996) conducted a comparison of sulphur dioxide measurement methods. In particular, they reviewed the collection efficiency of potassium carbonate coated Whatmann 41 cellulose filters (the same as those used in this study), carbonate-coated annular denuders, and two fluorescent sulphur analysers. The collection efficiency was determined by sampling a standard gas with 9.2 ppb SO_2 at a rate of 16.7 - 17.1 lpm for approximately two hours. The results of this study found that among the four methods, carbonate-coated filters

consistently had the lowest collection efficiency, with ratios of filter SO_2 to delivered SO_2 ranging from 0.48 to 0.90. By comparison, carbonate-coated denuders had collection ratios of 0.77 to 1.03. Sulphur analysers that relied on fluorescence had the highest collection ratios. The concentration of SO_2 used in this comparison is slightly lower than the average SO_2 concentration that was observed in samples of 34 ppb.

An interesting observation made in Schorran and Keislar's study is that all techniques underestimated the amount of delivered SO_2 when the sample relative humidity is greater than 70%. This was attributed to the fact water may nucleate onto PM at or above 70% relative humidity. The presence of liquid water in the sample lines was thought to inhibit the transfer of SO_2 to the analysers and the filter.

3.5 Conclusions on the Choice of Analytical Methods

This chapter has reviewed the methods for analysing the physical and chemical characteristics of PM in a dilute exhaust sample. Physical characterisation techniques included total mass and size distribution on a number or mass basis. The chemical analysis techniques that were reviewed included organic/elemental carbon quantification, analysis of trace metals, ions and organics, and quantification of gaseous precursors to PM.

A key element worth noting is that each method for collecting PM is wrought with limitations that stem from the fact that no single instrument is capable of analysing all characteristics at once. There are conflicting needs that polarise themselves. These needs are transient versus steady state testing, chemical characterisation versus physical characterisation, and real-time measurement versus time-averaged measurement.

The choice of whether to measure motor vehicle PM emissions while operating under steady state conditions or transient conditions more representative of real driving conditions will depend on the purpose of the experiment. Steady-state testing is effective when testing the analytical equipment for repeatability and for evaluating the effect of such factors as engine load, fuel-air ratio, and valve timing. Sampling during transient behaviour will be more

important when attempting to characterise the effect of control factors such as cold- versus hot-starts and rapid accelerations and to develop emissions inventories.

In addition to these engine issues, some particle sizing instruments, such as many electrical mobility particle sizers, have rather long resolution times (time to complete size distribution). These instruments require that the PM characteristics in the sample gas remain constant throughout the length of the resolution time. This necessitates the need to perform steady-state cycles when using the equipment.

The tug of war that arises between chemical characterisation and physical characterisation is exemplified by the issue of size distribution measurement. If it is desired that the material collected by a particle sizer such as a MOUDI, be analysed for chemical analysis, longer driving cycles, higher sampling flow rates and/or a more concentrated sample will be required to collect sufficient sample for analysis.

The evaluation of real time PM emission rates and size distributions may also interfere with future chemical characterisation. Many instruments that measure PM emissions in real-time contaminate the particles in some way or another to facilitate measurement. Examples of this contamination are condensation particle counters, which use the particles as condensation nuclei to produce large (approx. 12 μm) butanol particles for detection, or plates on cascade impactors that are greased to which minimise bounce during sampling.

It is true that the simple solution to marrying these conflicting interests is simply to use more than one type of equipment during an emissions test. There is virtually no operational limit to the number of analytical instruments or filter collection that could be performed. Nevertheless, emissions testing is an expensive business. Thus, it is necessary to be careful in selecting analytical equipment according to project resources and research priorities.

The purpose of this section was to describe the analytical procedures and put the results of analysis in context. A limited number of the characterisation procedures outlined in this chapter were actually performed by the author. Instead, filters were collected, labelled and sent

for analysis. In particular, organic/elemental carbon analysis was performed by the Mining and Mineral Science Laboratory of Natural Resources Canada in Sudbury using the NIOSH 5040 method of thermal optical transmittance. Ion analysis and SO₂/NH₃ analysis were performed at the Environmental Technology Centre.

The next chapter describes the sampling and analysis procedures that were performed for this particular study.

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Chapter 4 **Vehicle Emissions Testing Procedure**

Two groups of emissions tests were conducted in this study. Motorcycle testing was conducted to evaluate the effect of fuel type and driving cycle on spark ignition emissions while bus testing was conducted to assess the effect of ambient temperature and an oxidative catalytic converter on emissions from diesel engines.

Gaseous and PM_{2.5} emissions were collected. The characterised gaseous emissions included criteria pollutant emissions and speciated hydrocarbon and carbonyl emissions. The results for gaseous emissions can be found in Appendix B. PM_{2.5} emissions were characterised gravimetrically and chemically. The chemical characterisation of PM_{2.5} included accounting of elemental and OC, characterisation of metals and ions, and detailed organics analysis. In addition, sulphur dioxide and ammonia emissions were collected using coated cellulose filters.

4.1 Vehicle Operation

This section discusses all aspects of the operation of the vehicles during the testing campaign. Topics that are discussed include the driving cycle operated, the fuel used and description of emission controls.

4.1.1 Motorcycle Testing Operation

The two motorcycles used in this project were taken from Transport Canada's 1998 compliance fleet. Ideally, the engines of these vehicles would have had similar engine sizes to better assess how emissions are affected by vehicle design. However, one of the vehicles selected for testing (Kawasaki Vulcan VR-800) could not be used because a seal could not be made around the exhaust, resulting in a leaking exhaust system. The substitute vehicle was a Honda CBR 600. A summary of the specifications and emissions controls for these

motorcycles is found in Table 2. Emissions rates quoted in this table are from emissions testing conducted on vehicles in 1998.

Table 2. Motorcycle specifications.

	Suzuki GSX-R 750W	Honda CBR 600
Engine	0.8L, L4	0.6 L, L4
Transmission	Manual 6 speed	Manual 6 Speed
Emissions Controls	Electronic fuel injection Pulsed air	Engine Modification
Emission Rates (g/mi)	HC – 2.96 CO – 8.98	HC – 3.22 CO – 14.48

The emissions controls on these motorcycles are limited compared to light duty vehicle (LDV) controls. For the Suzuki, the pulsed air arrangement is installed just outside of the exhaust valve. The air is injected just as the exhaust valve opens, exposing the hot exhaust gases to fresh oxygen, which helps to complete the combustion of unburned fuel prior to exhaust exit (Collins, personal communication, 2000). Although ERMD had engine modifications listed as emission controls, Honda Canada was unaware of what these modifications were (Barry, personal communication, 2000).

The two motorcycles were tested on three different driving cycles and operated on two different fuels. The driving cycles conducted were the '4-phase Federal Test Procedure' (FTP), three repeats of the US-06 cycle and three repeats of the New York City Composite (NYCC) cycle. Detail on these driving cycles can be found in Section 3.1.2. The data from the FTP test is used primarily for emissions inventory and modelling purposes. The US06 cycle provides an indication of the change in emissions due to high speed and aggressive driving habits and the NYCC simulates vehicle operation in congested urban traffic.

The 4-phase FTP differs from US-75 cycle presented in Section 3.1.2 in that a second transient phase was included after the hot start. Thus, two complete LA4s were performed on the FTP with a hot soak in between. Ideally, each phase would have been sampled on separate filters. Unfortunately, because there is no pause between the Cold Start Phase and the Transient Phase of the FTP, using a separate set of filters for each phase was not possible. Instead, the

FTP cycle was expanded and a single set of filters was used for the first LA4, termed CS-LA4, and a second set of filters for the second LA4, termed HS LA4. This method facilitated a better comparison between the two cycles, since the only difference between the two filter sets is that the engine starts from cold in one of them. A composite $PM_{2.5}$ mass emission rate was calculated from the CS-LA4 (mg/mile) and HS-LA4 (mg/mile) portions by weighted sum ($0.43 \cdot \text{CS-LA4} + 0.57 \cdot \text{HS-LA4}$). This is identical to Equation 1, since each portion includes a transient phase.

The fuels used were a commercially available summer grade fuel and a low-sulphur summer grade produced from Oil Sands derived stock. A summary of the fuel quality is shown in Table 3.

Table 3. Characteristics of the test fuels used in motorcycle testing.

Parameter	Current SGC (Canadian)	Low Sulphur SGC (Canadian)
Sulphur (ppm_m)	338	2
Lead (mg/L)	<1.0	<1.0
Manganese (mg/L)	2.7	5.2
Specific Gravity	0.752	0.733
Reid Vapour Pressure (kPa)	59.7	76.2
Oxygenates (wt. %)	0	0
Aromatics (vol. %)	34.63	32
Olefins (vol. %)	10.99	0.99

Two complete sets of samples were collected for each test cycle for each fuel-vehicle combination. A summary of the complete set of tests is presented in Table 4.

Table 4. Summary of motorcycle testing conducted.

Date	Tests Completed	Fuel Type	Vehicle	Date	Tests Completed	Fuel Type	Vehicle
15 June	CS Set 1	SGC	Suzuki	7 July	CS Set 1	SGC	Honda
	HS Set 1				HS Set 1		
	US06X3 Set 1				US06X3 Set 1		
	NYCC Set 1				NYCC Set 1		
16 June	CS Set 2			8 July	CS Set 2		
	HS Set 2				HS Set 2		
	US06X3 Set 2				US06X3 Set 2		
	NYCC Set 2				NYCC Set 2		
22 June	CS Set 1	Low-Sulphur SGC		13 July	CS Set 1	Low-Sulphur SGC	
	HS Set 1				HS Set 1		
	US06X3 Set 1				US06X3 Set 1		
	NYCC Set 1				NYCC Set 1		
23 June	CS Set 2			14 July	CS Set 2		
	HS Set 2				HS Set 2		
	US06X3 Set 2				US06X3 Set 2		
	NYCC Set 2				NYCC Set 2		

Prior to testing on the first fuel (current Canadian SGC) the fuel tank of the motorcycle was drained and the test fuel added. The motorcycle was driven for 100 km, the fuel tank was then drained and filled with fresh test fuel and an additional 50 km was driven. The day before testing, the motorcycle was pre-conditioned as specified by the Federal Test Procedure (U.S. Code of Federal regulations: Title 40: Part 86). The same procedure was followed when switching from the SGC fuel to the low sulphur SGC fuel.

4.1.2 Bus Testing Operation

The bus used for this testing was a 1989 MCI Classic (12.2 m) urban bus DDC 6V92TA DDEC II (9.05 L two stroke: 189kW). It was operated with and without an oxidative catalyst at warm and cold ambient temperatures. Two sets of tests were conducted for each combination of parameters. Each set consisted of sampling the last two of three repeats of the Central Business District (CBD) cycle. Each repeat was separated by five minutes of idling. The CBD cycle is a synthesised saw-tooth cycle, which is discussed in 3.1.2. It consists of idle, acceleration up to 32 km/hour, cruise and deceleration modes repeated 14 times over 600 seconds. A summary of the sampling conducted is shown in Table 5.

Table 5. Summary of bus sampling conducted.

Date	Test Cycle Sampled		Ambient Condition	Exhaust Treatment
4 Feb.	Set #1	CBD #2 CBD #3	Warm (20 °C)	Catalyst
	Set #2	CBD #2 CBD #3		
7 Feb.	Set #1	CBD #2 CBD #3	Cold (-10 °C)	
	Set #2	CBD #2 CBD #3		
7 Feb	Set #1	CBD #2 CBD #3	Cold (-10°C)	Baseline
	Set #2	CBD #2 CBD #3		
23 June	Set #1	CBD #2 CBD #3	Warm (15 °C)	
	Set #2	CBD #2 CBD #3		

The diesel oxidation catalyst used on this vehicle was designed to reduce the soluble organic fraction of PM. The catalyst had a loading of platinum on a molecular sieve containing washcoat, which is stabilised against deterioration at elevated temperatures. The converter muffler designs used in this study were installed in the location of the original vehicle mufflers. The converter mufflers were designed to provide similar backpressure and sound attenuation to the original vehicle mufflers. When operating without the converter, a substitute muffler was used to ensure that the backpressure was also comparable to Original Equipment Manufacturer (OEM) specifications.

Operations were conducted at warm and cold temperatures to assess emissions rates for local conditions. The results from this testing will later be used in a local source apportionment study, where ambient samples will be taken in different microenvironments during both winter and summer conditions. Part of the source apportionment study is to determine whether emissions data taken using similar weather conditions result in better fits for the apportionment model.

Cold temperatures were simulated by operating the vehicle in a test cell where the temperature could be reduced to as low as -20°C , given the right testing conditions. The dilution tunnel and sampling equipment were also located in the cold test cell to better simulate on-road dilution in winter. Because the results of this bus testing were to be used in a source apportionment study and the testing was conducted in winter, the vehicle was operated in an "as received" condition. With the exception of running the vehicle through a warm-up cycle prior to sampling, the vehicle was neither preconditioned prior to testing nor was the fuel in the vehicle drained and replaced with a standard test fuel.

4.2 Sample Collection

Samples were taken from the dilution tunnel described in Section 3.1.3. Gaseous emissions of CO , CO_2 , NO_x and THC were determined in the manner specified in the FTP (U.S. Code of Federal Regulations: Title 40: Part 86), using emission analysers for each of these gases. Separate samples were collected for determination of CH_4 and detailed hydrocarbon analysis by gas chromatography (GC) and flame ionisation detection (FID). A Tenax cartridge was placed upstream of the hydrocarbon sample bag to collect semivolatile material. Emissions samples were collected for determination of carbonyl compound emission rates using 2,4-DNPH cartridges. In bus testing, heated lines were used to carry NO_x and THC to the analyser to prevent loss of sample.

A schematic of the PM sampling train is shown in Figure 34. Three probes were inserted into the tunnel along the axis of the flow, with an additional probe installed in the dilution air intake. Each of the dilute exhaust probes used a cyclone to remove PM larger than $2.5\text{ }\mu\text{m}$ at 91 lpm. Two of the sample streams were each passed through a two-stage filter pack containing 90 mm Pallflex Emfab™ filters (labelled S90-A/B -- see Section 3.4) at 91 lpm. The third stream was drawn through a 4-way flow splitter, where two-stage filter packs for 47-mm filters were used (labelled S47-A/B/C/D), each being sampled at 22.75 lpm so that flow through the cyclone would sum up to 91 lpm. During bus testing, equipment limitations dictated that only three channels of the 4-way splitter could be used. As a result, the flow through the 47 mm filter packs was increased to 30.33 lpm. In addition, one of the filter

cartridges was converted from two-stage to a three-stage. A summary of the filters used and their purpose is shown in Table 6

Figure 34. Schematic of $PM_{2.5}$ sampling set-up for motorcycles testing. (Filter terminology: S=Sample; 47/90=filter diameter (mm); A/B/C/D=identifier)

Dilution air was sampled for gaseous and $PM_{2.5}$ emissions rates calculations. The gaseous dilution air sample was collected according to the FTP and was analysed at the end of each test. Dilution air for PM calculations was collected on four filter packs (labelled A47-A/B/C/D) using a four-way flow splitter for the duration of a test day. Because the dilution air was pre-treated with a HEPA filter, it was assumed that no PM was present in the dilution air sample and no cyclone was necessary for $PM_{2.5}$ separation. It was found in testing that the net mass measurements on these filters were negligible, validating the assumption. A summary of the filter pack set-up for dilution air sampling is presented in Table 7.

Table 6. PM Filter set-up for dilute exhaust sampling.

Probe	Cartridge Ident.	Flow Rate (lpm)		Position	Filter type	Purpose
Motorcycle Testing						
1	S90-A	91		Upstream	Emfab	Detailed PM organics
				Downstream	Emfab	Organics corrections
2	S90-B	91		Upstream	Emfab	Detailed PM organics
				Downstream	Emfab	Organics corrections
3	S47-A	22.75	91	Upstream	Quartz	Organic / Elemental carbon
				Downstream	Quartz	OC/EC correction
	S47-B	22.75		Upstream	Teflon	Gravimetric
				Downstream	Quartz	OC/EC Correction
	S47-C	22.75		Upstream	Teflon	Gravimetric
				Downstream	Carbonate coated	SO ₂ collection
	S47-D	22.75		Upstream	Teflon	Gravimetric
				Downstream	Citric acid-coated	NH ₃ collection
Bus Testing						
1	S90-A	91		Upstream	Emfab	Detailed PM organics
				Downstream	Emfab	Organics corrections
2	S47-A	30.33	91	Upstream	Quartz	Organic / Elemental carbon
				Downstream	KOH coated Quartz	OC/EC correction
	S47-B	30.33		Upstream	Teflon	Gravimetric
				Downstream	Quartz	OC/EC Correction
	S47-C	30.33		Upstream	Teflon	Gravimetric
				Middle	Carbonate coated	SO ₂ collection
				Downstream	Citric acid-coated	NH ₃ collection

Table 7. Filter set-up for dilution air sampling

Cartridge Ident.	Flow Rate (lpm)	Position	Filter type	Purpose
Motorcycle Testing				
A47-A	16.7	Upstream	Emfab	Gravimetric / Detailed organics
		Downstream	Emfab	Organics correction
A47-B	16.7	Upstream	Quartz	OC/EC
		Downstream	Quartz	OC/EC Correction
A47-C	16.7	Upstream	Teflon	Gravimetric
		Downstream	Carbonate coated	SO ₂ collection
A47-D	16.7	Upstream	Teflon	Gravimetric
		Downstream	Citric acid-coated	NH ₃ collection
Bus Testing				
A47-A	15.0	Upstream	Quartz	OC/EC
		Downstream	Quartz	OC/EC Correction
A47-B	15.0	Upstream	Teflon	Gravimetric
		Middle	Carbonate coated	SO ₂ collection
		Downstream	Citric acid-coated	NH ₃ collection
A47-C	15.0	Upstream	Emfab	Gravimetric / Detailed organics
		Downstream	Emfab	Organics correction

Teflon membrane filters (Gelman Teflon R2PJ047, 2µm and 1 µm pore size, 47-mm diameter) were used for gravimetric determinations and for inorganic and organic ion analyses. Quartz fibre filters (Pallflex 2500QAT-UP, 47 mm diameter, pre-fired to 900 °C for 3 hours to remove all carbon) were used for the total elemental and OC analyses. Whatmann 41 cellulose filters were coated with potassium carbonate to determine emission rates of SO₂ or coated with citric acid to determine NH₃ emission rates. In bus testing, KOH-coated quartz filters were used for gaseous organic acid collection.

Quartz filters were pre-fired on-site in batches. Coated filters were also prepared in batches following coating procedures prescribed at ERMD. Quartz filters were stored in aluminium

foil then placed in a sealable bag while the coated filters were double-bagged using sealable bags. Both quartz filters and coated filters were stored in a refrigerator to reduce the possibility of the filters adsorbing gaseous material from the ambient air. Filter blanks were collected for each of the filter media used. Two blanks for each medium were collected either at the end of the testing campaign or prior to the depletion of a particular batch of filters, whichever occurred first. After sampling, the filters were stored in labelled petri dishes, placed in resealable plastic bags and stored in a freezer to await being sent for chemical analysis.

4.2.1 Gravimetric Determinations

All Teflon membrane filters were humidity and temperature equilibrated to $50 \pm 10\%$ RH and $22 \pm 2^\circ\text{C}$ before gravimetric determinations were performed. A Mettler MT5 microbalance, located in a controlled environment ($50 \pm 5\%$ RH, $21 \pm 2^\circ\text{C}$), was used for all mass measurements of Teflon filters. All Emfab filters were also humidity and temperature equilibrated to $50 \pm 10\%$ RH and $21 \pm 2^\circ\text{C}$ prior to gravimetric determinations and weighed using a Mettler A240-S. Masses determined using the Mettler MT-5 were accurate to within ± 0.002 mg while masses determined with the A240-S were accurate to within ± 0.02 mg.

4.2.2 Chemical Characterisation

Table 8 summarises the analysis performed on various PM samples collected.

Table 8. Particulate matter analysis scheme.

Target Compounds	Analytical Technique	Filter Media
Organic Carbon / Elemental Carbon	NIOSH 5040	Quartz (1&2) Quartz (3)
Gaseous Organic Acids (Bus only)	IC / CE	KOH coated Quartz
Gravimetric	Mettler MT-5	Teflon (1)
Ions + SO ₂	IC / CE	Teflon (1) Carbonate (2)
Ions + NH ₃	IC / CE	Teflon (1) Citric (2)
Detailed Organic Carbon Analyses	GC-MS LC-MS	Emfab (1&2)

Note: IC = Ion Chromatography
GC = Gas chromatography
CE = Capillary electrophoresis
LC = Liquid chromatography
MS = Mass spectrometry

PM samples collected on quartz filters were submitted for organic and elemental carbon analysis by Thermal Optical Transmittance (TOT), the method described by the NIOSH Method # 5040, at NRCan in Sudbury, Ontario. A description of this procedure can be found in Section 3.4.1. The quantification limits for detection of organic and elemental carbon are shown in Table 9. The quantification limit was calculated by determining the emission rate associated with the limit of detection associated with Method #5040, which is 3 µg for a 1.5 cm² sample. Note that the detection limit is much higher for NYCC than the other two driving cycles. This is due to the shorter distance travelled. Since distance is the denominator in emission rate calculations, shorter travelling distances result in larger uncertainties in results.

Table 9. Summary of quantification limits for emission rates of elemental and organic carbon (mg/mile).

	Organic Carbon and Elemental Carbon
CS or HS	0.33
US-06	0.44
NYCC	2.71
CBD (Bus Testing)	2.54

Table 10 summarises the complete suite of organic and inorganic ions determined with the quantification limits of each analyte. These quantification limits were determined by applying the quantification limit for the filter analysis to the sampling parameters for each driving cycle and calculating the respective emission rate following the procedures discussed in Appendix A.

Table 10. Target analytes for the organic and inorganic ion analyses and their quantification limits (mg/mile) for three sample types.

Ion	FTP	US06X3	NYCC	Ion	FTP	US06X3	NYCC
Acetate	0.03	0.02	0.14	Lithium	0.01	0.005	0.03
Propionate	0.06	0.06	0.34	Sodium	0.03	0.02	0.14
Formate	0.02	0.02	0.13	Ammonium	0.03	0.02	0.14
Methane-sulphonate	0.05	0.05	0.28	Potassium	0.05	0.05	0.29
Pyruvate	0.04	0.04	0.22	Magnesium	0.01	0.013	0.08
Glyoxylate	0.05	0.04	0.26	Manganese	0.04	0.04	0.23
Chloride	0.03	0.03	0.17	Strontium	0.07	0.06	0.35
Nitrite	0.03	0.03	0.15	Malonate	0.07	0.06	0.35
Bromide	0.02	0.02	0.13	Malate	0.09	0.08	0.46
Nitrate	0.01	0.013	0.08	Succinate	0.05	0.05	0.28
Benzoate	0.04	0.04	0.23	Glutarate	0.07	0.06	0.37
Sulphate	0.01	0.010	0.06	Adipate	0.07	0.06	0.36
Oxalate	0.01	0.008	0.05	Lactate	0.04	0.04	0.24
Azelate	0.09	0.08	0.46				
Phthalate	0.04	0.04	0.22				
Phosphate	0.02	0.02	0.11				

Chapter 5 **Results and Discussion**

This chapter presents the results of the vehicle testing for PM_{2.5} emissions. For reference, the gaseous emissions and tabulated PM emissions data are provided in Appendix B and Appendix C. Tabulated results for particulate matter emission rates are listed in Appendix D. This discussion is divided into the following analyses: reporting mass emission rates; apportioning PM_{2.5} emission rates to chemical species and performing balances of select fuel components; determining the statistical significance of the effect of the control parameters on PM rates; assessing whether there is a correlation between PM emission rates and the gaseous products of incomplete combustion; and comparing the results of emissions testing to published data. A listing of diversions from the originally scheduled test program is presented in Appendix F.

5.1 PM_{2.5} Mass Emission Rate

The PM_{2.5} mass emission rates for motorcycles under for each operating condition are summarised in Figure 35. The error bars in the figure represent the standard deviations calculated from the two repeats.

In general, it was found that variabilities in PM_{2.5} emission rates are significantly higher than the variabilities of gaseous emissions. The PM_{2.5} emission rates calculated in these experiments have Percent Residual Standard Deviation (%RSD – ratio of standard deviation to average value) values that range from 5% to 94%, while the gaseous emissions rates for the same tests have %RSD's in the range from 0.0004% to 21%.

Although the variability for PM_{2.5} emission rates is very high, the decision of whether two repeats of an emissions test were acceptable is based on variability in regulated gaseous emissions (e.g. CO, HC and NO_x). The variability of the emission rates for these compounds

consistently were within the criteria variability. The guidelines developed by the Auto/Oil research program defined acceptable repeatability provided the calculated emission rates were within 70% for CO, 29% for NO_x, and 33% for THC (Painter and Rutherford, 1992). Generally, ERMD use a stricter guideline of 20% for all regulated gases. There is currently no guideline for evaluating the repeatability of PM emission rates. Thus, it was decided that no additional testing was required over and above the scheduled testing program.

Figure 35. Comparison of PM_{2.5} mass emission rates for both motorcycles operating on SGC and low-sulphur fuel.

Admittedly, it may seem odd to base the assessment of repeatability on gaseous emission rates, given the fact that the emissions testing was specifically geared towards testing PM emissions and that PM_{2.5} emissions rates are exhibiting such high variability. However, it is important to keep in mind that vehicle emission test facilities are extremely busy. Vehicle testing is scheduled weeks in advance, often with another test program slated to use the test

facility as soon as a set of tests is completed. Immediately following a test cycle, a technician will review the results of the gaseous emissions sampling to ensure the quality of the test. The technicians are very knowledgeable with regards to the emission rates to expect and can quickly identify outliers in the results. By contrast, the filters used in testing PM emissions need to be placed in a dessicator for at least 24 hours following testing prior to measurement. It was found during testing that the net mass collected on the filters for motorcycle testing is very close to the analytical uncertainty of the Mettler balance, meaning that much of the variability observed in PM rates is not necessarily the result of a poorly performed test. Rather, it is the result of low sample on the filters. Thus, provided the gaseous emissions appear normal and nothing abnormal is observed in sampling flow rates or sampling set-up, two replicate tests were considered sufficient for repeatability.

The results for bus testing are shown in Figure 36. The emissions result for each combination of treatment and temperature were calculated by averaging the emissions data from four test cycles (two sets of three CBD cycles, sampling the last two cycles of each set) conducted for that combination. Prior to averaging the results of all four test cycles of a particular combination, the data were reviewed to determine whether there was any pattern among the repeats. Examples of possible patterns would be if the third cycle in each set had consistently higher or lower emission rates than the second cycle or if the second set that was sampled had consistently higher or lower emission rates than the first set. In fact, no patterns were observed within samples of a combination. In bus testing, the $PM_{2.5}$ mass emission rates were determined using the net mass and flow rate from either the 47 mm Teflon filters or the 90 mm Emfab filters. The emission rates from both methods are reported here for comparison.

Figure 36. Comparison of PM_{2.5} mass emission rates for buses.

It can be seen from the above data that the two methods of calculating the emission rate are comparable. It is also worth noting that in general, the %RSDs for bus emission rates are much lower than the %RSDs for motorcycle testing. This could be the result of a number of factors, including higher number of data points (two for motorcycle testing vs. four for bus testing) used to calculate the average emission rate, a simpler driving cycle to follow, and higher net mass of collected material on the filters. It is most likely the difference in net masses on filters that is the source of the difference in variability. The average net mass collected on Teflon filters for bus testing was 1.84 g while the average net mass for motorcycle testing was approximately 1/30th of the bus-testing average at 56 µg.

5.2 Organic / Elemental Carbon

The use of two filters in series for PM-bound carbon collection and the procedures employed to account for the adsorbed material on these filters was discussed in Section 3.4.1. Prior to

reporting organic and elemental carbon emission rates, it was necessary to evaluate which of the two correction methods produced a more accurate representation of carbon emission rates. One method was to subtract from the organic carbon on the primary or upstream quartz filter (Q_1) the organic carbon present on the secondary or downstream quartz filter (Q_2). The second method differs from the first in that the correction was performed using the organic carbon collected on the quartz filter downstream of a Teflon filter (T_1), termed Q_3 . For the purposes of this report, the emission rates for organic carbon and total carbon are prefixed by either " Q_2 -corrected" or " Q_3 -corrected". The comparison was conducted using motorcycle emissions rates alone.

The two methods of correcting for the positive artefact are compared in Figure 37. This figure presents a plot of corrected organic carbon versus the calculated $PM_{2.5}$ rate. The results of each individual test are plotted rather than the average emission rates to produce more data points and to better capture scatter of the data.

Figure 37: Comparison of organic correction methods for motorcycle data.

This plot shows that the Q_3 -correction method is more representative of actual organic carbon emission rates. The Q_2 -correction results in OC emission rates that are consistently greater than the PM emission rates, which is clearly undesirable. With the exception of two data points, Q_3 -corrected emission rates were consistently less than the total mass emission rate. This, combined with the fact that Q_3 -corrected results exhibited less scatter, indicated that Q_3 -corrected organic carbon emission rates were a better representation of actual organic carbon emission rates.

It should be noted that four data points in the Q_3 -corrected series were invalidated due to the fact that the OC collected on the correction filter (Q_3) was greater than the OC collected on the primary filter (Q_1). These cases were likely the result of the negative artefact from the upstream Teflon filter (T_1) becoming readsorbed onto Q_3 downstream. If sufficiently high,

the effect of the T_1 's negative artefact could result in more OC being adsorbed onto Q_3 than what was adsorbed onto Q_1 .

Although it may seem odd that a downstream filter could have collected more material than an upstream filter, remember that the OC on Q_1 is the sum of OC in the PM plus the positive artefact *minus* the negative artefact (See Figure 32). A large negative artefact decreases OC on Q_1 while potentially increasing the OC on Q_3 . The only way to eliminate the possibility of this error occurring would be to use denuders upstream and downstream of a single quartz filter, as described in Section 3.4.1.

When the OC emission rates are split between Honda results and Suzuki results, as shown in Figure 38, it is revealed that there is more scatter in Honda emission rates and that three of the four invalidated OC emission rates occurred during Honda tests. It is likely that these two observations are linked, since high scatter would lead to a higher likelihood that the data points would be close to zero emissions. The scatter itself is likely the result of the lower emission rates associated with the Honda, which have higher relative uncertainties compared to higher emission rates. Thus, the naturally low emission rates of the Honda both increase the relative uncertainty and make the calculated emission rates more sensitive to dilution air concentrations and artefacts, resulting in more invalidated tests.

Figure 38. Comparison of Suzuki and Honda OC emission rates.

Another interesting observation that can be made from Figure 38 is that OC emission rates relative to $PM_{2.5}$ emission rates were higher for the Honda than for the Suzuki. This has been attributed to differences in engine operation between the two vehicles. It was observed that the Honda had higher THC emission rates than the Suzuki did in spite of lower PM emission rates (see Appendix A). This higher concentration of THC relative to PM in the sample could have resulted in more adsorbed gaseous species on Honda samples, which could explain the high carbon emission rates.

Table 11. Averaged organic carbon (OC) and elemental carbon (EC) emission rates for motorcycles (mg/mile).

	Suzuki GSX-R 750W				Honda CBR 600			
	SGC		Low Sulfur		SGC		Low Sulfur	
	OC	EC	OC	EC	OC	EC	OC	EC
CS LA4	4.04	0.52	1.15		1.06		1.88	
%RSD	93%	122%	71%		126%		96%	
HS LA4	1.86	0.04	0.47		0.88		2.01	
%RSD	5%		116%		9%		25%	
4 Phase FTP	1.93	0.23	0.76		0.48		1.95	
%RSD	87%	123%	87%		110%		25%	
US06 x 3	19.82	0.86	13.16		11.55	0.37	9.10	0.36
%RSD	63%	28%	25%		8%	57%	2%	1%
NYCC x 3	3.18		11.34		1.66		3.37	1.34
%RSD	388%		15%		49%		280%	

The averaged OC and EC emission rates are reported in Table 11. One observes in this table that that the elemental carbon emission rates were, for the most part, barely detectable. The average elemental carbon detected on primary filters was 2.6% of the total carbon. After a correction is made for the blank concentrations and the emission is calculated according to standard emission rate methods, there are only 10 out of 32 samples that reported elemental carbon emission rates greater than zero. Cases where the elemental emission rate was calculated to be less than zero were considered to be invalid results and were ignored. The high number of cases where EC emission rates were non-detectable indicates that insufficient material is being collected on the filters.

The highest elemental carbon emission rates were observed for vehicles operating on the US06 cycle. This can be attributed to the fact that US-06 is an aggressive driving cycle where the engine is operated at high accelerations and loads, which are conditions conducive to soot formation. In addition, there appears to be high elemental carbon emission rates for Suzuki vehicles operating on summer grade commercial gasoline, with the highest rates occurring on the first day of the testing campaign. It was previously reported that in the first set of tests the driving wheel would occasionally slip on the dynamometer roll as the driver became

accustomed to the vehicle. As a result, the driver would have to accelerate more aggressively to catch up to the trace, favouring soot formation.

Figure 39. Comparison of carbon emission rates to total mass emission rates.

Figure 39 shows the comparison between averaged total carbon and total mass emission rates for vehicle and driving cycle. One observes in this figure that, with the exception of FTP tests with the Honda, total carbon is less than the total PM mass emission rate, which is as expected. It is also apparent that the biggest difference between total PM mass and total carbon occurs for NYCC tests. The reduced carbon emission rates for NYCC cycles can be explained by reviewing the calculated organic carbon emission rate by test cycle.

Figure 40 illustrates the OC emission rates relative to $PM_{2.5}$ emission rate by driving cycle. Also included in this figure is the average net mass measured on the respective Teflon filters to illustrate the link between collected material and the correlation between OC and PM. It can be concluded from the data that provided there is sufficient PM collected, there is a strong link between OC and $PM_{2.5}$ emission rates. There is a very good correlation between

OC and PM emission rates for US-06 points, which also happen to collect the most PM. The driving cycle with the next best fit is the CS LA4 cycle of the FTP. Both the Hot-Start phase of the FTP and NYCC driving cycles show poor correlation between OC and PM emission rates because of low amounts of material collected.

Figure 40. Summary of organic carbon emission rates by driving cycle.

Another conspicuous point is the fact that only two OC emission rates for NYCC cycles are considered valid. Of the points that are valid, the ratio between total carbon and total PM_{2.5} emission rates is dramatically lower compared to the other test cycles. This low proportion is likely due to the extensive idling periods throughout the NYCC cycle. This idling results in dilution factors for NYCC tests that were approximately 1.3 times greater than it is for FTP.

During idling periods, the proportion of dilution air to exhaust will be much higher and as a result, the sample that is being drawn through the filter will have very low concentrations of VOCs and PM. Because of these low concentrations, the Henry's law, which governs the equilibration between phases, dictates that some of the organic carbon will desorb from the quartz filter, resulting in lower proportions of carbon relative to total PM_{2.5}.

The Teflon-corrected organic and elemental carbon emission rates for bus testing are shown in Figure 41. Note that the variabilities associated with carbon emission rates from buses are much lower than the variabilities observed in motorcycle testing.

Figure 41. Organic and elemental carbon emission rates (g/mile) for bus testing.

The ratio of total carbon that is EC is much higher for bus testing than for motorcycle testing. This is a typical comparison of diesel engine emissions to gasoline engine emissions. Diesel engines are known to produce more soot due to the local fuel-rich zones in the combustion chamber during the diffusion combustion stage. A discussion of how organic and elemental carbon emission rates are affected by temperature and catalytic exhaust treatment is found in Section 5.7.

5.3 Ions analysis

This section reviews the ion emission rates for motorcycle testing. Emission rates for individual ions are presented in Appendix E. It was found that there was a great deal of scatter in the individual ion emission rates and, with the exception of manganese, no trends that were sustained across a particular control parameter. As a result, only total ion emission rates are presented here. Nevertheless, a description of the key ionic contributors is provided. In addition, the emission rates of manganese ion and sulphate ion are provided. Sulphate is of interest because of its contribution to PM_{10} in the atmosphere. Manganese is of interest for its neurotoxic potential. Manganese also happened to be one of the most prevalent and consistently quantified ion.

The most common ions observed in the motorcycle testing were manganese, sodium, nitrate, sulphate and phosphate. Sodium is a fuel component that is thought to be a remnant of the refining process (Graham, 1998). Sodium emission rates are highest during NYCC testing, with an average of 0.33 mg/mile for NYCC testing and 0.066 mg/mile for the remaining driving cycles. NYCC cycles also show the highest fuel consumption rates, validating the link between fuel consumption and sodium ion emission rates.

Manganese is present in fuel as MMT, an antiknock fuel additive that has replaced lead in Canadian gasoline fuels. Mn was present in greater quantities in low-sulphur fuel (see Table 3), presumably due to the originally lower octane number of the low-sulphur fuel. Manganese emission rates were accordingly higher for low-sulphur operation and are highest for NYCC tests. Because manganese has been found to be neurotoxic when inhaled in excessive amounts, and because of the prevalence of high manganese emission rates encountered, a determination of the fraction of manganese in the fuel that becomes manganese ion is presented later in Section 5.6.2.

The presence of phosphate in the emissions is due to detergents added to fuels and engine oils (Graham, 1998). Emission rates were highest for US-06 and NYCC tests, averaging 0.30 mg/mile for these two tests and 0.045 mg/mile for FTP tests.

Sulphate and nitrate were found in most of the dilute exhaust samples. These ions are of particular interest because of their contribution to PM in the atmosphere. It should be noted that the actual nitrate and sulphate contribution from these vehicles is likely to be much greater than the emission rates reported in this paper, however. This is because much of the sulphate and nitrate present in ambient PM is the result of conversion of SO_x and NO_x through photochemical interaction with VOCs and water. The determination of the degree of the conversion of SO_2 and NO_x is beyond the scope of this paper. As a result, only direct emissions of these ions were reported.

Nitrate emission rates were observed in most tests but emission rates were highest for NYOC tests (0.23 mg/mile for NYOC compared to 0.05 mg/mile for remaining tests). It was originally expected that a trend would be observed between sulphate emission rates and fuel sulphur consumption. The results of the comparison, shown in Figure 42, reveal that there is in fact no trend between sulphur consumption and sulphate emission rates. This phenomenon has been observed in previous emissions testing (Baumgard & Johnson, 1996). A possible cause insensitivity of sulphate emissions to fuel sulphur content is the contribution from a non-fuel source such as engine oil. Engine oil, which was not changed between tests as fuel was, typically has high concentrations of sulphur compounds.

Figure 42. Comparison of PM sulphate emission rates with fuel sulphur consumption rates.

The fact that emissions are not lower when operating with low-sulphur fuel indicates that the limiting factor in sulphate formation is not the fuel sulphur level. The formation of sulphate (SO_4^{2-}) and nitrate (NO_3^-) is the result of the oxidation of SO_2 and NO_x respectively. These oxidation reactions occur in all aspects of the combustion air system, as a result of complex reaction mechanisms. The production of sulphates from SO_2 consists of the conversion of SO_2 to SO_3 , followed by the oxidation of SO_3 to sulphate in water droplets. SO_3 can form during the combustion process provided excess air is available. It can also form in water droplets after SO_2 dissolves in the droplet. Similar mechanisms are at work in the formation of nitrates from NO_2 . These reactions all consist of oxidising the sulphur or nitrogen. It has been theorised that the presence of a catalytic converter can result in increased conversion of SO_2 and NO_x to sulphates and nitrates. Although it has been observed that the presence of a catalytic converter can produce more nuclei-mode sulphate particles (Baumgard and Johnson, 1996) the degree of conversion has not been quantified.

There were a number of ions that were observed on one vehicle but not the other. For example, acetate, formate, and ammonium ions were only observed during Suzuki testing. Acetate and formate were observed predominantly during NYCC testing, with average emission rates of 0.4 mg/mile for formate and 0.45 mg/mile for acetate. The average emission rate for the four samples where ammonium was observed was 0.083 mg/mile.

Chloride was almost exclusively observed during Honda testing and on the first day of Suzuki testing. The chloride emissions observed during Honda testing were highest during NYCC testing (0.38 mg/mile compared to .061 for remaining cycles). The prevalence of chloride in Honda samples could be due to the presence of chlorides in the engine oil of the Honda but not in the oil of the Suzuki. Although chemical analysis of the oil had been scheduled, the results of the analysis had not been completed at the time this report was written. The chloride found on the first day of testing could have been the result of cleaning residue.

Potassium was present in many of the Suzuki tests but on the first day of testing, emission rates were much greater than the emission rates of other ions (0.54 mg/mile compared to 0.09 mg/mile). Potassium is associated with cleaning products and is only present in trace amounts in fuel and lubrication oil. Another occurrence of high potassium concentration was on the ambient filter for 22 June testing. This filter happened to have the second-highest amount of potassium for any of the filters analysed, including dilute exhaust samples. Incidentally, the 22 June ambient filter also collected the highest gravimetric mass among dilution air filters. Considering that the emission rates of potassium are almost exclusively associated with the first day of testing and the presence of very high potassium levels on a dilution air filter, the most probable source of this high potassium is an artefact from the cleaning of the dilution tunnels and filter cartridges. Contamination of filters by cleaning product residue may also be the source of the relatively high chloride rates on the first day of testing.

As mentioned previously, the degree of scatter in the emission rates made the graphic representation of ion emission rates difficult. Instead, the total emission rate was plotted versus the total $\text{PM}_{2.5}$ emission rate and fuel consumption in an effort to identify the source

of the ions. Figure 43 presents the plot of ion emission rates relative to total $PM_{2.5}$ emission rates. It appears from this figure that there is little correlation between ion emission rates and total gravimetric emission rates.

Figure 43. Comparison of ion and gravimetric $PM_{2.5}$ emission rates for motorcycles.

Given that many of the observed ions have been attributed to components of the fuel and engine oil, a comparison was made between ion emission rates and fuel consumption. The results of this comparison are shown in Figure 44. It appears that there is a stronger correlation between ion emission rates and fuel consumption rates than there is between ion and PM emission rates. The poor correlation between ions and PM could be attributed to the low mass of PM collected, which resulted in many of the ion emission rates reported being close to detectable limits for the analytical method. The average detectable limit for ion analysis was 0.04 mg/mile. A review of Appendix E reveals that very few of the ion emission rates are above the detectable limits for the analysis.

Figure 44. Comparison of ion emission rates to fuel consumption rates.

5.4 Secondary PM Precursors (SO_2 , NH_3)

This section reviews the emission rates of SO_2 and NH_3 for motorcycle testing. A summary of the sulphur dioxide emission rates for each driving condition is presented in Figure 45. A comparison of fuel sulphur consumption to sulphur-based emissions is presented later in Section 5.6.1.

Figure 45. Comparison of sulphur dioxide emission rates for motorcycles.

The variability between samples for Honda tests appears to be much less than that for Suzuki tests. This could be the result of the more aggressive driving of the Suzuki on the first day of testing to match the driving cycle. The most evident trend is the effect of low-sulphur fuel on SO_2 rates. The ratio of SO_2 rates observed between SGC and Low-Sulphur testing are proportional to the sulphur content of the fuel, indicating that the primary source of sulphur dioxide in the exhaust is from gasoline.

Ammonia emissions are shown in Figure 46. Ammonia emissions were very low and highly variable for both sets of vehicles and fuels. The average emission rate is greater than the standard deviation for all Suzuki tests except for NYCC tests. The same cannot be said for Honda tests, however, where only the composite and the US-06 tests for low-sulphur fuel have average emission rates greater than the standard deviation. Also note that the range of emission for ammonia is two orders of magnitude less than that for sulphur dioxide.

Unlike the sulphur dioxide samples, the ambient ammonia concentrations were very high relative to dilute exhaust concentrations. In fact, of the 32 test samples collected, 10 had dilute exhaust concentrations that were lower than the ambient concentration for that day. Given that the most common source of ammonia emissions from vehicles is the reduction of elemental nitrogen in 3-way catalytic converters, it was not surprising that ammonia emission rates were at such low levels.

Figure 46. Ammonia emission rates for both motorcycles.

5.5 Chemical mass recovery

An attempt was made to chemically account for all the PM mass that was collected on the filters. To properly perform the balance, estimates were made to account for the additional elements bonded to organic carbon. In spite of the fact that elemental carbon may also have additional elements bonded to it, it was assumed in this report that any correction would be negligible.

It has been assumed in this study that the organic carbon of PM is from unburned lubrication oil that volatilises during the power and exhaust stroke. These compounds consist of straight chain alkanes with carbon numbers between 14 and 29. If the average carbon number of 22.5 is used, then the average mass ratio of hydrogen to carbon is 0.175. These calculations are outlined in Table 12.

Table 12. Determination of mass of hydrogen associated with organic carbon of PM.

		C₁₄	C₂₉
Atoms	Carbon	14	29
	Hydrogen	30	60
Mass	Carbon	168	348
	Hydrogen	30	60
	H:C Ratio	0.179	0.172
	Average	0.175	

It should be noted that this estimate accounts only for the hydrogen and not other components, such as oxygen and trace elements that may be bonded to the organic carbon portion. Norbeck *et al.* (1998) suggest a correction factor of 1.2 to account for the presence of hydrogen, oxygen and other trace elements associated with organic carbon. Their estimate is based on determining organic carbon by the Thermal Optical Reflectance method, a variation on the TOT method described in Section 3.4.1. Norbeck *et al.*'s carbon data were collected on a single quartz filter backed up with a vapour phase trap for the collection of polycyclic aromatic hydrocarbons (PAHs). It may be expected that Norbeck *et al.*'s estimate is representative of the PM characteristics in the present study.

The total speciated mass that results from summing the total ion emission rate, the estimate of organics based on the correction outlined above, and elemental carbon is plotted versus the PM_{2.5} emission rate measured gravimetrically is shown in Figure 47. The results of this comparison show that the speciation of PM is being underestimated. It is likely that the speciated mass would have accounted for more of the gravimetric mass if trace element analysis had been performed and if more material had been collected on the filters. As we saw in Section 5.2, the small amount of PM collected on the filters results in underestimates

of the organic and elemental carbon emission rates. It is also expected that more material would also result in reduced scatter.

Figure 47. Comparison of speciated mass emission rate to gravimetric mass emission rate.

An illustration of the comparison between the averaged gravimetric emission rate and the averaged total mass calculated by chemical speciation is shown in Figure 48. In this figure, the error bars represent the standard deviation for the averaging of the emission rate. The error bars for total speciation mass is the summed standard deviation for each component.

Figure 48. Total speciation mass versus total mass emission rate (motorcycles).

The results show that in general, the emission rates resulting from summing chemical speciation results are comparable to the total $PM_{2.5}$ emission rate. In five of the twelve cases considered, the error bars overlap. In all but one case where the error bars do not overlap, the speciation mass is less than the gravimetric mass. There appears that there is no discernible set of conditions that lead to consistent over- or under- estimates of the speciated mass.

The comparison of speciated mass emission rates to total $PM_{2.5}$ emission rates for bus testing is shown in Table 58. The comparison is illustrated in Figure 49.

Figure 49. Comparison of total PM_{2.5} emission rate to chemical speciation emission rates for bus testing.

From these results, it can be concluded that the correction for organic carbon may be overestimated for bus emission rates. For three of the four test conditions, the total speciated mass is slightly greater than the total mass determined by gravimetric methods. Given that the chemical accounting for buses does not include ionic species or trace elements, the fact that the speciation mass is so close to the gravimetric mass is an indication that the correction for total organics may not be appropriate.

5.6 Fuel Component Balances

This section is devoted to a discussion of accounting for fuel components through chemical speciation of emission rates. The two components considered here are sulphur and manganese.

5.6.1 Sulphur Balance

The sulphur balance for this set of tests is presented in Figure 50. Analysis for SO_2 was conducted through extraction from potassium carbonate-coated filters while the sulphate concentrations were determined through ion extraction from Teflon filters.

Figure 50. Sulphur balance calculations for motorcycle tests.

In general, the collection of the fuel-bound sulphur was very poor. The average proportion of fuel sulphur accounted for as SO_2 and SO_4 was 26%. When operating with SGC gasoline, the average proportion was 31% while the average for low-sulphur fuel was 13%. An interesting observation is that sulphur emission rates are reasonably constant for all fuel sulphur consumption rates. This could indicate that some sort of limiting condition is affecting the conversion of sulphur to sulphate and SO_2 .

Figure 51. Comparison of emitted sulphur species to fuel sulphur consumed.

Figure 51 shows the emission rate of sulphur species relative to the fuel sulphur consumption rate. In this figure, the rates are plotted on a logarithmic scale to capture the relatively low emission rates of sulphate ion relative to SO_2 emission rates. The error bars represent the standard deviation of the averaged results. There are six cases (five fuel consumption rates and one sulphate emission rate) where the lower error bar is missing. This occurs in cases where the standard deviation is greater than the emission/consumption rate. The most prominent sulphur component in emissions was SO_2 . While sulphate had an almost negligible contribution to tests where SGC fuel was used, its contributions to emissions with low-sulphur fuel are more pronounced.

It was not expected that sulphur dioxide emission rates would account for such a low fraction of the fuel sulphur consumed. There are three possible causes of the low capture of fuel sulphur: (i) some of the sulphur dioxide bypassed the filter; (ii) sulphur was emitted in a form

that was not captured by the analytical methods; and (iii) SO_2 was partially removed from the gas stream prior to exposure to the filter. It is suggested here that the first two causes were the key causes of the low sulphur capture.

The fact that using carbonate-coated filters may not be the most effective collection method was discussed in Section 3.4.4. This discussion mentioned that the ratio of collected SO_2 to delivered SO_2 ranged from 0.48 to 0.90. The reasons for this low capture have not been elaborated upon in the literature. The most likely scenario is that the carbonate filters may not have been moist enough to facilitate the of SO_2 to KHSO_3 . Recent testing at ERMD has ensured that carbonate coated filters remain moist up until testing and have noted much higher collection efficiencies.

It is unlikely that the poor capture is due to the carbonate coated filters reaching capacity. The capacity of 47-mm cellulose filters coated with sodium carbonate is 765 μg of SO_2 (Karakas and Tuncel, 1997). It is expected that similar capacities would be observed with potassium carbonate-coated filters. The maximum SO_2 collected was 364 μg and that was over two filters, which suggests that capacity issues are not a concern. In addition, risks of breakthrough were minimised by placing two carbonate filters together, doubling the SO_2 capacity for each test. The fact that sulphur capture rates do not improve with low SO_2 emission rates as would be expected to occur when operating with low-sulphur fuel also discounts the possibility that collection capacity was reached.

The possibility that the sulphur was emitted as species that were not captured during testing is also likely. Figure 52 shows the calculated equilibrium concentrations for an open-air propane flame with unconverted gases initially containing 1% SO_2 . In stoichiometric flames, almost all of the sulphur bound in fuel is converted to SO_2 . In fuel-rich conditions, however, stable sulphur products such as hydrogen sulfide, carbonyl sulfide, and elemental sulphur have been observed. Conversely, SO_3 begins to occur at increasingly fuel lean conditions. In fact, it has been observed that SO_3 conversion in flames is near 1-2 percent, which is much higher than the equilibrium concentration shown in Figure 52 (Glassman, 1996).

Figure 52. Equilibrium distribution of sulphur containing species in propane-air flames.

Given the broad range of air-fuel ratios that can be observed in spark ignition systems, it is possible that fuel-bound sulphur is being emitted in a form that is not captured by the present analysis scheme. The overall air/fuel ratios for motorcycle tests were calculated by determining the concentration of raw exhaust gases from the concentration of these components in the dilute exhaust. The results show that the average air-fuel ratio is slightly leaner than stoichiometric over the duration of the test. Although air/fuel ratios will fluctuate throughout the test, the weighting of the air-fuel ratio is clearly towards the lean side, suggesting that the predominant sulphur species will be SO_2 .

It has been observed in testing conducted at ERMD that there is a sulphur compound not shown in Figure 52 that may be accounting for a large proportion of the sulphur emitted. The compound is hydroxymethane sulphonic acid (HMSA - $\text{HOCH}_2\text{SO}_2\text{H}$). This compound is present in the gaseous form and has been observed in systems where SO_2 and

formaldehyde concentrations are particularly high. It was observed in gaseous analysis of the motorcycle testing results that formaldehyde emission rates were one of the most abundant organic species in the exhaust stream (Welburn and Graham, 2000). Emissions testing at BC Air Care observed high emission rates of HMSA in older vehicles and vehicles that failed the emissions test (Graham, personal communication, 2000). These vehicles are likely to have inoperative or non-existent catalytic converters, which would be a similar set-up to the motorcycles. The reason that HMSA was not captured in this study is that gaseous organic acids must be collected using KOH-coated quartz filters. This sampling method was only performed for bus testing. Preliminary analysis of the bus testing results reveals that HMSA concentrations in the dilute exhaust were substantial. Future testing should certainly include organic acid sampling to evaluate the contribution of HMSA for fuel sulphur balances.

It is also possible that SO_2 is somehow adsorbing onto elements of the sampling system prior to passing through the carbonate-coated filter. Tests conducted by Schorran and Keislar (1996) observed in their comparison of sulphur dioxide measurement methods that collection efficiencies of SO_2 dropped for all methods at relative humidities above 70%. This reduction in efficiency was attributed to water condensation occurring at high humidities, resulting in "line loss". This condensation in the sampling lines could provide a medium for SO_2 to partition between the gaseous phase and the aqueous phase, reducing the amount of SO_2 exposed to the filters. In the end, the likelihood of line loss is quite low, given that the maximum observed relative humidity observed during testing was 58%.

Another possible sulphur sink is the dilution tunnel and transfer pipe. It was mentioned in Section 3.1.4 that a black film was observed in the dilution tunnel immediately downstream of the mixing point. It was suggested earlier that this film could be PM that deposited due to cooling occurring in the last section of the transfer pipe just prior to mixing. This PM could potentially contain sulphur species. However, this effect is likely to be negligible relative to the effect of SO_2 bypass and possible HMSA contribution discussed earlier in this section. Future testing is planned at ERMD to determine if SO_2 is bypassing the filters and if there is a better method capable of capturing all the SO_2 .

Even if the systematic losses in sulphur sampling could be remedied, there is no guarantee that all of the collected sulphur would be account for. In fact, it could be found that collected sulphur exceeds the fuel sulphur consumption rate. Previous testing at ERMD has observed that sulphur emission rates reach a lower limit equivalent to fuel with 50 ppm sulphur even with fuel sulphur contents well below the 50 ppm level (personal communication, Graham 2000). This baseline emission rate of sulphur has been attributed to sulphur present in the engine oil and the transient release of sulphur stored in the catalyst when switching from high to low sulphur fuel.

5.6.2 *Manganese Balance*

Manganese is a neurotoxin that, in an airborne form as PM, can cause neurological effects similar to Parkinson's disease. It is most hazardous in its ionic form, which is more water-soluble and thus available to mix into the bloodstream if it is deposited in the alveolar region. The "inhalation reference concentration" (concentration where exposure for 24 hours per day over 70 years may cause symptoms) of air-borne manganese has been set at $0.4 \mu\text{g}/\text{m}^3$, with a ten fold uncertainty. The uncertainty adjusts the reference dose to a range of concentrations from 0.073 to $0.73 \mu\text{g}/\text{m}^3$. Assuming a widespread use of MMT and a coarse exposure model, the EPA has predicted that the American population would be exposed to the concentrations shown in Table 13. According to the model, the emission of approximately 25% of the manganese in the fuel as air-borne particles may represent a health hazard.

Table 13. Estimated exposure concentrations of PM-bound manganese (in $\mu\text{g}/\text{m}^3$) assuming widespread use of MMT in USA (Hammerle, 1992).

% of Fuel Mn converted to PM Mn	Ambient Concentrations for the typical office worker	Ambient concentrations for the 1 million most highly exposed in the U.S. Population
10%	0.05	0.16
20%	0.07	0.31
30%	0.08	0.45

Inhalation Reference Concentration: 0.073 to $0.73 \mu\text{g}/\text{m}^3$ - concentrations that are greater than the reference concentration are **bolded**.

Figure 53 presents the comparison of manganese emission rates to fuel consumption emission rates. In this figure, it is shown that manganese ion accounts for approximately one-third of manganese consumed in the fuel in Suzuki tests and just less than two-thirds of the fuel manganese consumed in Honda tests. The fact that the ratio between manganese consumption and ion emission rate is so different between the two motorcycles indicates that manganese conversion from fuel to PM may be sensitive to combustion conditions.

Figure 53. Comparison of manganese ion emission rates and fuel consumption.

A survey of $PM_{2.5}$ emission rates on in-use vehicles in BC included both ion and trace element analysis. It was observed in this survey that overall, manganese ion emission rates were approximately 50 percent of the total manganese emission rate as measured by XRF (Graham, personal communication 2000). Given that the average ratio of manganese ion to fuel manganese consumption is approximately 45% and assuming that the ratio of manganese ion to total manganese holds for motorcycle emission rates, we have a manganese collection efficiency of 90%, which is quite good.

The motorcycle manganese results are in agreement with studies conducted on the emissions from vehicles operating with MMT. A study of eight vehicles operating with fuel containing varying degrees of MMT found that 5% to 45% of the fuel manganese was emitted in the form of PM, and an average of 8% was found in the engine oil, leaving 50% to 80% of the manganese unaccounted for. (Hammerle *et al.*, 1992). In their study, the total manganese was analysed by extracting the material from the Teflon filters using an HCl solution. It was

suggested that unaccounted-for manganese could have been stored in the engine, catalyst and exhaust systems. It is worth noting that the manganese balance for motorcycles actually resulted in higher collection rates compared to Hammerle's estimates, in spite of the fact that only manganese ion was measured in motorcycle testing. One potential reason for the higher proportion of fuel manganese being measured on motorcycles is that there is less exhaust plumbing on a motorcycle upon which particles could deposit. Another reason is that the acid extraction method may not be extracting all of the manganese from the filter.

It remains uncertain what species of PM-bound manganese is the most toxic. A review of toxicological studies in Zayed *et al* (1999) found that the oxidation state of manganese may play a key role in the distribution and accumulation of manganese in various animal tissue. Thus, future manganese analysis should include more detailed studies to characterise the nature of manganese emitted.

5.7 Statistical Analysis of Results

This section focuses on the statistical analysis of PM_{2.5} emission rates. The motorcycle testing results were used to evaluate the effect of fuel and driving cycle on PM emissions, while bus testing results were used to evaluate the effect of test temperature and use of a PM control device on PM emissions.

To determine whether the effects of these factors were significant, analysis of variance (ANOVA) was conducted to statistically compare the average emission rates from different combinations of treatments. In particular, two-factor ANOVAs with replication were used to determine the significance of the factor effects on vehicle emissions. The effects of test factors were considered separately for each vehicle. Evaluating the effect of vehicle on emission rates was not considered appropriate since, even in the case of the two motorcycles, the vehicle cannot be considered a conditioning factor as fuel or driving cycle can be.

The output of the ANOVA quoted in the following discussion is the *p-value*. The *p-value* is the probability that the null hypothesis is correct. Throughout the analysis, the null hypothesis was that the two samples being compared were from the same population (i.e.

changing a particular parameter does not result in a significant change in emission rates). In essence, the p-value is a measure of how much the difference between average emissions for different test factors stands out from the overall variability in the data. If the p-value is sufficiently low, the effect of the test factor is considered significant. The benchmark against which the p-value is measured is called the level of significance (α). The level of significance is set by the researcher based on the variability of the data and the sensitivity of the decision. The significance level used in this analysis is $\alpha=0.05$, which is the commonly-used level for most scientific studies. Other studies that have evaluated the effect of test parameters on PM_{2.5} vehicle emissions have also used a significance level of 0.05 (Norbeck, 1998).

Two-factor ANOVA is particularly well suited for the assessment of the data presented, given the combined effects of driving cycle and fuel for motorcycle emissions and of temperature and control device for bus emissions. In addition to determining whether the effects of two factors are significant, the two-factor ANOVA determines the effect of an *interaction* factor. A significant interaction factor indicates that the effect of a particular factor is not consistent across all combinations of adjacent factors.

In some cases, multiple-comparison tests were performed subsequent to an ANOVA to determine whether there were significant differences between particular combinations of factors. Multiple-comparison tests simultaneously compare the means of each combination of factors in a particular data set while accounting for the variability of the entire set. These multiple-comparisons were performed whenever interaction was observed or where more than two permutations of a particular factor were considered in the ANOVA.

The multiple-comparison test used in this study was the Tukey test for significance. The Tukey “Honestly Significantly Different” test relies on calculating the q value, which is the ratio of the difference between two means to the overall variability in the data and is expressed as:

Equation 5

$$q = \frac{\mu_1 - \mu_2}{Q}, \quad Q = \sqrt{\frac{MSE}{n}}$$

Where: μ_1, μ_2 = The mean emission rate of the two combinations

MSE = Mean Sum of Squares for Error in ANOVA

n = Number of samples used to calculate the mean

The calculated q value is compared to the critical q value, known as the studentized range percent point function (*snappf*). The *snappf* is a function of the significance value, degrees of freedom and sample size. If the q -value is greater than the *snappf*, then there is a significant difference between the means.

The results of the following analyses are shown in more detail in Appendix G, with specific Table numbers referenced in the text.

5.7.1 Effect of Test Factors on Motorcycle Emissions

A summary of the statistical comparisons are presented in Table 14. The comparison of CS LA4 to HS LA4 PM_{2.5} emissions was based on the expectation that there would be higher PM emissions in the CS LA4. These higher emissions were expected in CS LA4 operation due to increased fuel enrichment required for starting a cold engine and the increased flame quenching as a result of cold cylinder walls (see Section 2.3.3). The US06 and NYOC tests were compared to the FTP composite because the FTP is the regulatory standard for testing vehicle emissions. Assessing their effect relative to FTP emission rates will help to decide whether inclusion of these supplemental cycles is worthwhile or whether the FTP is sufficient to represent the PM_{2.5} emission rates from all driving conditions.

Table 14. Summary of statistical evaluations.

Parameter evaluated	
Driving cycle	Fuel
<ul style="list-style-type: none"> • CS LA4 vs. HS LA4 • US06 vs. 4-Phase FTP • NYOC vs. 4-Phase FTP 	<ul style="list-style-type: none"> • SGC vs. Low Sulphur Fuel

The results of the statistical analysis of start type (cold start versus hot start) on LA4 emissions for both motorcycles are shown in Table 15, with more detailed summaries of the ANOVA calculations shown in Table 65 and Table 66. The p-value for both vehicles is well above the 0.05 limit so the null hypothesis (start type does not affect LA-4 emissions) is accepted. It is worth noting however that, with the exception of low-sulphur operations with the Suzuki, CS LA4 emissions are consistently almost twice as high as HS LA4 emission rates. It is possible that with reduced measurement uncertainty, a significant difference may have been observed.

Table 15. Statistical analysis of the effect of start type on PM_{2.5} emission rates for motorcycles.

Fuel	CS LA4 Average	HS LA4 Average	P value (Cycle)	Decision
Suzuki				
SGC	5.58	2.88	0.40	Accept CS = HS
Lo S	3.17	3.13		
Honda				
SGC	1.35	0.62	0.39	Accept CS = HS
Lo S	2.13	1.30		

The results of the statistical analysis of the comparison between emissions for the supplemental tests (US06 and NYOC) and those for the regulatory composite (4-Phase FTP) are shown in Table 16, with detailed ANOVA results shown in Table 67 and Table 68. Because there were more than two driving cycles being compared, Tukey tests were also performed to evaluate the difference between each cycle. Note as well that the interaction factor was significant for Honda tests.

Table 16. Statistical analysis of the effect of supplemental tests on PM_{2.5} emission rates for motorcycles.

Fuel	Average Emission Rate			P value (Cycle)	Decision
	4-Ph. FTP	US06	NYCC		
Suzuki					
SGC	3.94	32.92	26.55	0.02	Reject FTP=US06=NYCC
Lo S	3.18	22.91	23.32		
Honda					
SGC	0.88	16.18	6.12	$8.6 \times 10^{-6*}$	See below
Lo S	1.63	13.09	8.31		

* $P_{\text{interaction}}$ for Honda Emission tests = 0.04

The results of the Tukey test for Suzuki emissions are shown in Table 17. Because there was no interaction factor observed for the Suzuki tests and the effect of fuel was not considered significant, the vehicle emission rates for both fuels were grouped together. The q -value was calculated by determining the MSE for a Single factor ANOVA (Table 69), grouping the results of all Suzuki tests for a particular driving cycle together. The results of this evaluation showed that the emissions from the FTP Composite were significantly lower than both the NYCC and the US-06 cycles but that the US-06 and the NYCC were not significantly different from each other.

Table 17. Results of Tukey Test for evaluating effect of driving cycle on Suzuki PM_{2.5} emissions.

Cycle	4-Ph. FTP	NYCC	US-06	$Q = \sqrt{\frac{66.4}{4}} = 4.08$
Average (both fuels)	3.56	24.93	27.91	
Comparison	Difference	q	q(0.05,9,3)	Conclusion
US-06 vs. Comp	24.35	5.98	4.415	Reject H ₀ : US-06 = Comp
US-06 vs. NYCC	2.98	0.73	4.415	Accept H ₀ : NYCC=US06
NYCC vs. Comp	21.37	5.24	4.415	Reject H ₀ : NYCC=Comp
Decision: $\mu_{\text{FTP}} \neq \mu_{\text{NYCC}} = \mu_{\text{US06}}$				

It is worth noting here that if the 2-factor ANOVA data were considered, then the corresponding Q value would be 5.76 with $\text{snppf}(.05, 6, 6) = 5.628$. In this case, none of the differences would be considered significant (see Table 70). The key reason for the lack of

significance at the two-factor level can be accounted for by the results associated with the first day of testing, where emission rates were significantly higher than the remaining test days for the Suzuki. In the two-factor test, the variability of these high emission rates is spread over only two data points. When fuel is eliminated as a possible factor, and the tests for a particular driving cycle are grouped together, the variability of the first day of testing is spread over four data points, reducing the mean squared error and the associated *snappf*.

The results of the Tukey test for driving cycles on Honda PM emissions are shown in Table 18. The results show that, in spite of the significant interaction factor, the emission rates from each driving cycle are significantly different from each other. A review of the results show that the interaction factor was significant because operations with Low-Sulphur fuel resulted in lower PM_{2.5} emissions for US-06 tests and higher emissions for the remaining tests.

Table 18. Results of Tukey Test for evaluating effect of driving cycle on Honda PM_{2.5} emissions.

Cycle	4-Ph. FTP	US-06	NYCC	$Q = \sqrt{\frac{1.30}{2}} = 0.79$
SGC Average	0.88	16.18	6.12	
Lo-S Average	1.63	13.09	8.31	
Comparison	Difference	q	q(0.05,6,6)	Conclusion
SGC: US-06 vs. NYCC	10.06	12.72	5.628	Reject US06=NYCC
Lo-S: US-06 vs. NYCC	4.78	6.04	5.628	Reject H0: US06=NYCC
SGC: NYCC vs. Comp	5.24	6.62	5.628	Reject NYCC = Comp
SGC: NYCC vs. Comp	6.68	8.44	5.628	Reject NYCC = Comp
Decision (SGC): $\mu_{FTP} \neq \mu_{NYCC} \neq \mu_{US06}$				
Decision (Lo-S): $\mu_{FTP} \neq \mu_{NYCC} \neq \mu_{US06}$				

A review of the above ANOVA test results for the effect of fuel on PM emissions show that fuel is not a significant factor in PM emissions. In fact, what little effect fuel has is not consistent from Suzuki to Honda operations. Note that operations with low-sulphur fuel result in lower emission rates with the Suzuki and higher emission rates with the Honda.

Based on the fact that fuel was not considered significant in any of the above ANOVA tests, further analysis for the effect of fuel on PM emissions was not considered necessary.

Although PM_{2.5} mass emission rates are not significantly affected by fuel composition, certain chemical characteristics did change with fuel type. The obvious characteristic that changed with fuel type was the SO₂ emission rate. Another emission component that was affected by fuel type was manganese ion, which was observed at higher rates during low-sulphur operation. Both of these changes were expected, given the differences in the composition of sulphur and MMT between the two fuels, as shown in Table 3. Unfortunately, due to the invalidated data points discussed in Appendix F, there were not sufficient data to perform statistical analysis on these emission rates. As a result, only qualitative conclusions could be made.

5.7.2 *Effect of Conditions on Bus Emissions*

The emission rates for bus testing were also subjected to two-factor ANOVA testing, where the factors were ambient temperature and the use of exhaust after-treatment. The results of this analysis are shown in Table 19, with ANOVA calculations shown in Table 71. Note that the display of results is slightly different compared to what was presented in the motorcycle analysis. This is largely due to the fact that only a pair of permutations were considered for each factor. Pairs of emission rates with significant differences have been identified with a double line separating the units of the pair.

Table 19. Results of ANOVA for PM_{2.5} emission rates from bus testing.

Average Emission Rate (g/mile)	Baseline	Catalyst	P-Value (Temp.)
Warm	2.78	1.12	<u>0.0001</u>
Cold	2.15	0.89	
P-Value (Exhaust treatment)	<u>3×10^{-10}</u>		P-Value (Interaction) <u>0.025</u>

The p-values for both temperature, exhaust treatment and interaction were well below the significance level of 0.05. Because the interaction factor was significant, it was necessary to

perform multiple-comparison analysis on the results to determine significant pair-wise differences (See Table 72). The results in Table 19 show that PM emissions reduce with cold temperatures but are only significant in the absence of exhaust aftertreatment.

Also of interest in this study was the effect of the control parameters on the organic and elemental carbon rates. The comparison of carbon emission rates also provided insight into the possible reasons for the reduced effect of temperature when operating with a catalyst. Table 20 presents the results of 2-way ANOVA testing on these emission rates, with the detailed results presented in Table 73 through Table 76.

Because of the significant interaction factor for both OC and EC ANOVA tests, Tukey tests were performed to identify significant differences. The results show that operating with the catalyst results in a decrease in OC and an increase in EC (although there was not a significant increase for EC at cold temperatures). Also, cold temperatures produced significantly lower EC emissions when operating with a catalyst.

Table 20. Statistical analysis of organic and elemental carbon emission rates.

Average Emission Rate (g/mile)	Baseline	Catalyst	P-Value (Temp.)
<u>Organic Carbon</u>			
Warm	1.79	0.26	0.348
Cold	1.49	0.41	
P-Value (Exhaust treatment)	<u>7.0×10^{-10}</u>		P-Value (Interaction) <u>0.01</u>
<u>Elemental Carbon</u>			
Warm	0.54	0.82	<u>3.1×10^{-6}</u>
Cold	0.43	0.46	
P-Value (Exhaust treatment)	<u>0.0002</u>		P-Value (Interaction) <u>0.0013</u>

Note: Statistically significant differences are underlined.

Two inferences can be made from these results. The first is that the catalyst operates by converting the OC to CO₂ (and partially to EC). The second inference is that catalyst performance decays at lower temperatures. This second inference is evidenced by the fact

that the change in EC emission rates between baseline and catalyst conditions is only statistically significant in warm temperatures. In addition, the difference between OC emission rates from Baseline to Catalyst conditions is, while still significant, reduced in cold temperatures.

5.7.3 Analysis of Individual Test Results

In addition to evaluating the effect of control factors on emission rates, two-factor ANOVA tests were also performed on the individual PM emission rates from the urban bus. These ANOVA were designed to answer two questions: (i) was there a significant difference between the emission rates calculated from the two filter media (e.g. Teflon and Emfab); and (ii) was the variability observed between repeated tests the result of sampling conditions (i.e. control device, ambient temperature) or uncertainty in the analytical methods (i.e., filter weighing).

The ANOVA used to compare emission rates by filter media was organised by vehicle configuration as one factor and filter media as the other factor and is shown in Table 21 (see Table 77 for detailed ANOVA results). This analysis showed that Teflon emission rates were only a marginally lower (i.e. $p=0.075$) emission rates calculated using Emfab filters.

Table 21. Statistical analysis of the effect of filter media on emission rates.

Configuration	Average Emission Rate by Filter Media (mg/mile)		P (Configuration)
	Teflon	Emfab	
Catalyst Warm	1118	1099	1×10^{-18}
Baseline Warm	2779	2928	
Catalyst Cold	887	975	
Baseline Cold	2151	2348	
P (Media)	0.0752		P (Interaction) 0.5616

The results of the two-way ANOVA that assessed variability in the emission rates from repeated tests are shown in Table 22 (detailed ANOVA in Table 78). In this analysis, the means presented were calculated by averaging the emission rates for two Teflon filters that were sampled simultaneously for each individual test. These results show that very little of the

total variability was accounted for by variability between replicate filters, as measured by the MSE. The MSE had a value of 1559, which was appreciably less (as much as $1/22^{\text{nd}}$) than the MS associated with Repeat or Configuration.

Table 22. Statistical analysis of the variability in multiple tests.

Repeat Number	Average Emission Rate by Configuration (mg/mile)				P (Repeat)
	Warm Cat	Cold Cat	Cold Base	Warm Base	
1	1244	811	1923	2565	5.3×10^{-6}
2	1104	1012	2339	2647	
3	1028	844	2093	3037	
4	1096	880	2250	2867	
P (Configuration)	3.0×10^{-23}				P (Interaction) 1.1×10^{-8}

There would have been great value assessing motorcycle emission rates in a similar fashion but unfortunately, there was an insufficient number of valid samples in the motorcycle dataset to perform the analysis.

In summary, it was found that while cold starts increased motorcycle emission rates, the increment was not statically significant. The supplemental driving cycles (US06 and NYCC) resulted in significantly higher emissions compared to the 4-phase FTP composite. The supplemental driving cycles were only different from each other when considering Honda emissions. The $\text{PM}_{2.5}$ mass emission rates for the urban bus decreased significantly when operating with a catalyst. Organic emission rates decreased while elemental carbon emission rates increased to a lesser degree when operating with a catalyst. Cold temperature operation resulted in lower emission rates but only significantly when operating in the non-catalyst (baseline) condition. A review of individual test results for bus emission rates show that emission rates measured by material collected on Teflon filters is only marginally less than emission rate calculated from Emfab emission rates. Also, much of the variability observed between multiple tests is the result of variability in the test conditions, not in the filter weighing procedure.

5.8 Correlation of PM with Incomplete Combustion Gases.

It was discussed in Section 2.2 how exhaust PM is the result of incomplete combustion products. Other gaseous emissions species, such as total hydrocarbons (THC) and CO are also products of incomplete combustion. In this experiment, the emission rates of CO and THC for the FTP composite, the NYOC and the US06X3 cycles were plotted versus the respective $PM_{2.5}$ emission rate. The results for motorcycle testing are shown in Figure 54 and Figure 55.

Figure 54. Correlation of total hydrocarbon emission rates with $PM_{2.5}$ emission rates for motorcycles.

Figure 55. Correlation of Carbon Monoxide emission rates with $PM_{2.5}$ emission rates for motorcycles.

The results of motorcycle testing show a poor correlation for THC with PM emission rates, particularly for the Honda, which shows a negative correlation. There is a more consistent correlation between CO and PM emission rates. For the Honda tests, the US06 results result in the negative correlation with PM rates. It is possible that the reduced THC emission rates for the US06 cycle is the result of hotter engine temperatures, which would reduce flame quenching at the cylinder walls. Flame quenching is a dominant source of the THC observed in vehicle exhaust.

It has been observed in some studies (Cadle *et al.* 1997, Sagebiel *et al.* 1997) that poor correlations between gaseous products are observed in vehicles that are poorly maintained or have high oil consumption. It could thus be argued that the PM observed in the motorbikes is due largely to evaporated lubrication oil. The PM from evaporated engine oil will be in the form of condensed species. The high OC emission rates relative to EC emission rates observed in motorcycle testing lends support to the oil consumption theory.

Figure 56. Correlation between bus testing $PM_{2.5}$ emission rates and CO and HC emission rates.

The results of the gas correlation for bus testing are shown in Figure 56. It appears that CO and HC emission rates change very little compared to PM rates in this experiment. While the oxidative catalyst cuts PM emissions by a third or more, CO and HC emissions do not appear to be significantly affected. Thus, like motorcycle testing, there is no relation between the carbon monoxide or hydrocarbon emission rates with PM emission rates.

The search for a correlation between PM emission rates and emission rates of incomplete combustion products may not be appropriate for the testing performed for this study. Generally, the determination of correlation is performed when there is emission data from a large fleet of vehicles operating on the same driving cycle with reasonably constant ambient conditions. In both motorcycle testing and bus testing, the conditions for each data point are so unique that correlations may be lost in other confounding factors. This is particularly true for bus testing, where the configuration of the exhaust system is fundamentally different between the two series.

5.9 Comparison to Published Results.

As was previously mentioned, PM from motorcycles is rarely tested and present models do not adequately represent their chemical characteristics. By contrast, diesel generated PM is fairly well characterised. In fact, the TPM emission rates for this particular bus had been previously published (Brown *et al.*, 1997). This section compares the results of emissions testing performed in this study to previous tests conducted at ERMD and to results found in the literature.

The only motorcycle emission rates of $PM_{2.5}$ available for comparison were those found in the U.S. EPA's PM emission inventory model, PART5. The results of ERMD testing on two recent model light-duty gasoline vehicles (Graham, 1998) were also compared. The results of previous ERMD testing were considered a good comparison, since the LDV testing was conducted following similar test procedures to the motorcycle testing and bus testing presented here. It should be noted, however, that a different dilution tunnel was used and although the dilution air was not HEPA filtered in the 1998 LDV testing, PM concentrations for the dilution air were determined and accounted for in emission rate calculations.

A detailed discussion of PART5 and a comparison of its output are presented following the comparison of LDV emission rates to motorcycle emission rates. The results of this comparison are shown in Figure 57. In this figure, the emission rates from the two LDVs are indicated by "Bonneville" and "Cirrus". Also included in this figure are the estimated $PM_{2.5}$ emission rates from U.S. EPA's model PART5.

Figure 57. Comparison of test data with LDV data.

There are some important points to note in this figure. The emission rates from both motorcycles are below the emission rates estimated in PART5. Note that the PM emission rates of the motorcycles are comparable to those of the LDVs, in spite of the fact that the motorcycle engines are about one-third the size of the LDV engines. Comparisons of g/mile emission rates based on engine size are a deceiving measure, since it is not necessarily the indication of a "dirty" engine. Another way to consider this data is to calculate the PM emitted per unit fuel consumed. This comparison is presented in Figure 58.

Figure 58. Comparison of specific $PM_{2.5}$ emissions for motorcycles and LDVs.

The fuel-specific PM production results are quite revealing. They show that during FTP testing, the Suzuki emission rates are as much as three times greater than the LDV emissions. By contrast, Honda emissions are comparable to LDV emissions during the FTP. During US06 testing, PM production in light duty vehicle increases to such an extent that there is very little difference in production rates between the motorcycles and LDVs. The range of fuel-specific $PM_{2.5}$ emission rates for motorcycles and LDVs operating on the US06 cycle are barely distinguishable, although average motorcycle emission rates remain slightly higher. This change in relative rates indicates that the LDV emissions controls on the test vehicles could have been less effective at reducing PM during the US-06 tests. This is not surprising, given that the supplemental driving cycle did not apply to the model years of the test vehicles. Newer vehicles that must meet the supplemental FTP standards have had better US06 results

(Graham, personal communication, 2001). The reduced effectiveness of catalytic converters at high speeds was discussed in Section 2.4.2.

The PART5 emission rates presented were the result of output calculated by the model with the input conditions as per the values in Table 23.

Table 23. Summary of input parameters for PART5 modelling.

Parameter	Value
Vehicle Distribution	Not Applicable (Concerned with individual emissions)
Average Vehicle Speed	20.0 mph (Average of FTP and CBD cycles)
Reformulated Gasoline?	No
Idling Emission Factors:	Not included
Modelling Date	1999
Fuel Sulphur level	340 ppm (based on modelling year of 1999)
Particle Size cutoff	2.5 μm
Bus Driving Cycle:	Include CBD

A major limitation with the use of PART5 in emissions modelling is that no estimate is provided for the organic fraction of the carbon emitted in light duty vehicles or motorcycles. Whereas the total PM emission rate for heavy-duty vehicles is completely accounted for by the categories of SOF, remaining carbon portion (RCP) and direct sulphate, the SOF and RCP entries are blanked out for motorcycles and light duty vehicles. The reason for this is that the model assumes the carbon portion of PM from light duty vehicles to be so small that it cannot be reliably estimated. Although the emission of $\text{PM}_{2.5}$ by LDVs and motorcycles may be small relative to heavy-duty vehicles, the large share of trip distributions made by LDVs dictate that the organic fraction should be included in future emission models. The relevant results for motorcycle and bus testing are presented in Table 24.

Table 24. Output from PART5 for motorcycles and buses.

Parameter	Motorcycle Emission Rate (mg/mile)		Bus emission rates (g/mile)		
	PART5	Average Measured	PART5	Warm Baseline	Warm Catalyst
Lead	0	0	0	0	0
SOF	Not	Not	0.755	(OC) 1.79	(OC) 0.26
RCP	Available	Applicable	0.961	(EC) 0.54	(EC) 0.82
Direct SO₄	2	0.03	0.101	Not Available	
Exhaust PM	14	4.8	1.817	2.93	1.12
SO₂ Rate	32	14.1	0.949	Not Available	

PART5's estimates of sulphur emission rates appear to be consistent with fuel sulphur consumption measured for motorcycles. In the case of motorcycle emissions, PART5 estimates that SO₂ emissions should be 32 mg/mile. This estimate is based on fuel sulphur consumption rate minus the sulphate conversion value, which PART5 assumes to be 2%. Using calculated fuel sulphur consumption rates when operating with SGC and assuming 100% conversion of fuel sulphur to SO₂, the estimated range of SO₂ emission rates for motorcycles is in the range of 35 to 82 mg/mile. The fuel sulphur content assumed in PART5 is quite close to the fuel sulphur content of the SGC used (338 ppm). Thus, it is not surprising that the SO₂ emissions as estimated by fuel sulphur consumption would be so close to the PART5 estimate. Unfortunately the average measured SO₂ emission rate for SGC operations was 14 mg/mile, well below the values estimated above. Possible causes for the low sulphur collection were discussed in Section 5.6.1

The modelled PM_{2.5} emission rates for buses are approximately halfway between the emission rates measured for the warm baseline and warm catalyst conditions. The model assumes approximately 44% of the PM emitted from the vehicle will be in the form of SOF. By comparison, the measured results showed an OC proportion of approximately 61 % for baseline operation and 23% when operating with the catalyst.

A comparison of the bus testing results performed in this study to previously published results showed that the bus is emitting PM at a higher rate than what was observed in

previous tests. A comparison between the emission rates for the same bus in 1996 is shown in Table 25. Note that the results from 1996 are from a different test cycle and that emissions were based on TPM, not $PM_{2.5}$.

Table 25. Comparison of $PM_{2.5}$ emission rate (g/mile) for Bus 8910 to previous testing.

	Warm CBD (Feb 2000)	NY Comp (TPM) (1996)
Baseline	2.78	1.39
Catalyst	1.12	1.20

The baseline emission rates for this vehicle are much higher than what was observed in previous testing while the catalyst results are slightly lower. The higher baseline emission rate could be the result of engine age or improper tuning of the vehicle.

5.9.1 Organic and Elemental Carbon Emissions Rates

The results of the organic and elemental carbon emission rates for motorcycles were compared to results of ERMD testing on LDV vehicles (Graham, 1998). Overall, the results of LDV testing found significantly higher elemental carbon to total carbon ratios (17%-42%) than what was observed for motorcycle testing (2% - 15%). Other studies (Sagebiel, 1997; Norbeck, 1998) found results similar to the LDV results from ERMD.

It is likely that the low elemental carbon emission rate observed in the motorcycle testing was the result of elemental carbon emission rates being below the quantification limits outlined in Table 9. If we assume an OC/EC split of 70/30 (which is the median ERMD results), the corresponding EC emission rate would be below detectable limits for any FTP test where the organic emission rate was below 0.65 mg/mile. Of the 16 test conditions that were sampled, there are seven cases where the average OC emission rates would result in non-detectable EC emission rates. There are another three cases where the OC emission rate is within 0.1 mg/mile of the detectable limit for EC assuming the 70/30 split.

The average OC/EC split measured in a study of 19 light duty diesel vehicles (Norbeck *et al.*, 1998) was 31.4/68.6. This average is similar to the bus results when operating with catalyst, which were 49/51 (warm) and 24/76 (cold). The baseline condition for buses resulted in OC/EC of approximately 78/22 at both temperatures. There is no discussion in Norbeck's work of exhaust aftertreatment for the diesel vehicles tested, although it was mentioned that the majority (18) of the vehicles were built before 1986. Thus, it is unlikely that these vehicles would have had exhaust treatment devices installed.

5.9.2 Ion Emission Rates

The study of 23 in-service vehicles in Nevada (Sagebiel, 1997) measured the emission rates of three anions (sulphate, nitrate and chloride). The study found that the majority of vehicles had very low emission rates of these anions, with the exception of one vehicle, which recorded a sulphate emission rate of 13 mg/mile, accounting for 42% of the total PM mass. This emission rate was greater than the fuel-sulphur consumption rate and was attributed to material that had built up over time and become dislodged. Excluding this vehicle and another high emitter, the average sulphate emission rate was 0.12 mg/mile. Norbeck *et al.* (1998) observed a similar sulphate emission rate (0.10 mg/mile). In this test, the average sulphate emission rate was approximately 0.035 mg/mile, which is much lower than the results from the studies mentioned above. Once one accounts for the difference in fuel consumption, the sulphate emission rate of the motorcycles is still about half that of the LDV sulphate emission rate per quantity of fuel consumed. The fact that the motorcycles do not have oxidative catalysts may explain the lower sulphate emission rate.

The sulphate emission rate predicted for motorcycles by PART5 is 2 mg/mile for motorcycles and 9 mg/mile for LDVs. These are almost two orders of magnitude higher than the values observed above. PART5 estimates sulphate emission rates based on the assumption that 2% of sulphur in the fuel will be converted to sulphate. In this study, the sulphate conversion rate was an average of 0.05% for operation with SGC and 10% for low-sulphur fuel. Another point worth considering is that, the sulphate estimated by PART5 includes an estimation of the weight of water that adsorbs to the sulphate molecule. This

estimate increases predicted emission rates by almost 30%. This water was not accounted for in the reported sulphate emission rates.

This chapter has provided a summary of how emission rates vary with vehicle type, driving cycle, temperature and exhaust aftertreatment. The next chapter evaluates the effect of dilution path on sampled emission rates.

Chapter 6 Exhaust Dilution Modelling

The purpose of this chapter is to compare the dilution processes that the exhaust experiences as it exits into the atmosphere to the dilution and cooling processes that are experienced in the dilution tunnel. This comparison has been performed through (i) the development and evaluation of a simple model that estimates the temperature and dilution of vehicle exhaust as it mixes with surrounding air in an on-road scenario; (ii) the estimation of exhaust temperature throughout the exhaust collection and dilution system in the laboratory, (iii) the comparison of the time history of exhaust temperature between the two regimes, and, (iv) the inference of the effect of identified differences on the nature of the sampled PM in the laboratory.

A chemical characteristic of PM that has been discussed extensively in this report has been the organic fraction, termed organic carbon (OC) in Chapter 5 and soluble organic fraction (SOF) in Chapter 2. As was discussed in Chapter 2, the SOF can be highly sensitive to the dilution path. It is thus clearly desirable that the exhaust sampling system accurately simulate on-road exhaust dilution so that measured SOF values will be similar to the values for PM emitted to the atmosphere. Unfortunately, dilution path is a parameter that is very difficult to model and to control in the laboratory.

The SOF is but one of numerous PM characteristics that are in flux during the exhaust mixing process. In addition, PM conversion continues on a more gradual basis once the PM has completely mixed with the atmosphere and begins to interact with atmospheric components. Given the variety of processes at work, it is difficult to pinpoint the moment where post-exhaust conversions have ended and atmospheric processes have begun.

Ideally, we would like to track the saturation path of each species as it leaves the exhaust pipe. Clearly, this isn't possible so instead, we have to identify clues that can best estimate the effect of dilution path on the degree of saturation. One method is to evaluate the saturation curve for a characteristic condensable species, as was illustrated in Section 2.2.2. Another is to determine the time that it takes for vehicle exhaust to reach a stated end-condition, such as a certain level of dilution or an end temperature.

Two measures for the degree of exhaust dilution were considered in this report. On-road dilution was reported as dilution ratio in order to compare the results of the model to published work. The estimated conditions in the dilution tunnel model were compared to the results of the on-road dilution model using temperature, the reasons for which shall be discussed later in this chapter.

6.1 On-road Dilution Model

The dilution of vehicle exhaust is an extremely complex process. The various combinations of exhaust pipe alignment and vehicle geometry result in a seemingly endless variety of flow patterns, making the development of a characteristic exhaust dilution pattern extremely difficult. One of the most reliable methods for developing these flow patterns would be through the development of a flow visualisation model either through physical modelling or computational fluid dynamics. Unfortunately, there was not sufficient scope in this study to conduct flow of the on-road dilution process. As a result, some rather gross simplifications have been made. It is highly recommended for future analysis that these assumptions be verified to ensure the validity of these assumptions.

Two vehicle scenarios were considered in this model: light duty gasoline and heavy-duty diesel. A number of vehicle parameters were considered to affect the concentration decay profile. These parameters were (i) exhaust pipe alignment; (ii) temperature and flow rate of exhaust and temperature of the ambient air; and (iii) degree of air entrainment in the wake. The conditions of each of the control parameters are shown in Table 26. The development of these boundary conditions is discussed below.

Table 26. Boundary conditions for two vehicle scenarios.

Vehicle	Pipe Alignment	Temperature and Flow Rate	Wake Effect	Ambient Temp
Light duty gasoline	Coaxial	See Table 27	Relative velocity reduced by 1/3	20 °C
Heavy duty diesel	Cross flow	See Table 27	Not applicable	20 °C

The possible conditions for exhaust temperature and flow rate were determined from ERMD test data on exhaust flow rates and temperatures for a heavy-duty diesel vehicle and a light-duty gasoline vehicle. The exhaust flow rate was measured using a laminar flow element in the intake manifold. It was assumed that there were negligible differences between the mass flow rates of intake air and exhaust air. Temperature was measured with a thermocouple attached to the transfer pipe at the point where the exhaust would normally exit into the atmosphere.

Test data for the light duty vehicle was taken from two warm-start LA4 cycles. Heavy duty data was taken from an urban bus operating on a 5-mode test, which is a synthesised saw-tooth cycle consisting of five acceleration, steady-state operation and deceleration cycles. From this data, relationships were developed to calculate the temperature and flow rate of vehicle exhaust for any speed within the range of testing.

The driving cycle and measured parameters for the heavy-duty engine are presented in Figure 59. The exhaust temperature and exhaust flow rates are plotted versus vehicle speed in Figure 60.

Figure 59. Heavy duty test cycle with exhaust flow rate and temperature.

Figure 60. Temperature and flow rate of exhaust from a heavy-duty diesel engine.

It can be seen in the temperature plot that there are five regions with tight groupings of data points. These are associated with the steady state conditions (20, 25, 30, 35 & 40 mph) in the cycle. The points outside of these groups are associated with accelerations and decelerations. It was decided that exhaust temperature could be estimated with a straight regression line for all data points in the cycle. A review of the plot of the flow of air through engine reveals that it exhibits little or no dependence on vehicle speed. This is expected, given that the engine used for this study had a minimum 10-gear transmission, allowing the engine to operate at the rpm for optimum engine performance during each mode.

It should be noted that the mass flow rate of exhaust will differ from the mass flow of intake air by the mass flow of fuel into the engine. Fuel flow was determined by ERMD for the heavy duty cycle and is accounted for in the dilution tunnel model presented later in this section. Volumetric flow rate of exhaust will also be much higher than that of intake air, given the difference in temperature between intake and exhaust air. This exhaust temperature was accounted for when calculating the exhaust exit speed in the dilution model.

In summary, the following expressions were determined to predict the temperature and exhaust flow rate for diesel engines:

$$T (^{\circ}\text{C}) = 4.05 \times V (\text{mph}) + 176,$$

$$Q (\text{scfm}) = 327$$

The exhaust flow rate for light-duty vehicles was taken from a data set that measured the intake flow rate in standard cubic feet per minute and exhaust temperature for the last two of three repeats of the LA4 cycle. The speed profile with the associated flow rate and exhaust temperatures for one of the LA4 cycles is shown in Figure 61.

Figure 61. Speed, flow rate and exhaust temperature versus time in an LA4 cycle.

Figure 62. Plot of light-duty vehicle exhaust flow rates versus vehicle speed.

Intake flow rate is plotted versus vehicle speed in Figure 62. In this plot, there appears to be very little difference between the flow rates of the two LA4 cycles. When the two sets are combined into one data set, the predicted flow rate is expressed as:

$$Q \text{ (scfm)} = 0.44 \times V \text{ (mph)} + 12.9.$$

The plot of exhaust temperature versus vehicle speed is shown in Figure 63. The distinguishing feature in these plots is that there appears to be two distinct temperature regions. By comparing this figure to Figure 61, we find that the temperature is very low (approximately 150°C) at the beginning of the cycle. After the vehicle completes the high-speed acceleration/deceleration cycle (approximately 3.5 minutes into cycle), the exhaust temperature stabilises at a higher range. This jump in temperature is due to the light-off of the catalytic converter, which converts unburned fuel and CO to CO₂ exothermically. It was decided that only data collected after light-off would be used for predicting the temperature of the exhaust relative to speed.

Figure 63. Light duty vehicle exhaust gas temperature versus vehicle speed.

Figure 64 presents the plot of stabilised exhaust temperatures versus speed. It appears that stabilised temperatures are consistent and that temperatures can be approximated by averaging the slopes and intercepts to the following relationship:

$$T (^{\circ}\text{C}) = 0.44 \times V (\text{mph}) + 197$$

Figure 64. Isolated plot of exhaust temperature versus speed for LDV gasoline vehicle.

Table 27 summarises the predicted flow rates and temperatures for light duty gasoline and heavy-duty vehicles for use in the dilution model.

Table 27. Summary of equations for predicting temperature and exhaust flow rates with speed.

Vehicle	Temperature ($^{\circ}\text{C}$)	Exhaust Flow (scfm)
Light-Duty Gasoline	$T = 0.44 \times V (\text{mph}) + 197$	$Q = 0.44 \times V (\text{mph}) + 12.8$
Heavy-duty Diesel	$T = 3.3 \times V (\text{mph}) + 198$	$Q = 327$

It is important to mention here that a fundamental parameter of exhaust flow has not been captured by these relationships. Exhaust flow rate was estimated by measuring the intake volumetric airflow rate. While this is a fair estimate for determining the mass flow rate of exhaust air, it does not necessarily capture the concentration of pollutants in the exhaust. This is a particularly significant oversight for heavy-duty exhaust, where concentrations change significantly with load (see Section 2.3.1). At high loads and speeds, the concentrations of particular exhaust components are significantly higher than they would be at steady state. A review of Figure 8 on page 24 shows that higher concentrations of pollutants will result in an increased condensation of species onto PM. Thus, an important factor in the estimation of SOF has not been included in the equation.

6.1.1 Effect of Vehicle Wake

For the purposes of this discussion, the vehicle wake is considered the air that is entrained by the vehicle, resulting in a reduction in relative airflow as measured from the exhaust pipe. This reduction in airflow is referred to as the perturbation velocity, designated u . A schematic showing the conceptual model of the wake is shown in Figure 65. The model developed here assumes that light duty vehicle exhaust is directed behind the vehicle into the wake. By contrast, the theoretical heavy-duty vehicle was assumed to have an exhaust pipe aligned vertically and extending far enough above the vehicle so that the exhaust would exit perpendicular to the relative wind. This results in cross-flow mixing of the exhaust outside of the vehicle wake.

Figure 65. Schematic of the wake behind a vehicle moving the surface at speed, U and holding the vehicle fixed; $l(x)$ is the height of the wake and u is the perturbation velocity of the wake (Eskridge *et al.*, 1979).

The effect of vehicle wake on relative airflow behind the vehicle was reviewed by Eskridge *et al.* (1979) in their study of exhaust dilution. A summary of the solution of their wake calculation is shown in Figure 66. In this figure, $\xi = z/l(x)$ (the vertical distance divided by the wake height) and $\eta = y/l(x)$ (lateral distance from vehicle centreline over wake height).

Figure 66. Wake perturbation velocity for given distance (x), measured in car heights (h) downstream of vehicle travelling at 22.2 m/s. Wake modelled at centreline of vehicle.

It can be seen in the figure that at a distance of three car heights (approximately 5 metres for a sedan) downstream of vehicle travelling at 80 km/h, the perturbation velocity will be approximately one-third the speed of the vehicle. No indication is given what sort of perturbation velocities to expect at distances closer than three car-heights. However, given that the perturbation velocity appears to increase exponentially with proximity to the vehicle, it is likely that the exhaust is exiting into stagnant air relative to the pipe exit.

As the exhaust departs from the pipe, the perturbation velocity decreases steadily. From the perspective of the exhaust gas, the surrounding airflow shifts from stagnant at the exit to the full relative velocity of the vehicle some distance downstream. These changes in relative velocities and their effect on exhaust dilution are difficult, if not impossible to model accurately. Keeping in mind that the purpose of this modelling study was to develop an approximation for the time for the exhaust to reach ambient conditions, an intermediate

perturbation velocity was selected. A perturbation velocity of $1/3$ the vehicle speed was selected for all distances from the pipe.

This next part of the discussion of exhaust dilution will focus on previous research on the dilution of gas jets and will outline the model selected for this study. The aerodynamic mechanisms at work to dilute coaxial exhaust and cross-flow exhaust are quite different. These two flow conditions shall be reviewed in turn.

6.1.2 Effect of Pipe Alignment

The extreme conditions for pipe alignment were considered cross-flow and coaxial. Common to both conditions is the concept of a potential core, the region downstream of the exhaust exit point where flow conditions of the injected air are the same as those in the pipe. The fundamental difference between these two conditions is the mechanism by which the potential core decays upon exiting the jet.

6.1.2.1 Coaxial Flow Dilution

In coaxial flow, momentum and material is transferred across an often turbulent boundary layer with very little pressure differential. The mixing between phases is dependent on eddy diffusion and exhaust mixes with the ambient flow symmetrically. The exhaust jet is composed of three regions, shown in Figure 67. In the initial region, eddies have not completely penetrated the exhaust. Part of this initial region is the potential core, where flow qualities have not changed from the conditions in the pipe. The transitional region begins when the centreline concentration begins to decay. The similarity region is the point at which concentrations along the centreline decay according to Fick's Diffusion theory. A diagram of these regions is shown below.

Figure 67. Mixing regions between exhaust and surrounding air (Beér and Chigier, 1972).

It has been found that in turbulent flow regimes, the decay of centreline qualities (temperature, concentration and velocity) is a function of two variables. These are:

- (i) The centreline distance downstream of the jet exit; and

- (ii) The ratio of ambient or relative airflow conditions exhaust flow conditions. This ratio shall be designated by λ . In the following discussion, exhaust flow is designated by the subscript j (jet flow) and ambient flow designated by the subscript s (surrounding flow).

There is some contention as to what flow parameters should be used to define λ . Forstall and Shapiro (1950) defined λ as a velocity ratio u_j / u_s where u is the velocity of the stream.

Zakkay *et al.* (1964) later defined λ as a mass flux ratio $\left(\frac{\rho_s u_s}{\rho_j u_j} \right)$ (ρ = density, u = velocity) in systems with significant density variations. Given the temperature differences between exhaust and ambient air, it was decided that the mass flux ratio would be used to calculate λ .

The length of the potential core (i.e. the distance from the pipe exit where centreline conditions begin to decay) was estimated using the relationship developed by Forstall and Shapiro (1950):

$$L_{pc} / d_j = 4 + 12\lambda$$

Equation 6

, Where: L_{pc} = Length of Potential Core
 d_j = Diameter of jet
 $\lambda < 1.0$

To clarify, in the case where the exhaust was exiting into still air, the λ would be zero and the potential core would be the shortest for the range of applicable λ values. Conversely, a λ of unity would be associated with the case where the mass flux of the exhaust would be the same as that for the surrounding flow, resulting in minimum eddy diffusion and thus, the longest potential core.

For cases where λ is greater than 1, (i.e., surrounding flow greater than the exhaust flow), estimates for exhaust mixing were taken from a plot shown in Beér and Chigier (Figure 68), which shows the decay of centreline velocity for $0 < \lambda < 2.13$. This figure describes the potential core as x/d , instead of L/d . It can be seen in this figure that the velocity decay

profile for $\lambda=2.13$ is almost a mirror image of the profile for $\lambda=0$ with respect to u_c/u_o . An assumption was made that potential core lengths would follow Forstall and Shapiro's estimate and correlate linearly from the maximum potential core length of 16 at $\lambda=1$ to $L/d=4$ at $\lambda=2.13$. For λ s greater than 2.13, it was assumed that potential core length reduced asymptotically to zero. Table 28 summarises the calculation of the potential core depending on λ .

Figure 68. Velocity decay along the axis of a round jet in a co-current stream (Beér and Chigier, 1972)

Table 28. Summary of relationships used for determining length of potential core.

$\lambda = \frac{\rho_s u_s}{\rho_j u_j}$	Potential Core Length (L/d)
$0 \leq \lambda \leq 1$	$L/d = 4 + 12\lambda$
$1 < \lambda \leq 2.13$	$L/d = 4 + 12 \left(\frac{2.13 - \lambda}{1.13} \right)$
$\lambda > 2.13$	$L/d = 4 \left(\frac{2.13}{\lambda} \right)$

Forstall and Shapiro estimated the decay of jet velocity to be:

$$\frac{U - U_s}{U_p - U_s} = \frac{L_{pc} / d_j}{x / d_j}$$

Where:

U_s = Velocity of surrounding flow

U_p = Velocity of exhaust at pipe exit

U = Velocity of exhaust at x

L_{pc} = Length of potential core

x = Centreline distance from pipe exit

d_j = diameter of nozzle

Equation 7

For the purposes of this study, this relationship applies equally well to centreline concentration and temperature, as was discussed in Section 2.2.2. The conversion of velocity relationships to concentration relationships is shown in Equation 8. For a component where the background concentration is much less than the concentration in the raw exhaust.

$$\frac{C_m}{C_0} = \frac{1}{DR} = \frac{U - U_s}{U_0 - U_s}$$

Where:

C_m = Concentration of exhaust component at x

C_0 = Concentration of exhaust at pipe exit

Equation 8

We can see from Equation 7 that the velocity ratio varies inversely with x . We can also say that concentration has an exponential decay coefficient of 1. If concentration varied inversely with x^2 , the exponential decay coefficient would be 2. Table 29 presents a summary of the results of experiments that measured the exponential decay coefficients for temperature (P_T), momentum (P_v) and concentration (P_C). The average decay coefficients for all three qualities is less than -1 but no consistent relationship could be found between momentum and mass. This is likely because eddy diffusivities are highly variable and difficult to predict with certainty. As a result, it was assumed that all exhaust flow qualities (temperature, momentum and concentration) have a decay exponent of -1 for all flow regimes where $\lambda < 1$.

Table 29. Summary of exponential decay coefficients. (Schetz, 1980).

Study	V_s/V_j	ρ_i/ρ_e	λ	P_v	P_t	P_c
Corrsin	0	0.95	0	-1	-1	
	0	0.52	0	1.18	1.2	
Forstall	0.25	0.92	0.27	1		1
	0.5	0.92	0.54	1		1
Pabst	0.05	0.45	0.11	1.29	1.05	
	0.26	0.45	0.58	1.28	0.94	
	0.44	0.45	0.98	0.88	0.74	
Landis and Shapiro	0.25	0.92	0.27	1	1	
	0.25	0.77	0.32	1.04	1.04	
	0.46	0.92	0.50	1.25	1.14	
	0.5	0.77	0.65	1.03	1.08	
	0.5	0.84	0.60	1.33	1.33	
	0.5	0.84	0.60	1.02		1.02
	0.5	0.84	0.60	1.22	1.22	1.22

Note that none of the studies above considered conditions where λ was greater than unity. Figure 69 summarises the results of studies that measured the decay of centreline jet concentration in axis-symmetric flows. It can be observed in this figure that when the surrounding flow is greater than the exhaust flow, the decay exponent shifts from 1 to 2.

Figure 69. Experimental determination of asymptotic concentration decay exponent. (Schetz, 1980)

Based on the data in Figure 69, it was decided that in conditions where $\lambda > 1$, the exponential decay coefficient would be set to 2. Admittedly, there appears to be a transition region for λ greater than one but without more data, it is difficult to predict how decay coefficients will be affected in this transition region.

6.1.2.2 Cross-flow Dilution

The mechanisms at work in cross-flow mixing are more complicated than the mechanisms that define coaxial mixing. A schematic of cross-flow mixing is shown in Figure 70. The air exiting the jet acts as a cylinder around which the surrounding flow circulates. The surrounding flow is decelerated on the upstream side of the jet creating a region of stagnation pressure while a low-pressure region develops in the wake of the jet. The mixing between the

jet and the main stream is accelerated by the additional lateral shearing stresses, which induce vortices in the exhaust jet, thus shortening the potential core.

Figure 70. Schematic of cross-flow injection. (Schetz, 1980).

An empirical formula for concentration decay is presented in Beér and Chigier (Equation 2-19), shown below.

$$\frac{C_0}{C_m} = DR = \left[\left(\frac{x}{D_j} \right) \exp(7.8\lambda - 1.85) \right]^{1.18}, \text{ Where}$$

C_0 = Initial Concentration

C_m = Centreline concentration downstream of jet exit

x = Distance downstream

D_j = Diameter of jet

$$\lambda = \left(\frac{\rho_s}{\rho_j} \right)^{0.5} \frac{u_s}{u_j},$$

$$0 < \lambda < 0.152$$

Equation 9

A number of elements are worth noting in this relationship. The first is that the model is not applicable for distances where x is less than the pipe diameter. Since this distance range is within the potential core, it is not considered a problem for modelling purposes. Note also that in the cross-flow model, the flow ratio is weighted differently than in the coaxial model. The ratio used here appears to be a momentum-weighted model, given the relative powers that have been assigned to density and speed. The increased weight of velocity in the λ expression is likely due to the increased shear due to the angle of injection.

Another major factor to consider is the limited range of λ 's for which the relationship is applicable. We shall find later that the range of λ for heavy-duty vehicles is between 0.01 and 0.74. An inspection of the relationship reveals that the limits placed on λ are to ensure that the exponential function $(7.8\lambda - 1.85)$ remains negative. This indicates that the exponential function is a curve-fitting feature in order to fit the empirical function to the data. Note that no other relationship could be found for cases where $\lambda > 0.152$. However, if we assume that the exponential function was included in the relationship merely to account for reduced diffusion in low- λ scenarios, the function can be removed from the relationship in $\lambda > 0.152$ cases. This assumption implies that there is no effect of the relative wind on the rate and degree of initial dilution, which is clearly incorrect (Wark, Warner and Davis, p. 145).

Another source of potential data and relationships is the study of dispersion of exhaust gases from roof-level stack and vents. Roof-level dispersion has parallels with the dilution of vehicle exhaust from the theoretical heavy-duty vehicle. The key difference between rooftop dispersion and vehicle exhaust dispersion is the surrounding flow will generally be much faster in the vehicle scenario. Wilson *et al.* (1994) defined DR_0 , the initial dilution ratio, as:

$$DR_0 = 1 + 7\lambda^2 \quad , \text{ where} \quad \text{Equation 10}$$

$$\lambda = \left(\frac{\rho_s}{\rho_j} \right)^{0.5} \frac{u_s}{u_j}$$

$$0 \leq \lambda \leq 2.0$$

Note that Wilson *et al.* (1994) also used a momentum-weighted flow ratio. This initial dilution accounts for flow entrainment that bends the vertical jet to the direction of relative airflow and any concentration reduction that is a result of buoyant forces on the jet. Wilson's relationship provides an indication of how the relative wind affects the concentration, which is not accounted for in Equation 9. Thus, Equation 10 was included in the cross-flow model for λ 's greater than 0.152 but less than 2.0.

6.1.3 *Summary of Model Used*

Based on the considerations discussed above, a model was developed to estimate the dilution ratio and exhaust temperature relative to distance (x) downstream from the exhaust pipe for six representative vehicle speeds. Based on the limitations of the relationships discussed earlier, the relationship between dilution ratio and distance is slightly different for the various ranges of λ .

A summary of the relationships used to calculate the dilution ratio for each flow regime is presented in Table 30. In the first column, the regimes are annotated by LD (for light-duty) or HD (for heavy-duty) and a case number. The second column outlines the range of λ for which the case number applies. The last set of columns describes the applicable Dilution Ratio (and potential core length in the case of the light-duty model).

Table 31 summarises the various vehicle speeds with their calculated λ and the modelling flow regime that applies for that speed.

Table 30. Summary of expressions used to determine dilution ratio.

Vehicle	Flow Ratio Definition and Range	Dilution Ratio Relationships	
Light Duty Flow Regime	$\lambda = \frac{\rho_s u_s}{\rho_j u_j}$	Potential Core Length (L/d)	Decay Expression
LD-1	$0 \leq \lambda \leq 1$	$L/d = 4 + 12\lambda$	$DR = \frac{x}{L}$
LD-2	$1 < \lambda \leq 2.13$	$L/d = 4 + 12\left(\frac{2.13 - \lambda}{1.13}\right)$	$DR = \left(\frac{x}{L}\right)^2$
LD-3	$\lambda > 2.13$	$L/d = 4\left(\frac{2.13}{\lambda}\right)$	
Heavy Duty Flow Regime	$\lambda = \left(\frac{\rho_s}{\rho_j}\right)^{0.5} \frac{u_s}{u_j}$	Temperature Decay Expression	
HD-1	$0 \geq \lambda \geq 0.152$	$DR = \left[\left(\frac{x}{D}\right) \exp(7.8\lambda - 1.85)\right]^{1.18}$	
HD-2	$0.152 > \lambda \geq 2.0$	$DR = \left[\left(\frac{x}{D}\right)\right]^{1.18} (1 + 7\lambda^2)$	

Using the temperature and volumetric flow relationships derived in the previous section, the mass and momentum flux ratios were calculated a range of cases a function of vehicle speed. A summary of these fluxes for the light duty and heavy duty vehicle is presented in Table 31. The six cases shown on this figure are the driving conditions that were selected for estimating exhaust dilution.

It is worth noting that the original relationships found in the literature (LD-1, HD-1) are applicable for a limited range of the λ 's calculated for this study. There are three light duty cases and two heavy duty cases where the λ defined for each vehicle scenario fits within the empirical relationship presented in the literature. In the remaining cases, estimates were made of how the relationships should be adjusted for the remaining high- λ cases. Thus, the predicted dilution profiles should only be considered rough estimates that should be reviewed if applicable data becomes available in the future.

Table 31. Mass flux ratios for heavy-duty vehicles and light-duty vehicles.

Case Number	Vehicle Speed (km/h)	Heavy-Duty Model		Light-Duty Model	
		λ (mass based)	Flow scenario	λ (mass based)	Flow scenario
1	0.65	0.01	HD-1	0.04	LD-1
2	64	0.07		0.32	
3	16	0.17		0.69	
4	FTP Average*	0.30	HD-2	1.13	LD-2
5	60	0.57		1.51	
6	80	0.74		1.70	

Note: FTP average is 34 km/h for LDV testing and 30 km/h for HDV testing (see p. 48 and p. 51).

The dilution profiles for light-duty and heavy-duty vehicles are presented in Figure 71 and Figure 72, respectively. Superimposed on these profiles is the critical dilution ratio range of 5:1 to 50:1. In these figures, the dilution profile is plotted versus time, rather than distance, to account for the fact that the condensation of semivolatile species is a rate function. In order to plot versus time, the time t that the diluting exhaust passes a particular point x downstream was calculated using $t = x/U$. The exhaust velocity U was calculated by applying the conversion relationship shown in Equation 8.

Figure 71. Dilution profiles for light duty vehicle at various speeds.

What is immediately apparent is that the time for exhaust to dilute through the critical dilution range covers two orders of magnitude. The logarithmic mean time across all speeds is 6 seconds for the light-duty model and 4 seconds for the heavy-duty model. This range of dilution can be easily observed by comparing the persistence of the exhaust plume from a heavy-duty vehicle accelerating from a stop to the same vehicle operating at steady state on the highway. Given the right conditions, the puff of black smoke from the slow-moving vehicle remains visible for a number of seconds. On the highway, however, smoke is only apparent on very poorly maintained vehicles and even then, for only an instant before it disappears into the ambient air. The higher emission rate from the accelerating vehicle no doubt contributes strongly to this perception but the sharp difference in the persistence of the visible plume is nonetheless quite prominent.

Figure 72. Dilution profiles for heavy-duty vehicle at various speeds.

The results of the model were compared to two on-road dilution measurement studies performed by the University of Minnesota. The first study was conducted by Kittelson *et al.* (1988) on dilution from heavy-duty vehicles. The first study (Field Study II) measured the emissions of a heavy-duty diesel flatbed truck from its trailer as it travelled between 50-55 mph. The second (Field Study V) used a mobile laboratory that followed behind the tractor at a constant distance.

Dilution ratios were calculated by dividing the volume concentration of TSP in the exhaust plume by the product of the mass concentration in the stack and the average volume to mass ratio of PM in the plume. Background concentrations of PM were measured prior to testing to correct for background concentrations where necessary. The results of the two field studies are shown in Figure 73.

Figure 73. Relationship between dilution ratio and sampling distance. (Kittelson, et al. 1988).

The data from the trailer fit the following expression for dilution ratio:

$$DR(x) = 7.01x^{0.955} \quad , \text{ Where} \quad \text{Equation 11}$$

X = Distance downstream of exhaust pipe
DR (x) = Dilution ratio as a function of x

Data taken beyond ten meters from the exhaust stack showed a diversion from Equation 11. This was attributed to more intense eddies in the wake. An important observation made in this study is that dilution models that use constant eddy diffusivities for highly turbulent regimes such as vehicle exhaust scenarios are only valid for short times and distances. This observation infers that it may be necessary to develop staged dilution relationships that

change with progressive distance from the exhaust pipe. One observes in Kittelson's data that the dilution ratio at the approximate point of divergence due to the wake region is already near 100. Thus, accounting for the wake may not be required for the range of distances that are considered in this report. Although Kittelson *et al.*'s data is a valuable comparison to the model presented here, their curve-fitting relationship was not directly applicable for calibration of the model, since Kittelson's results give no measure of how dilution changes with vehicle speed.

The results of the 1988 study indicate that exhaust dilution at high speeds may, in fact, be slower than what is described by the model presented here. For a vehicle travelling at 55 mph (88 km/hr), the distance to pass through the 5:1 - 50:1 range was approximately 6.25 m, which is associated with 0.25 s. This time is slightly longer than the 0.18 s determined by the model for 80 km/hr. Given the numerous parameters that affect the dilution ratio, such as minor differences in pipe exit alignment, wind direction, and wake effects, that have not been quantified in the measured data, the model appears to be quite a good fit. In addition, there is no mention whether the distances were corrected for prevailing wind, which would confound results.

The other on-road dilution study measured on-road exhaust concentrations from light duty vehicles (Dolan and Kittelson, 1979). Two sets of tests were conducted in this study. The first consisted of measuring the NO concentrations of an idling vehicle facing into a 20-km/hr wind. The second set of tests measured NO concentrations of vehicle exhaust behind two vehicles approximately 1 second after emission at 16, 48 or 80 km/hr. In this study, dilution ratios were calculated by the ratio of NO measured in the plume to NO measured in the raw exhaust during chassis dynamometer tests.

The study found for the idling vehicles that dilution ratios were near 100 one meter from the tailpipe. At 20 km/hr and 1 meter downstream, the modelled dilution ratio is approximately 1.6, which is two orders of magnitude below Kittelson's estimate. Kittelson's measurements taken one second behind a moving vehicle estimated dilution ratios near 1000 at 16 km/h and up to 5000 at 80 km/h. The model calculates a significantly lower dilution ratio of 8 after 1

second in the 16 km/h range. For 80 km/hr, the dilution ratio calculated by the model (2600) is much closer to the measured result, although still one half of the measured value.

There are numerous potential sources of the discrepancy between our light duty dilution model and the values measured in the field. Some of the key sources are the effect of the vehicle wake, differences in exhaust pipe alignment with the direction of motion, and the effect of the tailpipe being so close to the ground. In our model, the wake was assumed to simply reduce the relative airflow by a set perturbation velocity. In reality, the perturbation velocity changes with downwind distance from the vehicle. In addition, the eddies associated with the vehicle wake appear to intensify at a point downstream of the vehicle, as shown in Figure 73. The tailpipe alignment selected in the model is the extreme case that results in the lowest dilution rate. Many light duty vehicles have tailpipe alignments that are partially deflected from the direction of motion, which would increase the dilution rate.

The proximity of the exhaust pipe to the ground is likely the most significant unaccounted for variable in the light duty dilution model. Light duty exhaust exits into a region of high shear that results from the strong velocity gradient between the air close the ground, which remains stagnant relative to the road to the air immediately behind the vehicle, which is moving at the speed of the vehicle. The differences in these air speeds will result in intense eddies in the region that the exhaust exits, resulting in much more rapid diffusion than the model predicts. The evaluation of the complexities associated with the interaction between the vehicle wake and the layer of stagnant air close to the ground was beyond the scope of this study.

The fact that times to pass through the Critical DR range can vary so much with vehicle speed has far reaching implications for emissions testing and PM emissions inventory collection. The fact that these critical dilution times can be linked to the degree of condensation of semi-volatile material in the exhaust means that the PM emitted from a vehicle will have significantly different characteristics depending on its average speed over and above the effects of the engine. In other words, if we compare the dilution regime associated with high speed driving conditions, to that in congested areas with low vehicle speeds, one can expect that the PM in congested areas may be greater in mass and number and have

higher SOF values. One might presume that this theoretical scenario is what occurs in the dilution tunnel but we shall discover in the next section that not only is this not the case but, in fact, the situation is reversed!

6.2 Dilution Tunnel Model

As mentioned earlier, the dilution tunnel should simulate dilution processes on the road so that the PM emission rates calculated from laboratory tests properly represent the actual PM emitted. Where it does not, efforts should be made to characterise the differences and estimate what ramifications these differences will have on the measured PM emission rates and composition. For example, on-road dilution is a continuous mixing process that can be assumed to occur adiabatically while tunnel dilution is either a single stage or two-stage discrete mixing process that is not necessarily adiabatic. The implications of these differences will be discussed below.

Implicit in this discussion is an evaluation of the dilution tunnel used for the emissions testing discussed earlier in Section 3.1.3. Where it is appropriate, references may be made in a more general sense regarding the nature of dilution tunnels used in the emissions testing sector.

The dilution profiles compiled in the previous section applied the relationships for dilution interchangeably between concentration and temperature. We could do this in part under the assumption that the dilution process was adiabatic. Applying the adiabatic assumption allows us to use the 5-50:1 critical dilution range as a guide for predicting the degree of condensation of semi-volatile species into PM. We do not have the luxury of assuming adiabatic conditions when considering tunnel dilution because of the potentially large temperature gradient between the exhaust and the walls of the transfer pipe (or dilution tunnel), leading to non-adiabatic conditions. As a result, the cooling profiles developed for the dilution tunnel account for heat transfer across the tunnel walls.

A fairly simplified mixing and cooling model was prepared using the following assumptions:

1. Exhaust from the transfer pipe is mixed instantly and completely with dilution air at the mixing point.
2. Cooling due to heat transfer through the tunnel walls occurs uniformly across the cross section of the dilution tunnel and transfer pipe.

These assumptions are verified in the following discussion.

6.2.1 Dilution Ratio Estimates

The first assumption was verified by applying the coaxial dilution model, developed in the previous section, to the mixing process in the dilution tunnel. The flow parameters for ERMD's dilution tunnel are shown in Table 32. Note that two different venturis were used in emissions testing, depending on the size of the vehicle being tested. The flow parameters in the transfer pipe were calculated for each of the six operating cases presented in the Section 6.1.3. The limiting conditions (Cases 1 and 6) will be discussed here. The flow parameters for the dilution tunnel and the transfer pipe at these limiting conditions are presented in Table 32 and Table 33, respectively.

Table 32. Description of flow parameters of dilution tunnel.

<u>Common Parameters</u>		<u>Common Factors</u>
Tunnel diameter (m)		0.254
Length of tunnel between exhaust inlet and sampling region (m)		10.0
Ambient Temperature (°C)		20.0
<u>Vehicle Specific Parameters</u>	<u>Light Duty Testing</u>	<u>Heavy Duty Testing</u>
Venturi size (scfm)	762	2000
Residence time (s)	1.41	0.54
Gas Velocity (m/s)	7.10	18.63
Reynolds Number	120,177	315,425

While the exhaust density was adjusted for temperature, the values for such parameters as heat capacity, viscosity and thermal conductivity were set at those for air at standard

conditions. Table 34 presents the calculated potential core length, using the coaxial mixing model developed in Section 6.1.2.1 and the dilution ratio, based on the ratio of standard flow rates.

Table 33. Description of flow parameters in transfer pipe.

<u>Common Parameters</u>	<u>Value</u>			
Length of transfer pipe between vehicle and tunnel (m)	4.0			
<u>Vehicle Specific Parameters</u>	<u>Light Duty Cases</u>		<u>Heavy Duty Cases</u>	
	Case 1 0.65 km/h	Case 6 80 km/h	Case 1 0.65 km/h	Case 6 80 km/h
Pipe diameter (m)	0.10		0.127	
Flow rate (scfm)	13.02	34.86	327.7	332.6
Temperature (°C)	197	219	199	362
Gas Velocity (m/s)	0.81	2.27	20.50	27.28
Residence time (s)	4.93	1.76	0.20	0.15
Reynolds Number	125,663	335,897	3,159,630	3,126,961

Table 34. Dilution parameters for full range of operating parameters.

	<u>Light Duty Cases</u>		<u>Heavy Duty Cases</u>	
	Case 1 0.65 km/h	Case 6 80 km/h	Case 1 0.65 km/h	Case 6 80 km/h
Ratio of dilute exhaust to raw exhaust flow rates (scfm basis)	58.5	21.9	6.1	6.1
Potential core length (cm)	3.4	9.4	38.6	38.6
Potential core duration (s)	0.090	0.089	0.019	0.014

It can be seen that the potential core length is much longer for heavy duty testing conditions than it is for light duty testing conditions. The longer potential core for heavy-duty dilution means that there is a longer section of the dilution tunnel where the exhaust is not completely mixed with the dilution air. If the exhaust flow is at all deflected from the centreline during mixing, hot spots along the tunnel walls could occur. Thermophoretic losses (discussed in Section 3.1.4) could be exaggerated at these hot spots. In terms of the duration of the potential core, however, mixing occurs on a much shorter time frame in heavy duty testing compared to light duty testing, which reduces the probability that condensation will occur as a

result of tunnel cooling in heavy duty testing. Thus, it appears that the assumption that the exhaust is mixed instantaneously is valid.

Figure 74 shows the estimated dilution ratios, calculated by the standardised flow balance between the raw exhaust and dilute exhaust flow rates, in the dilution tunnel for the two theoretical vehicles over a range of operating speeds. Since the sampling equipment should simulate on-road dilution, it is desirable that the exhaust spend at least some time in the critical dilution ratio range so that the amount of condensed material is comparable to on-road emissions. It can be seen that, with the exception of light duty vehicle travelling at speeds below 10 km/h and the heavy-duty vehicles for speeds above 60 km/h, dilution ratios in the dilution tunnel are within the critical range of 5:1 - 50:1.

Although the implications of diluting the exhaust by a single step rather than a gradual dilution process are worth assessing in future studies, their evaluation is beyond the scope of this study. The next section evaluates how the exhaust cools in the dilution tunnel and compares it to the cooling that occurs during mixing in on-road dilution.

Figure 74. Estimated dilution ratios for exhaust in dilution tunnel at various speeds.

6.2.2 Temperature Modelling

Regulatory emissions testing of diesel vehicles dictates that the temperature in the primary mixing zone is a maximum of 190°C and that the peak filter face temperature does not exceed 52°C (Kittelson and Johnson, 1991). To determine whether the dilution tunnel is capable of meeting these criteria, a simple model was developed to estimate the exhaust temperature decrease from heat transfer to the tunnel walls and from mixing.

In the review of heat transfer, two limiting scenarios were considered. The first was where the walls of the tunnel were non-insulating. In this case, it is assumed that the wall temperature was approximately the same as the ambient air temperature. The temperature difference between the wall and the exhaust is a maximum at the upstream end of the tunnel/pipe and decreases along the length of the tunnel. The second limiting scenario assumed that the walls were partially insulating. In the partially insulated case, the temperature difference between the dilute exhaust and the tunnel wall is constant along the length of the tunnel. Schematics of these regimes are shown in Figure 75.

The exhaust cools more rapidly with the first scenario, since the temperature difference between the exhaust and the wall is consistently greater. To determine which of these scenarios best fit the actual heat transfer in the dilution tunnel, the outside temperature of the dilution tunnel was measured during vehicle testing at seven equally spaced intervals using an infrared temperature sensor. The results of this survey found that, with the exception of the section immediately downstream of the mixing point, temperatures were constant along the length of the tunnel at approximately 33 °C. The section of tunnel downstream of the mixing point was 37 °C. The higher temperature of the first section of the dilution tunnel could have been the result of conductive heat transfer from the transfer pipe. Unfortunately, it had not been possible to measure the temperature of the transfer pipe at the time.

Where:

T_o = Ambient air temperature (°C)

T_a = Gas temperature at the beginning of the pipe.

T_b = Gas temperature at the end of the pipe.

T_{wall} = Temperature of the tunnel/pipe wall.

ΔT_a = Temperature difference between wall and gas inside pipe at start of pipe (°C)

ΔT_b = Temperature difference between wall and gas inside pipe at end of pipe (°C)

ΔT_L = Logarithmic mean temperature difference between wall and gas inside pipe along length of pipe.

Figure 75. Limiting conditions for the modelling of exhaust cooling in the dilution tunnel.

Based on the temperature survey, it was assumed that the temperature of the walls of the pipe or dilution tunnel was constant along their respective length. The gas temperature decrease with distance downstream was determined using the following expression:

$$T_b = T_w + (T_a - T_w) \exp\left(\frac{h_i \pi D_j L_p}{c_p m}\right) \quad \text{Equation 12}$$

Where:

- T_a = Gas temperature at the beginning of the pipe (°C)
 - T_b = Gas temperature at the end of the pipe (°C)
 - T_w = Temperature of the wall (°C)
 - h_i = Convective heat transfer coefficient (W/m²°C)
 - D_j = Pipe diameter (m)
 - L_p = Length of pipe (m)
 - c_p = Heat capacity (Joules/kg·°C)
 - m = Mass flow rate (kg/s)
- (McCabe, Smith & Harriot, p. 338)

The values for the tunnel wall temperatures and heat transfer coefficients are shown in Table 35. The heat transfer coefficient was calculated by the Dittus-Boelter equation, presented in McCabe, Smith and Harriot (p. 341). The selected wall temperature of the dilution tunnel for heavy duty testing was based on the temperature measured on the outside of the tunnel wall during bus testing. The dilution tunnel wall temperature for light duty testing was rated down from the heavy-duty value based on the dilute exhaust temperatures for heavy duty and light duty testing relative to an ambient air temperature of 20 °C. The transfer pipe wall temperature for heavy duty testing was assumed to 144 °C, which is halfway between the average exhaust temperature and the ambient air temperature. For light duty vehicle testing, the transfer pipe was covered with an insulating blanket that was heated to 100°C. Thus, the temperature of the inside of the transfer pipe was assumed to be 153°C, which is halfway between the average light duty dilute exhaust temperature and 100 °C.

Table 35. Heat transfer coefficients for dilution tunnel, transfer pipe.

Dilution Tunnel	<i>Light Duty Testing</i>		<i>Heavy Duty Testing</i>	
Ambient Temperature	20		20	
Dilution Tunnel Wall Temperature (°C)	21.6		33	
Convective Heat Transfer Coefficient - h_i (W/m² °C)	7.25		31.05	
Transfer Pipe	Case 1 0.65 km/h	Case 6 80 km/h	Case 1 0.65 km/h	Case 6 80 km/h
Transfer Pipe Wall Temperature (°C)	153		144	
Heat Transfer Coefficient (W/m² °C)	4.0	8.9	53.4	53.0

One observes in the above flow parameters that the highest heat transfer coefficient occurs for heavy duty testing and that it is not particularly sensitive to vehicle speed.

In addition to cooling to the tunnel walls, we must also consider the substantial temperature reduction due to mixing of raw exhaust with dilution air. If we assume adiabatic conditions at the mixing point, the temperature of the exhaust gas after mixing with dilution air can be calculated using an energy balance relationship, shown in Equation 13.

$$T_x = \frac{T_{RAW}(\dot{m}_{RAW}) + T_D(\dot{m}_V - \dot{m}_{RAW})}{\dot{m}_V} \quad \text{Equation 13}$$

Where:

- T_x = Temperature after mixing (°C)
- T_{RAW} = Temperature of raw exhaust (°C)
- T_D = Temperature of dilution air (°C)
- $\dot{m}_{RAW}$ = Standardized flow rate of raw exhaust in transfer pipe (scfm)
- $\dot{m}_V$ = Standardized flow rate of dilution tunnel venturi (scfm)

Combining these expressions with the flow data for the dilution tunnel and transfer pipe and the vehicle exhaust data from the previous section, the temperature of the exhaust gas along the length of the transfer pipe and the dilution tunnel were calculated. Table 36 documents the temperature decay in the transfer pipe and the dilution tunnel for both a heavy-duty vehicle and a light-duty vehicle operating at high and low speeds. The data show that cooling

to the walls occurs predominantly in the transfer pipe. This is to be expected, given the larger temperature difference between the raw exhaust and the walls compared to the dilute exhaust to the walls.

Table 36. Exhaust temperature at key points in dilution tunnel for both vehicles at high and low speeds exhaust in dilution tunnel.

Stage	Temperature (°C)			
	LDV		HDV	
	0.65 km/ h	80 km/h	0.65 km/ h	80 km/h
Exhaust Exit	197	219	199	362
End of Transfer Pipe	178	195	185	306
After Mixing Point	23	28	47	67
Sampling Point	21	24	42	56

The heat transfer to the tunnel and pipe walls could lead to more condensation of species during mixing. Consider the discussion in Section 2.2.2, which noted that decreases in raw exhaust temperature result in a higher probability of condensation during the mixing process. From these results, it can be concluded that the condensation of volatile species may be exaggerated by cooling to the walls. The fact that much of the heat transfer occurs in the transfer pipe, which is upstream of the mixing point, means that higher degrees of condensation can be expected to occur in the dilution tunnel. The large temperature gradient between the exhaust and the walls of the transfer pipe can also lead to thermophoretic losses of PM sample, which will be discussed in Section 3.1.4.

Based on the results shown in Table 36, the dilution tunnel is capable of meeting the maximum mixing zone temperature limit but may not be capable of satisfying the filter face temperature limits for the heavy-duty vehicle at high speeds. It was assumed that the temperature of the dilute exhaust at the sampling point is approximately the same as the temperature of the sample at the face of the filter. It can be seen that for the most part, the dilute exhaust temperature is lower than the critical temperature for sampling particles except for the heavy-duty vehicle at speeds above approximately 50 km/hr.

To verify the cooling model, the estimated temperatures of the sampling point were compared to measured sampling point temperatures. Temperatures at the sampling station were measured during bus testing conducted in February 2000 using a thermocouple that was inserted into one of the sampling points. The dilute exhaust temperatures were found to be in the ranges shown in Table 37.

Table 37. Measured dilute exhaust temperature at sampling station for various cell temperatures.

Test Cell Temperature	Dilute Exhaust Temperature at Sampling station	
	High (°C)	Low (°C)
20°C	54.2	45.0
15°C	49.8	41.0
-10°C	25.0	8.0

These temperatures were measured during a CBD test, described in earlier in Section 3.1.2. The high temperature presented in the above table was the maximum temperature observed during an acceleration/deceleration cycle. These temperatures show reasonable agreement with the model shown in Table 36, which estimates an exhaust temperature between 42°C and 60°C for heavy-duty vehicles. It should be noted that any comparison between these results is tenuous, given that it is unknown whether the design parameters of the bus that was used for flow and temperature mapping were at all similar to the bus used to develop the estimated flow rates and temperatures.

Although it appears in Table 36 that temperatures at the sampling point are occasionally above the critical temperature, this does not necessarily mean that the filter face temperature will exceed the regulatory limit in transient testing. Recall that this cooling model only accounts for cooling up to the sampling point. It does not account for cooling through the sampling lines or the cyclone, which could be substantial. Thus it is expected that in most, if not all, cases, the dilution tunnel can be used for regulatory testing. Nevertheless, it is recommended that the filter face temperature be investigated more thoroughly to assess the acceptability of the dilution tunnel for performing high-speed steady state tests.

The concept of hot spots in the dilution tunnel warrants a discussion of the second assumption of uniform heat transfer in the cross section. In most cases, this assumption will be valid, provided the geometries of the transfer pipe and dilution tunnel are not excessively circuitous. Any bends or sharp corners can potentially result in recirculation regions where a portion of the flow separates from the streamlines. These separated flow regions result in a restricted region where particle deposition is more likely to occur. This was discussed earlier in Section 3.1.3.

To ensure that filter face temperatures remain below 52 °C, many laboratories use two-stage dilution to sample PM. The purpose of the secondary dilution tunnel is to increase the dilution of the exhaust to better simulate on-road dilution and to bring it to a level where the exhaust temperature is below the regulatory limit of 52°C. A typical two-stage dilution arrangement consists of a primary dilution tunnel with similar characteristics to the dilution tunnel discussed here. A fraction of the diluted exhaust is transferred to the secondary dilution tunnel and then sampled for analysis. Typical parameters for such an arrangement are presented in Table 38.

Table 38. Primary and secondary dilution values and typical residence times.
(Kittelson, 1998)

	Dilution Ratio Range	Residence at Primary Dilution
Primary	2 – 50	0.5 - 2 (s)
Secondary	2.5 – 200	0.5 - 3 (s)
Total	5 – 1000	

We have seen that a great deal of variability in dilution ratio and temperature can occur both between laboratories and within the same dilution tunnel between different tests. The remainder of this chapter will consider how these variabilities will affect the amount of PM that will be present in the dilution tunnel and where potential losses of PM can occur.

6.3 Comparison of Tunnel Cooling to On-Road Dilution

What remains to be done is to determine whether the exhaust is cooling at a comparable rate in the dilution tunnel compared to that which occurs during on-road dilution. Figure 76 and Figure 77 present the plots of exhaust temperature versus time for the dilution tunnel and for on-road dilution.

The performance of the dilution tunnel can be evaluated in two ways. One is to compare the exhaust temperatures of the two models at the time associated with the dilute exhaust reaching sampling the sampling point. This time has been annotated in the figures by a vertical dashed line and is referred to as “sampling time”. The second method is to determine how close the sampling time is to the time that the exhaust temperature has reached a state where PM conversion process have “frozen” according to the on-road dilution model. This “freeze point” has been identified as 1% of the original temperature spread between raw exhaust temperature and ambient temperature. The freeze point was calculated by the mixing model, presented in Section 2.2.2, and is identified as “freeze time” in each plot in Figures 76 and 77.

The following comparison must be considered with a substantial caveat. While temperature is a common measure between the two models, the methods used to determine temperature is substantially different between the two models. The calculated temperature for the on-road dilution model is calculated using a stochastic model that is used interchangeably for dilution ratio and temperature decay calculations. As a result, the “freeze time” where T_{mixed} is 1% of T_{ex} is also associated with a dilution ratio of 100. However, the temperature reduction model for the dilution tunnel was derived by a combination of an energy balance between the exhaust and the dilution air and a heat transfer model for the hot gases in the sample collection system. As long as future studies do not disprove these two methods of temperature estimation, the comparison is acceptable.

It can be seen that in all cases, the initial cooling in on-road dilution occurs more quickly than what occurs in the dilution tunnel. As the vehicle speed increases, the temperature at the sampling point increases. The comparison shows that, for light-duty vehicles, sampling

temperatures are cooler than the modelled temperature at low speeds and approach the modelled temperature as the vehicle speed increases. Conversely for heavy-duty vehicles, the sampling temperatures are similar to modelled temperatures at low speeds but diverge from the modelled temperature as the vehicle speed increases. It can thus be concluded that the sampling point temperature is generally cooler than on-road exhaust for light duty vehicles and hotter than on-road exhaust for heavy-duty vehicles.

The implications of these differences are difficult to determine. Based on the principles outlined earlier in Section 2.2, it would appear that the shorter time for initial cooling could result in less condensed species in on-road samples compared to PM samples collected from dilution tunnels. In comparing the freeze time to the sampling time, one observes that at low speeds, the freeze time is significantly longer than the sampling time for both vehicles. The reverse is true for high-speed operations. This could mean that at low speeds, the PM in the sample is being taken before it has fully evolved as it would in the on-road scenario. This is less problematic than the implications of the high speed scenario, where not only are the particles being sampled well after the freeze time, the window between freeze time and sampling time is being spent at high temperatures where particle conversion can continue to occur.

It can thus be inferred that sampling conducted during prolonged high speed operations may have higher SOF values because of the higher temperature at sampling time, leading to more conversions. It is also likely that light duty operations will be more greatly affected, since the freeze-time for light duty vehicles at high speeds occurs before the exhaust has even reached the mixing point in the dilution tunnel. This could be easily prevented through the modification of transfer pipe dimensions (i.e. shorter length and diameter) in order to reduce residence time.

Figure 76. Comparison of cooling in dilution tunnel to cooling from mixing for light-duty vehicles.

Figure 77. Comparison of cooling in dilution tunnel to cooling from mixing for heavy-duty vehicles.

6.4 Conclusions on Exhaust Dilution Processes and PM Sampling

In this chapter, a simulation of on-road dilution was developed and compared to a simulation of exhaust mixing and cooling in a dilution tunnel. A review of the on-road dilution model showed that the model approximated heavy-duty exhaust dilution fairly well but severely underestimated light-duty exhaust dilution.

The comparison of the on-road dilution model to the dilution tunnel simulation revealed that the commonly-used sampling system allows the exhaust to spend too much time in the transfer tunnel, where cooling to the tunnel walls can have a significant impact on SVOC condensation. This cooling could result in thermophoretic losses and potentially more condensed species in the PM than what is present in naturally mixed exhaust.

To reduce the degree of cooling to the walls of the transfer pipe, it has been suggested that dilution air be introduced at the vehicle exhaust exit point (Dolan and Kittelson, 1993). This pre-dilution method allows temperature and the concentration of condensable species to reduce concurrently and provides a better simulation of the mixing processes that occur in the atmosphere. A pre-dilution design, combined with heating the transfer pipe, is the most efficient method for reducing excessive condensation and thermophoretic losses.

An area that will certainly need to be assessed in future studies is the applicability of temperature and exhaust flow rates as the sole parameters used in estimating the degree of condensation of exhaust species. Keeping in mind the curves in Figure 9, one observes that the saturation at pipe exit is a key parameter in the likelihood of condensation. Unfortunately, exhaust temperature and flow rate do not provide a measure of saturation ratio and how it may vary with vehicle operation. This is an acceptable omission for spark ignition engines, where air-fuel ratios do not change considerably in the range operation. However, the same cannot be said for compression ignition engines.

A review of estimated fuel flow rates over the length of the heavy-duty cycle was performed since the study was completed. The data show that dilution ratios do not vary significantly with steady state speed. However, the estimated HC concentrations in the raw exhaust are

1.5 ppm at low speed of 20 mph and increase to approximately 4.8 ppm at the high speed of 40 mph. If this three-fold increase in raw hydrocarbon concentration is considered analogous to the effect of speed on saturation ratio, then it can be expected that more condensation will occur at high speeds both on the road and in the dilution tunnel. Thus, it is suggested that better estimates of SVOC condensation could be made through the inclusion of fuel flow in the dilution modelling of compression-ignition engines.

Chapter 7 Conclusions

This study has evaluated the conditions that affect the characteristics of $PM_{2.5}$ emitted from on-road vehicles. Emissions testing was conducted to assess the effects of driving behaviour and fuel composition on $PM_{2.5}$ emissions from two motorcycles and the effect of ambient temperature and exhaust aftertreatment on $PM_{2.5}$ emissions from an urban bus. The effect of dilution history on $PM_{2.5}$ was estimated by developing an on-road exhaust dilution model and comparing it to the estimated dilution profiles in the dilution tunnel.

Emissions testing and exhaust dilution modelling are linked by the dependence of the organic fraction of PM on the time spent at dilution ratios conducive to condensation. It has been estimated that much of the organic fraction of PM from on-road vehicles is formed during dilution through the range of 5:1 to 50:1. The path by which exhaust dilutes in the dilution tunnel should simulate the path by which it will dilute in the on-road case. Where it does not, efforts should be made to characterize the differences and to estimate what ramifications these differences will have on the measured PM emission rates and composition.

The significant conclusions of the study can be summarized as follows:

1. The uncertainties associated with gravimetric determination of $PM_{2.5}$ mass emission rates are much higher for motorcycles (5-81% RSD) with emission rates on the order of mg/mile than the mass emission rates for buses (8-10% RSD), which were on the order of g/mile. Uncertainties associated with $PM_{2.5}$ emissions from motorcycles were also higher than the respective emission rates for regulated gaseous pollutants (0-21% RSD for motorcycles; 1-20% RSD for buses). The high uncertainties of motorcycle PM rates are directly related to the small mass of filter sample collected from motorcycles during

standard test cycles. The small amount of sample collected on the filters also resulted in insufficient material being available for trace metal analysis and detailed organics analysis and suggests that an alternative methodology should be considered for these cases.

2. Statistical analysis of FTP PM_{2.5} mass emissions revealed that there was not a significant difference in PM_{2.5} emission rates between a Cold-Start LA4 cycle and a Hot-Start LA4 cycle. Compared to FTP composite emissions, both NYCC and US06 cycle are associated with higher mass emission rates with a significance level of 0.05 for both motorcycles. PM_{2.5} emission rates were significantly different between NYCC and US06 tests for the Honda but not for the Suzuki. The highest emission rates were consistently associated with the US06 cycle.
3. The organic and elemental carbon (OC and EC) emission rates determined by Thermal/Optical Transmittance (TOT) method on quartz filters were generally higher than the total mass emission rates determined gravimetrically from Teflon filters. This is attributed to the adsorption of gaseous OC on the quartz filter. It was found that this adsorbed OC can be better estimated by measuring the carbon collected on a quartz filter placed downstream of a Teflon filter, rather than the carbon collected on a second quartz filter placed downstream of the quartz filter used collecting PM-bound carbon.
4. OC/EC analysis of the collected PM from emissions testing of motorcycles exhibited much higher scatter than the bus testing results. Much of the scatter is explained by the small amount of sample collected on the filters during motorcycle testing. One eighth of the dilute exhaust samples for organic carbon were invalidated by over-correction of the positive artefact (gaseous carbon material that adheres to the filter medium). Only one third of elemental carbon samples were valid, which was attributed to emission rates being too close to the detectable limits of the measurement. By contrast, bus testing results were much more reliable and none of the filter samples were invalidated.

5. Measurements of the detailed ion content of $PM_{2.5}$ exhibited a high scatter that was also attributed to the paucity of sample collected. Total ion emission rates showed a better correlation with fuel consumption than they did with $PM_{2.5}$ mass emission rates.
6. The effect of low-sulphur fuel on $PM_{2.5}$ mass emission rates for motorcycles was not statistically significant. However, due to differences in the fuel composition (i.e. more MMT and less sulphur in low-sulphur fuel), emission rates of manganese ion were consistently higher and SO_2 emission rates were consistently lower when operating with low-sulphur fuel.
7. The measured gaseous SO_2 and PM bound SO_4 accounted for only 30% of the sulphur in the SGC fuel and 15% of the sulphur in the low-sulphur fuel. This discrepancy was attributed to 1) bypass of SO_2 on the filter and 2) sulphur species that escaped detection.
8. The measured manganese ion content of motorcycle PM accounted for 30-75% of the manganese in the fuel, with good coefficients of correlation observed ($R^2 \approx 0.70$) between manganese consumption rates and manganese ion emission rates when data were divided between the two vehicles. Based on other observations by ERMD that approximately half the PM manganese is in ionic form, the manganese accounting is much better than the sulphur accounting.
9. An oxidative catalytic converter on the urban bus reduced $PM_{2.5}$ mass emission rates by 60% at both temperatures. Use of the catalyst also resulted in a decrease in organic carbon portion of the PM and an increase in the elemental carbon portion. At colder temperatures, $PM_{2.5}$ mass emission rates were reduced, although it was only significant when operating without the catalyst. It was inferred that the catalyst was less effective at cold temperatures.
10. Measured mass emission rates were compared to the U.S. EPA emissions model, PART5. $PM_{2.5}$ emission rates were similar for both motorcycle and average bus emission rates. However, it was found that sulphate emission rates were two orders of magnitude higher in PART5 compared to both the measured sulphate emission rates in motorcycle testing

and sulphate emission rates observed in the literature. In addition to the oversights discussed above, a review of the model reveals that the output exhibits no dependence on temperature, altitude or vehicle deterioration.

11. Evaluation of the dilution model developed in this study indicates that the time for exhaust to dilute through the 5-50:1 range varies from 0.1 - 0.2 seconds at 80 km/h to 20-30 seconds at idle. Comparisons to measured dilution profiles indicate that the dilution model simulates heavy-duty and light-duty exhaust dilution at high speed quite well but severely underestimates dilution at low speeds for the light duty vehicle. This underestimation was attributed to the failure of the model to account for the strong velocity gradient between the air close to the ground and the vehicle wake. It was also observed that the dilution model has limited applicability at extended distances from the exhaust pipe due to the high variability in the eddies associated with the vehicle wake.
12. The dilution model was compared to estimated temperature profiles for the exhaust sampling system used at ERMD. An important difference is that while the dilution ratio increases gradually from one towards infinity during on-road dilution, the dilution process in the laboratory is a one- or two-step process. Another potential limitation is that the relationship between vehicle speed and dilution rate is reversed in the tunnel compared to on-road dilution.

The comparison of the on-road model to the dilution tunnel model indicates that at low speeds, the time from exhaust exit to sampling in the dilution tunnel is much shorter than the time for the exhaust to reach ambient conditions in the on-road scenario. At high speeds, the exhaust is being sampled at a time well after the exhaust would reach ambient temperatures. The largest discrepancy between on-road dilution and mixing in the tunnel is for light duty vehicle at high speeds, where the exhaust spends too much time in the transfer pipe.

13. This study estimated the likelihood of SVOC condensation in the dilution tunnel through the analysis of engine air intake rates and exhaust temperatures versus speed data. These two parameters may not be sufficient to properly estimate condensation for compression ignition engines. Data from ERMD shows that while the degree of dilution (as measured by exhaust flow rate) changes by only 2-3% over the considered speed range, hydrocarbon concentrations are estimated to have a threefold increase over the same range. As a result, peak saturation ratios at the mixing stage are also expected to vary greatly with speed.

Recommendations

The major recommendation of this study is that elements of the dilution tunnel should be modified for the future PM sampling of light duty vehicle and motorcycle emissions. Presently, the PM concentrations in the dilute exhaust are so low that insufficient material is being collected on the filters.

Cheap and easy options for improving the amount of material collected include increasing the sampling flow rate, increasing the dilute exhaust concentration by reducing the venturi flow rate, and increasing sampling time by using more repeats. Unfortunately, all of these solutions have potential limitations. Increasing the sampling flow rate could increase gas partitioning of organic material adhered to the PM, increasing the negative artefact associated with carbonaceous PM. Unless the sampling equipment is adjusted, decreasing the dilution tunnel flow rate would increase the difference between sampling velocity and tunnel velocity. In addition, the slower flow rate in the tunnel could enhance particle deposition by increasing the residence time in the dilution tunnel or result in more condensed species due to reduced dilution of raw exhaust.

Increasing the testing time may be the best option of these three, since sampling considerations are not being modified. However, there may be issues associated with particles on the filter ageing due to extended exposure to sampling and the cost of extended testing may be greater than the benefit of collecting more sample.

The more expensive but technically sounder solution is to design a smaller dilution tunnel. Producing a tunnel that is tailored to light duty emissions would allow for meeting the demands of acceptable dilution ratio and tunnel residence time as well as isokinetic sampling. Certainly, if PM emissions become more strictly regulated and exhaust flow rates decrease with improved engine efficiency, this last option may be the most attractive.

A second recommendation is that the testing methodology should be reevaluated to reduce the potential of particle loss in the transfer pipe and dilution tunnel and to ensure that filter face temperatures are meeting criteria for regulatory testing. Particle loss leads to differences in PM composition compared to on-road conditions, potentially reduces the amount of collected material and limits the applicability of accounting for fuel and oil components in the PM. The potential for PM loss in the sampling system was greatest during light-duty testing. The effect of the transfer pipe on PM losses could be reduced through the judicious selection of transfer pipe dimensions. In particular, care should be made to limit residence time in the transfer pipe to as short as possible.

There are three main considerations in the testing methodology that should be evaluated. First, the raw exhaust inlet in the dilution tunnel is not insulated over the last two and a half feet of its length. Second, the dilution air is ducted into the tunnel at a T-junction, directing large amounts of cool air across this last length of pipe. These first two considerations result in strong cooling conditions, which could lead to thermophoretic losses and/or condensation of SVOCs into particles. The fact that dilution air is introduced at a T-junction may also lead to separated flow downstream of the edge of the junction, which may result in incomplete initial mixing of the exhaust across the cross section of the tunnel. Options should be considered for either insulating the exhaust inlet or shortening it to reduce its exposure to cool air.

The third element of the testing methodology that should be examined is the sampling inlet during light duty sampling. While the sampling probes are drawing air almost isokinetically in heavy-duty testing, the sampling velocity is almost three times the speed of tunnel velocity

during light duty testing. At the cut diameter of $2.5\ \mu\text{m}$, this discrepancy results in aspiration efficiencies of 82 percent.

The effect of these elements on exhaust collection and sampling should be more thoroughly reviewed. The dilution model used in this study relied on rudimentary tools developed in the middle of this century. These tools have since been developed into very sophisticated models, such as computational fluid dynamics. The application of fluid dynamics to the considerations presented here may provide some enlightening insights into areas of concern and opportunities for improving sampling efficiency. Some of the key areas that need to be addressed in future models include improved estimation of on-road dilution for light-duty vehicles at low to moderate speeds, detailed evaluation of the flows at the mixing point of the dilution tunnel, and the development of better indicators for the probability of condensation, particularly for heavy-duty exhaust mixing in the dilution tunnel.

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APPENDIX A: EMISSIONS RATE CALCULATION.

This section elaborates on the methods for collecting gaseous and PM emission rates and how emission rates are collected. Figure 78 illustrates the sampling and analysis procedures for the complete suite of gaseous emissions collected from a vehicle. The exhaust is collected in a constant volume sampling system, which ensures that a constant flow rate of diluted exhaust is flowing past the sampling probes for the duration of the test. The concentration of a pollutant in the dilution tunnel averaged over the duration of the test is thus proportional to the total mass of pollutant emitted.

Samples for regulated emissions (carbon monoxide (CO), nitrogen oxides (NO_x), total hydrocarbons) and CO₂ and speciated hydrocarbons are collected in non-reactive Tedlar bags during the length of the driving cycle. Carbonyl species can be sampled using a DNPH charged cartridge. PM samples are collected on Teflon filters and other filter media depending on chemical analysis performed. A separate sample of dilution air is collected during the sampling run.

At the end of the driving cycle, samples are drawn from the bags for chemical analysis. CO and CO₂ are analysed using non-dispersive infrared adsorption, NO_x are determined by chemiluminescence and THC by flame ionisation analysers. Methane is determined by gas chromatography using flame ionisation detection. The time to complete these analyses is between five and ten minutes. The results of these chemical analyses are gas concentrations in ppmv (% for CO₂) by volume. The concentrations are converted to mass concentrations by applying the molecular weights of the analyte and air.

For gravimetric PM determination, the filter is equilibrated for a period of 24 hours, after which it is weighed using a gravimetric balance. For chemical determination, the material collected by a filter, cartridge or denuder, the material is extracted from the media then detected by the prescribed analytical method. The amount of the material extracted and

detected on the filter is then divided by the amount of air that flowed through the sampling medium to determine the sample concentration, generally expressed as g/L.

Equipped with these concentrations, the total emission for the duration of the test can be determined using the following relationship:

$$GPP = V_a \left[C_a - \left(1 - \frac{1}{DF} \right) C_a \right] \quad , \text{Where} \quad \text{Equation 14}$$

GPP = Grams per phase of pollutant

VE = Volume of dilute exhaust, L

C_E = Concentration of Dilute Exhaust (g/L)

C_A = Concentration of Ambient Air (g/L)

DF = Dilution Factor

The dilution factor, outlined above, is the factor by which the raw exhaust has diluted in the air. It is calculated by comparing the concentration of carbon species expected in the raw exhaust (assuming stoichiometric combustion) to the observed concentration of these species in the diluted exhaust. The dilution factor is calculated using the following equation, provided in CFR 86.1342-90 (U.S. EPA, 1999b), determines the dilution ratio for a carbonaceous fuel with the composition ($C_xH_yO_z$):

$$DF_{\text{fuel } C_xH_yO_z} = \frac{100 \times \left(\frac{x}{x + y/2 + 3.76 \times (x + y/4 - z/2)} \right)}{CO_{2e} + (HC_e + CO_e + C_{\text{alcohol}} + C_{\text{carbonyl}}) \times 10^{-4}} \quad \text{Equation 15}$$

, Where: x, y & z = co-efficients of carbon, hydrogen and oxygen in the fuel.

CO_{2e} = The dilute exhaust concentration of carbon dioxide (% vol)

HC_e = Dilute exhaust concentration of total hydrocarbons (ppmv_c)

CO_e = Dilute exhaust concentration of carbon monoxide (ppmv)

C_{alcohol} = Dilute exhaust concentration of alcohol (ppmv)

C_{carbonyl} = Dilute exhaust concentration of carbonyls (ppm_c)

To determine the emission rate in grams per mile, the emission rate in grams per phase (GPP) is divided by the distance travelled on the dynamometer during the emissions test.

Figure 78. Schematic of the sampling and analysis of gaseous emissions using CVS emissions testing. (EPA, 2000)

APPENDIX B: GASEOUS EMISSION RATES FOR MOTORCYCLES AND BUSES

The results from motorcycle testing are drawn from the ERMD report #99-68: "On-Road Motorcycle Emissions - Characterisation of Particulate Matter and Gaseous Emissions". (Welburn and Graham, 2000)

Table 39. 4-Phase FTP, US06 x 3, and NYCC x 3 gaseous emission rates (g/mile) and fuel economy (MPG) for Suzuki running on Ottawa SGC (average of two tests).

Parameter	Phase 1	Phase 2	Phase 3	Phase 4	4-Phase FTP	US-06 x 3	NYCC x 3
CO	10.96	15.09	8.48	16.86	12.95	7.06	25.91
%RSD	7.20%	3.31%	3.31%	3.81%	1.22%	20.92%	2.20%
CO₂	181.18	203.39	172.15	196.41	188.19	171.94	331.95
%RSD	1.4%	4.5%	4.5%	0.4%	1.7%	1.1%	2.5%
NO_x	0.33	0.20	0.36	0.20	0.27	0.78	0.38
%RSD	10.4%	4.6%	4.6%	1.0%	1.7%	4.8%	30.8%
THC	3.23	3.07	2.15	2.80	2.77	1.76	4.20
%RSD	2.7%	8.2%	8.2%	4.5%	5.4%	5.3%	26.8%
NMHC	3.15	2.99	2.10	2.71	2.70	1.76	4.20
%RSD	2.4%	8.4%	8.4%	4.6%	5.6%	5.3%	26.8%
CH₄	82.97	88.95	53.68	96.37	80.24	42.19	142.93
%RSD	11.7%	1.8%	1.1%	6.4%	0.4%	15.5%	1.9%
Fuel Economy	52.17	45.98	56.62	46.96	50.09	56.87	27.62
%RSD	1.9%	3.8%	3.8%	0.4%	1.4%	2.3%	1.1%

Table 40. 4-Phase FTP gaseous emission rates (g/mile) and fuel economy (MPG) for Suzuki running on Scotford Low Sulphur fuel (average of two tests).

Parameter	Phase 1	Phase 2	Phase 3	Phase 4	4-Phase FTP	US-06 x 3	NYCC x 3
CO	10.41	16.05	8.62	15.63	12.72	7.52	23.05
%RSD	0.12%	12.83%	12.83%	0.20%	5.39%	18.45%	3.25%
CO ₂	176.21	197.37	162.68	189.08	181.03	169.53	306.88
%RSD	3.5%	0.6%	0.6%	0.6%	1.2%	3.8%	2.5%
NO _x	0.35	0.19	0.36	0.21	0.28	0.81	0.47
%RSD	1.8%	8.5%	8.5%	0.8%	1.9%	11.1%	0.5%
THC	2.95	3.49	2.42	2.97	2.93	1.94	5.75
%RSD	0.0%	4.1%	4.1%	1.9%	3.8%	6.6%	3.1%
NMHC	2.89	3.39	2.37	2.89	2.86	1.94	5.75
%RSD	0.4%	4.1%	4.1%	1.8%	4.0%	6.6%	0.0%
CH ₄	65.11	111.65	53.86	89.26	79.54	42.54	130.58
%RSD	16.7%	4.0%	2.7%	5.3%	2.9%	14.5%	3.5%
Fuel Economy	52.30	45.16	57.41	47.35	50.19	55.10	28.54
%RSD	3.0%	1.7%	1.7%	0.5%	1.3%	3.9%	0.0%

Table 41. 4-Phase FTP, US06 x 3, and NYCC x 3 gaseous emission rates (g/mile) and fuel economy (MPG) for Honda running on Ottawa SGC (average of two tests).

Parameter	Phase 1	Phase 2	Phase 3	Phase 4	4-Phase FTP	US-06 x 3	NYCC x 3
CO	14.43	20.18	12.00	16.79	15.74	17.78	22.36
%RSD	1.35%	1.01%	1.01%	2.92%	0.14%	3.73%	3.82%
CO ₂	137.53	130.25	128.75	131.90	131.82	135.46	202.50
%RSD	0.1%	1.5%	1.5%	0.0%	0.5%	1.0%	3.1%
NO _x	0.39	0.17	0.38	0.20	0.28	0.54	0.42
%RSD	0.2%	1.9%	1.9%	3.9%	1.3%	5.1%	4.5%
THC	3.13	3.92	2.57	4.01	3.41	1.88	7.58
%RSD	1.8%	1.6%	1.6%	0.2%	2.6%	0.1%	1.8%
NMHC	3.04	3.82	2.51	3.92	3.33	1.88	7.58
%RSD	1.8%	1.6%	1.6%	0.2%	2.6%	0.1%	1.8%
CH ₄	98.66	109.05	64.89	92.06	89.75	66.67	124.14
%RSD	1.1%	2.7%	1.0%	1.2%	1.5%	3.2%	5.3%
Fuel Economy	64.01	62.42	69.96	63.67	65.06	63.62	40.93
%RSD	0.1%	1.5%	1.5%	0.4%	0.5%	0.1%	3.0%

Table 42. 4-Phase FTP gaseous emission rates (g/mile) and fuel economy (MPG) for Honda running on Scotford Low Sulphur fuel (average of two tests).

Parameter	Phase 1	Phase 2	Phase 3	Phase 4	4-Phase FTP	US-06 x 3	NYCC x 3
CO	12.34	12.16	9.77	10.95	11.19	17.74	16.52
%RSD	1.95%	1.63%	1.63%	0.38%	0.39%	1.49%	3.64%
CO₂	142.37	131.80	134.15	139.52	136.91	130.34	217.54
%RSD	5.7%	1.0%	1.0%	5.0%	4.4%	3.7%	6.7%
NO_x	0.39	0.18	0.38	0.19	0.28	0.52	0.37
%RSD	1.7%	3.2%	3.2%	1.5%	0.3%	2.3%	0.7%
THC	3.24	4.30	2.78	4.23	3.64	1.94	8.64
%RSD	0.4%	5.1%	5.1%	4.1%	3.7%	1.7%	2.9%
NMHC	3.16	4.22	2.73	4.17	3.58	1.94	8.64
%RSD	0.6%	5.1%	5.1%	4.3%	3.8%	1.7%	2.9%
CH₄	86.93	78.36	57.70	70.61	72.18	62.79	107.98
%RSD	6.8%	4.1%	3.7%	2.3%	1.2%	0.7%	7.2%
Fuel Economy	61.49	64.18	66.80	62.15	63.66	63.65	38.37
%RSD	4.5%	1.4%	1.4%	4.0%	3.3%	3.4%	4.4%

Figure 79. Comparison of 4-Phase FTP emissions for Honda and Suzuki operating on SGC and Scotford Low Sulphur fuels.

Figure 80. Comparison of FTP composite, US06 x 3 and NYCC x 3 gaseous emissions for Honda and Suzuki operating on SGC and Scotford Low Sulphur fuels.

Table 43. Regulated emissions rates for bus testing (average of four tests).

	Warm Baseline	Cold Baseline	Warm Catalyst	Cold Catalyst
NO_x	26.9	27.3	20.2	25.3
%RSD	2%	1%	4%	13%
CO	7.6	6.4	7.9	5.2
%RSD	9%	4%	4%	20%
THC	2.6	2.7	1.9	2.7
%RSD	3%	2%	2%	2%
NMHC	2.7	2.7	1.9	2.7
%RSD	5%	1%	8%	0.2%
CO₂	2787.4	2713.7	2733.9	2712.0
%RSD	2%	3%	0.2%	3%
CH₄	0.0032	0.0000	0.0052	0.0046
%RSD	141%	0%	11%	76%

Figure 81. Graphic representation of CBD gaseous emissions for bus testing (average of four tests).

APPENDIX C - DETAILED ORGANICS ANALYSIS

Table 44. Hydrocarbon emission rates (mg/ mile) for Suzuki operating on SGC fuel.

Hydrocarbon	Suzuki - SGC					
	4-PHASE COMP		US06 x 3		NYCC x 3	
	Avg	RSD	Avg	RSD	Avg	RSD
methane	80.24	0.4%	42.19	15.5%	142.93	1.9%
ethylene	198.72	0.3%	150.41	3.2%	364.68	1.3%
acetylene	102.34	0.5%	58.26	5.2%	184.70	2.0%
ethane	29.99	0.7%	17.32	5.4%	57.72	4.5%
propylene	94.64	0.4%	77.85	6.3%	183.76	2.6%
isobutene/ 1-butene	35.70	1.4%	28.64	9.6%	70.47	2.3%
1,3-butadiene	16.36	0.8%	9.98	15.2%	31.23	3.7%
n-butane	47.79	7.9%	29.02	5.1%	90.62	3.8%
2m-butane	113.30	7.2%	68.93	5.3%	210.74	5.1%
n-pentane	76.28	7.2%	46.88	6.4%	140.74	5.6%
2m-pentane	78.39	5.7%	47.89	7.7%	148.31	4.3%
3m-pentane	47.87	5.6%	29.17	8.4%	90.68	4.2%
n-hexane	44.32	4.9%	27.21	8.9%	82.22	4.4%
m-cyclopentane	24.59	5.5%	15.16	8.2%	46.56	4.5%
benzene	55.27	0.0%	36.96	7.5%	105.38	7.7%
2m-hexane	24.37	4.5%	15.08	3.5%	48.17	2.9%
3m-hexane	27.30	5.1%	16.91	3.6%	53.34	5.1%
n-heptane	26.46	5.1%	16.43	2.2%	51.31	6.8%
toluene/ 2,3,3-trimethylpentane	161.29	3.0%	118.72	11.1%	310.76	12.0%
o-benzene	50.38	1.3%	38.57	6.0%	95.33	10.3%
m&p-xylene/ 2,3-dimethylheptane	163.83	0.0%	125.24	5.2%	310.03	9.7%
o-xylene	65.31	0.5%	49.91	2.7%	124.31	7.6%
3-methyltoluene	38.41	4.6%	31.20	3.0%	69.99	9.0%
1,3,5-trimethylbenzene	21.84	5.3%	16.68	1.3%	41.85	8.4%
2-methyltoluene	18.00	3.8%	14.29	2.6%	34.65	7.5%
1,2,4-trimethylbenzene/ 1-decene	55.67	6.8%	43.69	4.4%	106.29	8.2%
Sum of List	1785.78		1239.19		3362.95	
Total NMHC Rate	2697.63		1489.8		4079.10	
% accounted for	66%		83%		82%	

Table 45. Hydrocarbon emission rates (mg/ mile) for Suzuki operating on Scotford low sulphur fuel.

Hydrocarbon	Suzuki Lo-S					
	4-PHASE COMP		US06 x 3		NYCC x 3	
	Avg	RSD	Avg	RSD	Avg	RSD
methane	79.54	2.9%	42.54	14.5%	130.58	3.5%
ethylene	205.74	2.1%	158.95	5.1%	354.10	2.6%
acetylene	98.91	1.3%	55.73	1.3%	160.92	1.2%
ethane	28.47	2.4%	15.97	9.0%	53.71	2.2%
propylene	104.64	5.3%	88.44	10.3%	194.14	3.2%
isobutene/1-butene	31.34	0.7%	27.40	11.8%	59.72	4.0%
1,3-butadiene	11.29	0.1%	7.58	6.2%	21.29	2.8%
n-butane	90.23	4.1%	55.56	1.2%	183.75	8.2%
2m-butane	249.36	4.3%	159.15	4.6%	497.07	5.0%
n-pentane	129.23	4.3%	83.16	4.6%	255.20	5.9%
2m-pentane	127.05	5.8%	81.75	6.6%	256.04	2.7%
3m-pentane	76.74	5.8%	49.36	6.5%	155.07	2.4%
n-hexane	72.31	5.8%	47.11	6.4%	142.68	3.0%
m-cyclopentane	46.52	5.4%	30.06	5.9%	94.23	3.6%
benzene	38.77	3.0%	25.46	5.1%	67.71	5.8%
2m-hexane	20.87	3.9%	13.02	5.6%	42.87	4.9%
3m-hexane	23.59	3.7%	14.72	5.6%	48.51	4.5%
n-heptane	19.92	3.3%	12.55	4.6%	40.20	6.4%
toluene/2,3,3-trimethyl-pentane	67.33	1.2%	46.77	3.3%	126.17	10.1%
o-benzene	55.44	0.4%	40.99	3.3%	108.08	8.8%
m&p-xylene/2,3-dimethyl-heptane	217.22	1.2%	161.30	3.2%	425.88	8.0%
o-xylene	101.92	1.5%	75.87	4.5%	201.51	6.7%
3e-toluene	48.17	2.2%	36.95	3.9%	91.29	8.6%
1,3,5-trimethyl-benzene	24.30	3.6%	18.25	3.6%	49.56	6.3%
2e-toluene	18.40	4.2%	14.19	4.1%	37.92	6.3%
1,2,4-trimethyl-benzene/1-decene	67.88	5.4%	53.42	3.0%	140.86	4.7%
Sum of List	2181.40		1510.38		4190.12	
Total NMHC Rate	2859.59		1623.63		4553.08	
% accounted for	76%		93%		92%	

Table 46 Hydrocarbon emission rates (mg/mile) for Honda operating on SGC

Hydrocarbon	Honda- SGC					
	4-PHASE COMP		US06 x 3		NYCC x 3	
	Avg	RSD	Avg	RSD	Avg	RSD
methane	89.75	1.5%	66.67	1.1%	124.14	5.3%
ethylene	213.18	2.8%	147.88	4.1%	332.94	2.0%
acetylene	118.03	3.0%	72.76	2.8%	171.15	5.3%
ethane	39.89	1.6%	26.01	13.6%	62.24	0.9%
propylene	102.57	2.1%	74.42	289.0%	175.06	1.2%
isobutene/ 1-butene	37.62	4.6%	25.90		74.17	6.4%
1,3-butadiene	21.07	5.2%	11.13		35.14	5.5%
n-butane	52.34	8.7%	26.38		141.00	3.7%
2m-butane	136.11	1.9%	65.31	0.0%	353.18	5.2%
n-pentane	93.63	3.8%	45.20	0.0%	243.85	5.1%
2m-pentane	96.00	2.5%	46.02	0.0%	249.37	3.0%
3m-pentane	58.65	2.4%	28.07	0.0%	152.69	3.0%
n-hexane	55.52	0.7%	26.48	0.0%	142.12	6.1%
m-cyclopentane	30.54	2.1%	14.81	0.0%	78.46	2.9%
benzene	65.77	2.7%	38.46	0.0%	121.01	15.8%
2m-hexane	29.67	1.2%	14.20	0.0%	74.19	4.3%
3m-hexane	32.27	1.4%	15.40	0.0%	83.32	4.1%
n-heptane	31.50	2.1%	14.98	0.0%	80.10	5.7%
toluene/ 2,3,3-trim-pentane	190.86	2.5%	107.96	0.0%	419.10	16.2%
e-benzene	61.62	4.6%	32.55	0.0%	137.18	10.9%
m&p-xylene/ 2,3-dim-heptane	205.63	4.9%	110.46	0.0%	450.76	9.4%
o-xylene	81.23	4.2%	42.76	0.0%	179.48	6.8%
3e-toluene	51.62	5.8%	27.38	0.0%	114.40	5.7%
1,3,5-trim-benzene	28.29	1.2%	13.93	0.0%	62.78	6.9%
2e-toluene	23.19	0.1%	11.73	0.0%	51.06	7.7%
1,2,4-trim&tb-benzene/ 1-decene	72.11	0.9%	36.20	0.0%	153.72	6.3%
Sum of List	1785.78		1239.19		3362.95	
Total NMHC Rate	2697.63		1489.8		4079.10	
% accounted for	66%		83%		82%	

Table 47. Hydrocarbon emission rates (mg/mile) for Honda tests conducted on Scotford low-sulphur fuel.

Hydrocarbon	Suzuki Lo-S					
	4-PHASE COMP		US06 x 3		NYCC x 3	
	Avg	RSD	Avg	RSD	Avg	RSD
methane	72.18	1.2%	62.79	0.7%	107.98	7.2%
ethylene	191.82	1.0%	139.96	0.7%	311.43	5.1%
acetylene	98.02	1.7%	67.50	2.4%	152.20	4.1%
ethane	32.37	1.9%	22.01	0.2%	56.11	2.6%
propylene	102.37	0.9%	75.45	0.9%	180.07	1.3%
isobutene/ 1-butene	30.02	1.0%	21.84	0.8%	56.52	6.2%
1,3-butadiene	13.57	0.7%	8.66	1.3%	23.41	5.4%
n-butane	106.40	1.4%	52.76	2.1%	269.84	6.2%
2m-butane	321.37	2.5%	152.90	1.9%	825.98	5.6%
n-pentane	167.94	2.7%	80.48	1.5%	437.92	6.7%
2m-pentane	166.36	4.1%	78.62	0.3%	450.60	3.6%
3m-pentane	100.46	4.2%	47.34	0.2%	273.30	3.4%
n-hexane	96.60	4.7%	46.37	0.7%	263.27	3.9%
m-cyclopentane	61.51	4.3%	29.69	0.9%	168.11	4.0%
benzene	41.58	1.5%	29.06	3.0%	78.18	11.7%
2m-hexane	13.79	139.5%	12.83	0.1%	74.46	4.5%
3m-hexane	20.47	72.5%	14.47	0.1%	84.06	4.4%
n-heptane	25.73	3.5%	12.69	0.1%	71.11	5.4%
toluene/ 2,3,3-trim-pentane	82.66	0.4%	58.71	0.1%	185.11	12.9%
e-benzene	68.89	2.8%	40.49	1.9%	175.46	11.5%
m&p-xylene/ 2,3-dim-heptane	276.29	3.1%	166.82	1.0%	697.10	10.3%
o-xylene	129.28	3.4%	75.40	0.3%	328.16	8.8%
3e-toluene	62.65	2.2%	36.53	0.4%	155.52	10.6%
1,3,5-trim-benzene	31.99	2.6%	18.25	0.1%	80.84	8.9%
2e-toluene	24.17	3.4%	13.73	0.8%	60.35	9.5%
1,2,4-trim&tb-benzene/ 1-decene	90.96	4.2%	52.83	1.0%	228.50	10.4%
Sum of List	2181.40		1510.38		4190.12	
Total NMHC Rate	2859.59		1623.63		4553.08	
% accounted for	76%		93%		92%	

Table 48. Carbonyl emission rates (mg/mile) for all Suzuki operating on SGC.

Carbonyl	Suzuki - SGC					
	4-PHASE COMP		US06 x 3		NYCC x 3	
	Avg	RSD	Avg	RSD	Avg	RSD
Formaldehyde	90.94	11%	458.84	10%	1252.42	7%
Acetaldehyde	19.44	13%	122.79	9%	373.75	9%
Acrolein	6.78	13%	53.76	41%	121.81	12%
Acetone	6.86	12%	30.02	7%	111.67	9%
Methacrolein	3.90	17%	22.13	11%	54.24	13%
Benzaldehyde	13.81	5%	98.08	7%	222.99	14%
o-Tolualdehyde	3.63	9%	29.63	4%	75.08	22%
m&p-Tolualdehyde	12.97	12%	99.84	9%	274.56	15%
Sum of List	158		915		2487	
Total Carbonyl Rate	171		1001		2716	
% Accounted For	92%		91%		92%	

Table 49. Carbonyl emission rates (mg/mile) for all Suzuki operating on Scotford low-sulphur.

Carbonyl	Suzuki Lo-S					
	4-PHASE COMP		US06 x 3		NYCC x 3	
	Avg	RSD	Avg	RSD	Avg	RSD
Formaldehyde	95.46	0%	730.10	12%	1312.36	2%
Acetaldehyde	19.17	1%	189.76	16%	382.53	4%
Acrolein	5.25	19%	93.86	13%	108.81	16%
Acetone	5.06	7%	29.51	3%	84.56	2%
Methacrolein	2.58	7%	22.13	11%	40.58	1%
Benzaldehyde	12.21	9%	99.15	15%	237.37	3%
o-Tolualdehyde	5.73	5%	55.04	16%	114.02	14%
m&p-Tolualdehyde	20.62	5%	163.14	21%	404.19	5%
Sum of List	166		1383		2684	
Total Carbonyl Rate	177		1447		2908	
% Accounted For	94%		96%		92%	

Table 50. Emission rates (mg/mile) for representative hydrocarbons for bus testing (average of four tests).

	Baseline Warm		Catalyst Warm		Baseline Cold		Catalyst Cold	
	AVG	%RSD	AVG	%RSD	AVG	%RSD	AVG	%RSD
ethylene	163.82	0.1%	145.90	1%	125.21	3%	129.83	10%
propylene	72.55	5%	64.33	1%	51.38	9%	53.41	22%
n-octane/t12-dm-cyH	51.22	3%	50.83	8%	47.07	8%	50.54	10%
m&p-xylene/34-dm-heptane	41.13	4%	42.08	9%	27.81	1%	34.10	2%
n-nonane	119.62	3%	118.33	3%	107.88	5%	120.18	6%
3e-toluene	36.32	3%	35.43	1%	18.46	7%	24.48	20%
4e-toluene/23-dm-octane	27.61	10%	28.35	4%	21.41	9%	27.41	28%
2m-nonane	31.99	1%	36.19	10%	32.19	32%	42.72	13%
2e-toluene	41.02	3%	40.84	3%	29.66	1%	35.83	1%
3m-nonane	26.32	6%	26.74	6%	24.28	6%	26.49	11%
124-tm-benz/tb-benz/1-decene	61.22	2%	63.19	9%	33.78	1%	46.04	4%
n-decane	147.06	3%	147.78	1%	134.99	4%	148.84	2%
3-np-toluene	31.08	6%	25.36	0.0%	27.90	30%	23.63	7%
4-np-toluene/nb-benz/13dm5e-benzene	42.31	11%	42.26	19%	37.62	31%	38.19	10%
14dm-2e-benzene	41.66	11%	42.44	2%	23.36	9%	31.35	1%
n-undecane/12-dm-3e-& 1245-ttm-benzene	161.99	4%	150.53	3%	125.22	9%	144.97	0.1%
124-te-benzene	70.39	6%	62.40	5%	39.33	15%	49.39	29%
n-hexyl-benzene	46.39	16%	23.56	15%	20.93	3%	16.43	35%
n-c13	70.39	6%	62.40	5%	39.33	15%	49.39	29%
n-c14	46.39	16%	23.56	15%	20.93	3%	16.43	35%
Sum of List	1330.46		988.75		1232.50		1109.65	
Sum (HC)	1894.91		1462.58		1813.62		1667.75	
% Represented	70%		68%		68%		67%	

Table 51. Emission rates (mg/mile) for representative carbonyls for bus testing (average of four tests).

Carbonyl	Warm Baseline		Warm Catalyst		Cold Baseline		Cold Catalyst	
	AVG	%RSD	AVG	%RSD	AVG	%RSD	AVG	%RSD
Formaldehyde	153.26	2%	155.42	3%	124.58	7%	159.26	5%
Acetaldehyde	48.68	5%	61.73	1%	45.80	6%	72.64	8%
Acrolein	11.40	6%	7.01	12%	16.65	23%	10.42	8%
Acetone	15.26	8%	26.72	3%	14.26	20%	27.23	21%
Propionaldehyde	9.73	3%	10.53	1%	9.51	6%	13.65	9%
Crotonaldehyde	7.47	2%	4.26	0.1%	6.73	33%	4.11	32%
Methacrolein	4.26	4%	4.12	6%	3.67	20%	4.25	11%
Valeraldehyde	8.21	17%	5.31	4%	4.77	33%	5.55	18%
Sum of List	258.29		275.10		225.98		297.11	
Total Carbonyls	268.30		282.79		236.81		304.73	
% Represented	96%		97%		95%		98%	

Table 52. Sulphur dioxide emission rates (mg/mile) for all vehicles and fuels with quantification limits.

	Suzuki GSX-R 750W		Honda CBR 600		Quantification limits
	SGC	Low Sulfur	SGC	Low Sulfur	
CS LA4 %RSD	14.04	0.02 141%	10.23 12%	ND	0.009
HS LA4 %RSD	15.04 3%	0.12 100%	9.57 2%	ND	0.009
FTP Composite %RSD	11.91 34%	0.08 71%	9.86 4%	ND	0.009
US06 x 3 %RSD	44.60 7%	0.12 107%	43.85 4%	0.02 70%	0.002
NYCC x 3 %RSD	28.18	ND	12.50 32%	ND	0.013

Note: ND = Non-Detectable emission rates

Table 53. Emission rates of ammonia (mg/mile) for each vehicle and fuel.

	Suzuki GSX-R 750W		Honda CBR 600		Quantification limits
	SGC	Low Sulfur	SGC	Low Sulfur	
CS %RSD	0.41 43%	0.44	0.03	0.47	0.03
HS %RSD	0.40 22%	0.22		0.49	0.03
4 Phase FTP %RSD	0.40 31%	0.31		0.25	0.03
US06 x 3 %RSD	1.91 14%	1.51 36%	0.78	1.26 21%	0.01
NYOC x 3 %RSD	0.21	0.27	0.11	0.57	0.04

APPENDIX D: PARTICULATE MATTER EMISSION RATES FOR MOTORCYCLES AND BUSES

Table 54. Particulate matter (PM_{2.5}) mass emission rates (mg/mile) for motorcycle testing (average of 2 tests)

	Suzuki GSX-R 750W		Honda CBR 600	
	SGC	Low Sulphur	SGC	Low Sulphur
CS LA4	5.58	3.17	1.35	2.13
%RSD	68%	30%	79%	80%
HS LA4	2.88	3.13	0.62	1.30
%RSD	44%	9%	26%	81%
4-Phase FTP	3.84	2.73	0.86	1.36
%RSD	60%	34%	76%	80%
US06x3	32.92	22.91	16.18	13.09
%RSD	58%	14%	5%	8%
NYCCx3	26.55	23.32	6.12	8.31
%RSD	38%	6%	5%	24%

Note:

- %RSD = % residual standard deviation based on two repeats for each emission rate.
- 4-Phase FTP is the composite of the CS LA4 and HS LA4 phases of the 4-Phase FTP.

Table 55. PM_{2.5} mass emission rates (10³ mg/mile) for bus testing (average of four tests).

Test Date	8 Feb. Morning	7 Feb. Afternoon	4 Feb. Afternoon	7 Feb. Morning
Method of Determination	Warm Baseline	Cold Baseline	Warm Catalyst	Cold Catalyst
Emfab	2.93	2.35	1.10	0.98
%RSD	8%	9%	8%	10%
Teflon	2.78	2.15	1.12	0.89
%RSD	8%	9%	8%	10%

Note:

- %RSD = % residual standard deviation based on four repeats for each emission rate.

Table 56. Averaged organic carbon (OC) and elemental carbon (EC) emission rates (g/mile).

		OC		EC		TC		OC/EC split	
		Avg.	%RSD	Avg.	%RSD	Avg.	%RSD	OC	EC
Baseline	Warm	1.79	13%	0.54	6%	2.33	5%	77%	23%
	Cold	1.49	11%	0.43	13%	1.92	5%	78%	22%
Catalyst	Warm	0.26	2%	0.82	8%	1.08	5%	24%	76%
	Cold	0.41	20%	0.42	3%	0.83	10%	49%	51%

Table 57. Chemical account of PM_{2.5} emissions for bus testing.

	Warm Baseline	Cold Baseline	Warm Catalyst	Cold Catalyst
Emission Rate (g/mile)				
Organic Carbon	1.79	1.49	0.26	0.41
Total Organics	2.15	1.79	0.31	0.49
Elemental Carbon	0.54	0.43	0.82	0.42
Total Speciation Mass	2.69	2.22	1.13	0.91
Gravimetric Mass	2.78	2.15	1.12	0.89
Ratio Speciation/Gravimetric	0.97	1.03	1.01	1.03

APPENDIX E: IONIC EMISSION RATES FOR MOTORCYCLE TESTING

Table 58. Emission rates of selected ions (mg/mile) for Suzuki operating on SGC.

	Comp		US06		NYCC	
	avg	std dev	avg	std dev	avg	std dev
Lithium						
Sodium	0.080		0.051	0.027		
Ammonium	0.016		0.155	0.025		
Potassium	0.496		0.673			
Magnesium	0.024					
Manganese	0.081		0.083	0.015		
Strontium						
Acetate	0.030		0.057			
Propionate						
Formate	0.026		0.083			
Methanesulphate						
Pyruvate						
Glyoxylate						
Chloride	0.057		0.126			
Nitrite						
Bromide						
Nitrate	0.032		0.127	0.064		
Benzoate						
Sulphate	0.035		0.160	0.017		
Oxalate			0.016			
Azelate						
Phthalate						
Phosphate	0.042		0.333	0.233		
Malonate						
Malate						
Succinate						
Glutarate						
Adipate						
Lactate			0.120			

Table 59 Emission rates of selected ions (mg/ mile) for Suzuki operating on Scotford low sulphur fuel..

	Comp		US06		NYCC	
	avg	std dev	avg	std dev	avg	std dev
Lithium						
Sodium			0.057	0.014	0.301	0.064
Ammonium						
Potassium			0.083		0.577	
Magnesium						
Manganese			0.264	0.021	1.015	0.304
Strontium						
Acetate					0.454	
Propionate						
Formate			0.036		0.409	0.059
Methanesulphate						
Pyruvate						
Glyoxylate						
Chloride			0.050			
Nitrite						
Bromide						
Nitrate			0.064	0.010	0.242	0.086
Benzoate						
Sulphate			0.022	0.001	0.546	
Oxalate						
Azelate						
Phthalate						
Phosphate			0.278	0.036	0.435	0.016
Malonate						
Malate						
Succinate						
Glutarate						
Adipate						
Lactate			0.233			

Table 60. Emission rates of selected ions (mg/ mile) for Honda operating on SGC.

	Comp		US06		NYCC	
	avg	std dev	avg	std dev	avg	std dev
Lithium						
Sodium	0.067		0.043	0.016	0.207	
Ammonium						
Potassium						
Magnesium						
Manganese	0.077		0.190	0.027	0.568	
Strontium						
Acetate						
Propionate						
Formate						
Methanesulphate						
Pyruvate						
Glyoxylate						
Chloride	0.065		0.059	0.017	0.301	
Nitrite						
Bromide						
Nitrate	0.036		0.046	0.000	0.185	
Benzoate						
Sulphate	0.028		0.070	0.041	0.049	
Oxalate						
Azelate						
Phthalate						
Phosphate	0.045		0.229	0.006	0.257	
Malonate						
Malate						
Succinate						
Glutarate						
Adipate						
Lactate						

Table 61. Emission rate of selected ions (mg/mile) for the Honda operating on Scotford low-Sulphur fuel.

	4-Ph FTP		US06		NYCC	
	avg	std dev	avg	std dev	avg	std dev
Lithium						
Sodium	0.070		0.136	0.106	0.513	
Ammonium						
Potassium						
Magnesium			0.010			
Manganese	0.189		0.514	0.032	1.387	
Strontium						
Acetate						
Propionate						
Formate			0.037			
Methanesulphate						
Pyruvate						
Glyoxylate						
Chloride	0.053		0.065	0.011	0.451	
Nitrite						
Bromide						
Nitrate	0.018		0.040		0.254	
Benzoate						
Sulphate	0.030		0.134	0.154	0.089	
Oxalate						
Azelate						
Phthalate						
Phosphate	0.060		0.238	0.024	0.397	
Malonate						
Malate						
Succinate						
Glutarate			0.107			
Adipate						
Lactate						

APPENDIX F: ERRORS AND OMISSIONS

This section is intended to document diversions from the originally planned emissions testing and what was done to either remedy or account for errors, mistakes and malfunctions.

F.1. PM Sampling

F.1.1.

It was decided that the dilution air concentrations for PM_{2.5} emission rates and OC-EC emission rates were not consistent enough to be reliably used in the calculation of emission rate. A large number of OC emission rates would have been invalidated if the concentration of OC in the dilution air had been accounted for. It is likely that the dilution air's OC concentration is actually an overestimate. Figure 82 shows the comparison of collected OC mass (calculated using Q_2 -correction) to collected PM mass from the dilution air. The vertical error bars represent the analytical error associated with the OC measurement while the horizontal error bars represent the standard deviation from averaging the net mass on the two Teflon filters used in dilution sampling.

This comparison reveals that the PM-bound OC is greater than the gravimetrically measured PM. This provides an indication that the ambient OC concentration is likely an overestimate. The overestimate is the result of calculating the OC concentration of dilution air using a Q_2 -correction (which under-corrects for the positive artefact as we saw earlier) rather than a Q_3 -correction. This overestimate of PM-bound OC in dilution air is exaggerated when sampling dilution air sampling because of the relatively higher efficiency of clean quartz filters for absorbing OC. This, combined with the Q_2 -effect of reduced available carbon (discussed in Section 3.4.1), results in an exaggerated correction in the ambient dilution air. Unfortunately, the setup of the dilution air filters did not facilitate a Q_3 correction. As a result of these factors, the dilution concentration for both PM and OC/EC were neglected.

Given that the efficiency of OC collection is very high for clean quartz compared to particle laden quartz, it may have been better to neglect the ambient OC collected on the quartz altogether. It was decided that the ambient OC concentrations would remain in the calculation for consistency.

Figure 82. Comparison of OC to PM collected from dilution air.

F.1.2.

The variability that was observed between simultaneously sampled filters was much higher for motorcycles than it was for buses. This was attributed to possible leaks in the filters and the low amount of sample that was collected on the filters. This variability was partially reduced through the elimination of outliers in the simultaneously-sampled filters. The identification of these outliers was performed through the comparison of the ratio of average Emfab filter emission rates to individual Teflon emission rates calculated for each simultaneously-sampled filter.

F.2. Gaseous Sampling

F.2.1.

There were a number of incidences near the end of the motorcycle testing where the CO₂ sensor under-read the sample concentration. When noted, the problem was remedied by cycling the meter switch. Because the error was the result of a metering problem and not necessarily a sampling problem, it was determined that additional tests were not necessary. Where CO₂ tests were invalidated, substitute data from other tests were used in order to determine the dilution ratio. A summary of these tests is shown in Table 64. The dilution factor of tests that did not have CO₂ was estimated by replacing invalid CO₂ emission rates with emission rates from other tests with comparable driving parameters.

On the last test of the campaign (NYCC - 14 July), the dynamometer speed sensor went offline, resulting in the cursor on the Driver's aid no longer responding to the rotation of the dynamometer roller. This resulted in the distance travelled calculated by the computer to be 1.52 miles, 0.3 miles longer than dictated in the NYCC test. Given that the driver was experienced and very competent and that the NYCC is test in predominantly an idling cycle with simple accelerations and decelerations, it was assumed that the driver properly followed the trace and that the distance travelled was actually 1.22 miles.

Table 64. Summary of Corrections and Omissions

Test Date	Erroneous reading	Substitute reading
7-Jul-1999	CO ₂ in Repeat 2 & 3 of US-06x3	Omitted readings, used CO ₂ emission rate from Repeat 1.
13-Jul-1999	CO ₂ in Bag 2 of CS-	CO ₂ in Bag 2 of CS on 7-Jul-1999
	CO ₂ in Repeat 1 & 2 of US-06x3	Omitted readings, used CO ₂ emission rate from Repeat 3
14-Jul-1999	CO ₂ in Repeat 1&2 of CS	CO ₂ in Repeat 1&2 of CS on 8-Jul-1999
	Distance in Repeat 3 of NYCCx3 (1.52 miles)	Adjusted distance to 1.22

F.3 Test Procedures

In bus testing, the first series to be conducted (*Warm Baseline* - 4 February) was determined to be invalid and the series was repeated later in the testing program. The test series was invalidated because filters were becoming clogged due to of excessively long sample times. It was originally planned that one filter was to be used to collect two repeats of the CBD. The sampling time proved to be too long and by the end of the sampling period, the Teflon filters became clogged and the mass flow controllers were not able to maintain a constant flow. Subsequent tests used a single filter set per driving cycle to ensure that clogging did not occur.

It was originally planned that an additional bus would be tested for emissions. This second bus was a new technology bus that would be tested for comparison of emissions from different engine designs. It was anticipated that this bus would also be tested at warm and cold temperatures. During the first series of tests on the new technology bus, the dynamometer roller failed. Due to scheduling conflicts at the test facility, the new technology bus was not tested.

APPENDIX G: RESULTS OF STATISTICAL ANALYSES.

Table 65. Two-factor ANOVA Comparisons of PM emissions of CS LA4 to HS LA4 (Suzuki).

PM Rates		Test Date	CS LA4	HS LA4
Suzuki SGC		June 15	8.28	3.77
		June 16	2.88	1.98
Suzuki Lo-S		June 21	3.83	3.34
		June 22	2.50	2.93

Source of Variation	SS	df	MS	F	P-value	F crit
Fuel	2.32	1	2.32	0.54	0.50	7.71
CS vs. HS	3.75	1	3.75	0.88	0.40	7.71
Interaction	3.56	1	3.56	0.83	0.41	7.71
Within	17.13	4	4.28			
Total	26.76	7				

Table 66. Two-factor ANOVA Comparisons of PM emissions of CS LA4 to HS LA4 (Honda).

PM Rates		Test Date	CS LA4	HS LA4
Honda SGC		July 7	0.59	0.51
		July 8	2.10	0.74
Honda Lo-S		July 13	0.92	0.55
		July 14	3.34	2.04

Source of Variation	SS	df	MS	F	P-value	F crit
Fuel	1.06	1	1.06	0.82	0.42	7.71
CS vs. HS	1.21	1	1.21	0.94	0.39	7.71
Interaction	0.01	1	0.01	0.00	0.95	7.71
Within	5.19	4	1.30			
Total	7.48	7				

Table 67. Two-factor ANOVA for significance of extra test cycles on PM emissions (Suzuki).

PM Rates		Test Date	4-Ph FTP	US-06	NYCC
Suzuki SGC		June 15	5.50	46.44	33.75
		June 16	2.38	19.40	19.34
Suzuki Lo-S		June 21	3.54	25.13	22.26
		June 22	2.83	20.69	24.38

Source of Variation	SS	df	MS	F	P-value	F crit
Fuel	65.2	1	65.2	0.80	0.40	5.99
Driving Cycle	1411.8	2	705.9	8.70	0.02	5.14
Interaction	45.9	2	23.0	0.28	0.76	5.14
Within	486.7	6	81.1			
Total	2009.7	11				

Table 68. Two-factor ANOVA for significance of extra test cycles on PM emissions (Honda).

PM Rates		Test Date	4-Ph FTP	US-06	NYCC
Honda SGC		July 7	0.44	16.73	5.90
		July 8	1.32	15.63	6.34
Honda Lo-S		July 13	0.76	12.36	9.69
		July 14	2.50	13.81	6.92

Source of Variation	SS	df	MS	F	P-value	F crit
Fuel	0.008	1	0.0	0.01	0.94	5.99
Driving Cycle	359.4	2	179.7	143.66	8.6E-6	5.14
Interaction	14.9	2	7.5	5.97	0.04	5.14
Within	7.5	6	1.3			
Total	381.9	11				

Table 69. Single-factor ANOVA for significance of extra test cycles FTP, US-06, NYCC (Suzuki).

PM Rates		Test Date	4-Ph FTP	US-06	NYCC
Suzuki		June 15	5.50	46.44	33.75
		June 16	2.38	19.40	19.34
		June 21	3.54	25.13	22.26
		June 22	2.83	20.69	24.38

Source of Variation	SS	df	MS	F	P-value	F crit
Driving Cycle	1411.8	2	705.9	10.6	0.00427	4.3
Within	597.9	9	66.4			
Total	2009.7	11				

Table 70. Results of Tukey Test for evaluating effect of driving cycle on Suzuki PM_{2.5} emissions (two factor case).

Cycle	4-Ph. FTP	US-06	NYCC	$Q = \sqrt{\frac{81}{2}} = 6.37$
SGC Average	3.94	32.92	26.55	
Lo-S Average	3.18	22.91	23.32	
Comparison	Difference	q	q(0.05,6,6)	Conclusion
SGC: US-06 vs. FTP (Max-Min)	29.98	4.55	5.628	Accept US-06 = FTP
Decision (SGC): $\mu_{FTP} = \mu_{NYCC} = \mu_{US06}$				
Decision (Lo-S): $\mu_{FTP} = \mu_{NYCC} = \mu_{US06}$				

Table 71. Two-factor ANOVA test for PM emission rates from urban bus.

PM Rates (mg/mile)	Test Date	Warm	Test Date	Cold
Cat	4 Feb	1244	7 Feb (Morning)	811
		1104		1012
		1028		844
		1096		880
Baseline	8 Feb	2565	7 Feb (Afternoon)	1923
		2647		2339
		3037		2093
		2867		2250

Source of Variation	SS	df	MS	F	P-value	F crit
Baseline/Catalyst	8558492	1	9E +06	358.3	3E-10	4.7
Temperature	738037	1	738037	30.9	0.0001	4.7
Interaction	157325	1	157325	6.6	0.025	4.7
Within	286669	12	23889			
Total	9740522	15				

Table 72. Tukey test for significance of operating conditions on PM emissions from urban bus.

Combination	Baseline (Warm)	Baseline (Cold)	Catalyst (Warm)	Catalyst (Cold)	$Q = \sqrt{\frac{23889}{4}} = 77.3$
Average (mg/mile)	2779	2151	1118	887	
Comparison	Difference	q	q(0.05,9,3)		Conclusion
Warm vs. Cold (Baseline)	627.9	8.12	4.199		Reject Warm = Cold (Baseline)
Warm vs. Cold (Catalyst)	231.2	2.99	4.199		Accept Warm = Cold (Catalyst)
Catalyst effect (Warm)	1661.1	21.49	4.199		Reject Catalyst = Baseline (Warm)
Catalyst effect (Cold)	1264.4	16.36	4.199		Reject Catalyst = Baseline (Cold)

Table 73. Two-factor ANOVA test for OC emission rates from urban bus.

OC Rates (g/mile)	Test Date	Warm	Test Date	Cold
Cat	4 Feb	0.25	7 Feb (Morning)	0.34
		0.26		0.52
		0.26		0.40
		0.26		0.38
Baseline	8 Feb	1.58	7 Feb (Afternoon)	1.28
		1.67		1.66
		2.12		1.54
		1.79		1.49

Source of Variation	SS	df	MS	F	P-value	F crit
Baseline/Catalyst	6.82	1	6.82	305.20	7.0E-10	4.75
Temperature	0.02	1	0.02	0.95	0.348	4.75
Interaction	0.20	1	0.20	8.98	0.01	4.75
Within	0.27	12	0.02			
Total	7.31	15				

Table 74. Tukey test for significance of operating conditions on OC emissions from urban bus.

Combination	Baseline (Warm)	Baseline (Cold)	Catalyst (Warm)	Catalyst (Cold)	$Q = \sqrt{\frac{0.02}{4}} = 0.075$
Average (mg/mile)	1.789	1.492	0.259	0.410	
Comparison	Difference	q	q(0.05,9,3)	Conclusion	
Warm vs. Cold (Baseline)	0.297	3.9732	4.199	Accept Warm = Cold (Baseline)	
Warm vs. Cold (Catalyst)	-0.151	-2.021	4.199	Accept Warm = Cold (Catalyst)	
Base vs. Cat (Warm)	1.530	20.467	4.199	Reject Catalyst = Baseline (Warm)	
Base vs. Cat (Cold)	1.082	14.473	4.199	Reject Catalyst = Baseline (Cold)	

Note: Negative Differences indicate that second value (Cold, Catalyst) is greater than first value (Warm or Baseline)

Table 75. Two-factor ANOVA test for EC emission rates from urban bus.

EC Rates (g/mile)	Test Date	Warm	Test Date	Cold
Cat	4 Feb	0.90	7 Feb (Morning)	0.43
		0.81		0.40
		0.75		0.42
		0.81		0.57
Baseline	8 Feb	0.51	7 Feb (Afternoon)	0.41
		0.53		0.51
		0.57		0.40
		0.57		0.39

Source of Variation	SS	df	MS	F	P-value	F crit
Baseline/Catalyst	0.09	1	0.09	26.75	0.0002	4.7472
Temperature	0.23	1	0.23	67.00	3.1E-6	4.7472
Interaction	0.06	1	0.06	17.33	0.0013	4.7472
Within	0.04	12	0.00			
Total	0.43	15				

Table 76. Tukey test for significance of operating conditions on EC emissions from urban bus.

Combination	Baseline (Warm)	Baseline (Cold)	Catalyst (Warm)	Catalyst (Cold)	$Q = \sqrt{\frac{0.035}{4}} = 0.029$
Average (mg/ mile)	0.54	0.43	0.82	0.46	
Comparison	Difference	q	q(0.05,9,3)	Conclusion	
Warm vs. Cold (Baseline)	0.12	4.02	4.199	Accept Warm = Cold (Baseline)	
Warm vs. Cold (Catalyst)	0.36	12.35	4.199	Reject Warm = Cold (Catalyst)	
Base vs. Cat (Warm)	-0.28	-9.33	4.199	Reject Catalyst = Baseline (Warm)	
Base vs. Cat (Cold)	-0.03	-1.01	4.199	Accept Catalyst = Baseline (Cold)	

Note: Negative Differences indicate that second value (Cold, Catalyst) is greater than first value (Warm or Baseline)

Table 77. Two-way ANOVA Comparisons of PM emissions by filter media.

PM Rate (mg/mile)		Teflon		Emfab	
Cat Warm		1244		1081	
		1104		1018	
		1028		1086	
		1096		1210	
Baseline Warm		2565		2705	
		2647		2795	
		3037		3220	
		2867		2993	
Cat Cold		811		954	
		1012		942	
		844		1120	
		880		883	
Baseline Cold		1923		2123	
		2339		2555	
		2093		2291	
		2250		2423	

Source of Variation	SS	df	MS	F	P-value	F crit
Vehicle configuration	20362103	3	6787368	272.93	1E-18	3.01
Filter Media	86052	1	86052	3.46	0.0752	4.26
Interaction	52180	3	17393	0.70	0.5616	3.01
Within	596838	24	24868			
Total	21097174	31				

Table 78. Two-way ANOVA Comparisons of PM emissions by filter media.

Test Number	Emission Rate (mg/mile)			
	Warm Catalyst	Cold Catalyst	Cold Base	Warm Base
1	1258	837	1920	2593
	1230	784	1925	2536
2	1123	1024	2386	2658
	1085	1001	2292	2636
3	1033	845	2113	3115
	1023	844	2072	2959
4	1102	903	2267	2891
	1091	858	2233	2844

Source of Variation	SS	df	MS	F	P-value	F crit
Repeat of Test	106047	3	35349	22.7	5.3E-06	3.24
Vehicle configuration	18907707	3	6302569	4042.8	3.0E-23	3.24
Interaction	467290	9	51921	33.3	1.1E-08	2.54
Within	24944	16	1559			
Total	19505988	31				