**Particle Size Distribution Measurements of Light Duty Motor Vehicle
Exhaust:
Evaluating Different Measurement Techniques
and Vehicle Technologies**

By

Kristine Tracey, B.A.Sc

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

Master of Applied Science

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Ottawa, Ontario, Canada
2002

Abstract

The Electrical Low Pressure Impactor (ELPI), the Scanning Mobility Particle Sizer (SMPS) and the Condensation Particle Counter (CPC) are used to examine nanoparticle number concentrations and particle size distributions from eight vehicles representing different engine technologies. Five drive cycles along with several steady state cycles were used with two exhaust dilution methods.

The test set-up for studies of particle size distribution should include an aerosol neutralizer, since particles exit the tailpipe with a charge. To minimize particle formation and losses, heat is needed for dilution (particularly the mini-diluter, the dilution ratio is higher in the tunnel so heat is not essential). In addition, dilution with diesel vehicles requires a second mini-diluter.

According to the particle size distributions collected for the various vehicles, the electric hybrid has the lowest emissions, followed by the multi-port fuel injected spark ignition engine, the direct injection gasoline engine and the direct injection diesel engine.

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List of Abbreviations

A/F	Air/Fuel Ratio
CPC	Condensation Particle Counter
CVS	Constant Volume Sampling
DDI	Diesel Direct Injection Engine
DMA	Differential Mobility Analyzer
EGR	Exhaust Gas Re-circulation
ELPI	Electrical Low Pressure Impactor
EP	Explosion Point
ERMD	Emissions Research Measurement Division
FTP	Federal Test Procedure
GDI	Gasoline Direct Injection Engine
HEPA	High Efficiency Particulate Air
HWFET	Highway Fuel Economy Test
IBP	Initial Boiling Point
LDV	Light Duty Vehicle
MON	Motor Octane Number
MPFI-SI	Multi-Port Fuel Injected Spark Ignition
NAAQO	National Ambient Air Quality Objective (Canada)
NAAQS	National Ambient Air Quality Standard (United States)
NYCC	New York City Cycle
PM _{2.5}	Particulate Matter with an aerodynamic diameter of 2.5 microns or less

PM ₁₀	Particulate Matter with an aerodynamic diameter of 10 microns or less
RON	Research Octane Number
RVP	Reid Vapour Pressure
SFTP	Supplemental Federal Test Procedure
SMPS	Scanning Mobility Particle Sizer
TSP	Total Suspended Particulate Matter
US06	Part of Supplemental Federal Test Procedure

Chapter 1: Introduction

1.1 Sources of Particulate Matter Air Pollution

Particulate Matter (PM) air pollution comes from either natural or anthropogenic sources. A natural source contributes fine (those less than 2.5 microns) or coarse particles (those between 2.5 and 10 microns), and determines background particulate matter levels. Anthropogenic sources are divided into stationary and mobile sources. Stationary sources include point sources, which are generally large commercial or industrial operations, and area sources, which are several points in close proximity emitting the same pollutants, such as a residential area. Mobile sources are highway vehicles (cars, trucks, buses, motorcycles), and off-highway vehicles (trains, airplanes, farm & construction equipment).³⁶ The emissions from both the natural and anthropogenic sources can form particles in the atmosphere by secondary reactions.²

The primary sources of particle emissions are fuel-burning plants and industrial or commercial processes. Although mobile sources account for less than half of the particulate matter emitted, the number of vehicles on the road (in the United States) has increased from approximately 75 million in the 1940's to 250 million in 1990. In addition, in the 1940's drivers used approximately 25 billion gallons of gasoline, while in 1990 the gasoline consumption was 175 billion gallons. This is a 600% increase in the use of gasoline (approximately 12% a year), while the reduction in PM_{10} was 3% between 1981 and 1990 (0.3% a year).³⁶

Table 1 shows the emission characteristics of different sources, displaying the prominent particle size for each source.

Table 1: Dominant Particle Sizes Emitted from Various Sources²

Source Type	Dominant Particle Size
Motor Vehicle	Fine (0 to 2.5 µm)
Vegetative Burning	Fine (0 to 2.5 µm)
Residual Oil Combustion	Fine (0 to 2.5 µm)
Incinerator	Fine (0 to 2.5 µm)
Coal-Fired Boiler	Fine (0 to 2.5 µm)
Oil-Fired Power Plant	Fine (0 to 2.5 µm)
Smelter Fire	Fine (0 to 2.5 µm)
Antimony Roaster	Fine (0 to 2.5 µm)
Paved Road Dust	Coarse (2.5 to 10 µm)
Unpaved Road Dust	Coarse (2.5 to 10 µm)
Construction	Coarse (2.5 to 10 µm)
Agriculture Soil	Coarse (2.5 to 10 µm)
Natural Soil	Coarse (2.5 to 10 µm)
Lake Bed	Coarse (2.5 to 10 µm)
Marine	Both (0 to 10 µm)

It shows that the dominant particle size emitted in over half of the sources listed is the fine particle fraction. This indicates that particulate matter studies should include effects associated with this fine particle fraction.

1.2 Emergence of PM as a Key Pollutant from a Public Health Perspective

Particulate matter has a variety of health effects, including such things as impaired pulmonary function, medication use, reduced physical performance, excess visits with physician, emergency room visits, hospital admissions and mortality. A way to visualize these effects is with the 'Health Effects Pyramid' in figure 1, which relates different health effects to the strength of the scientific evidence that links them to particulate matter.

Figure 1: The Health Effects Pyramid¹⁴

Large amounts of evidence support the link between PM and the effects at the base, while there is less evidence for those at the peak

The effects found on the base of the triangle have large amounts of data supporting the theory that the population is affected by PM emissions, while the effects near the peak have less supporting evidence. This lack of evidence is due to the severity of the effect. The least severe effects are common to a large population when exposed to particulate matter, however those of increasing severity are localized to a smaller population with weak immune systems (mainly young children and elderly people).

1.3 The Role of Mobile Sources in PM Emissions

Particulate matter from motor vehicles is divided into exhaust particles, road dust, tire wear and brake lining.² As shown in table 1, the majority of the particulate matter

from motor vehicles falls in the fine particulate range, however, the exhaust composition is more variable. "The composition of exhaust particles depends on where and how they are collected. As the exhaust is diluted and cooled, nucleation, condensation, and absorption transform volatile materials to solid and liquid particulate matter."²⁰ In the engine, combustion occurs and carbon is formed in locally rich regions, most of which is then oxidized. If some of the fuel does not combust, the exhaust contains organic compounds from the unburned fuel. The sulfur in the fuel oxidizes to SO_2 and SO_3 . The SO_3 reacts with water to form sulfuric acid and if the sulfuric acid is neutralized it forms sulfates. As a result of these reactions, when the exhaust gas exits the engine, the particles are mainly composed of solid carbonaceous material, ash, organic compounds and sulfur compounds.²⁰

1.4 Objectives and Summary of the Study

The study of particulate matter emissions from motor vehicles has been an on-going process for years, with the focus on heavy-duty diesel vehicles. Within the light duty category, light duty diesel vehicles get the most attention, since diesel vehicles emit more particles. Although this is a valid concern, the lack of focus on other relevant light duty vehicles is disappointing.

When discussing particulate matter, the immediate thought falls to the mass of particles, more than any other measure, since current standards focus on this. There are many other ways to classify particles: number, area, and shape to name a few, all of which are emerging as possibilities for further study.

This study is concerned with the mass and the number of particles emitted from the tailpipe of the major light duty vehicle types on the market today; the direct injection

diesel (DDI), the multi-port fuel injected spark ignition gasoline (MPFI-SI), the direct injection spark ignition gasoline (GDI), and the electric hybrid. The vehicles chosen are mainly European and Japanese imports, only two of the 8 vehicles are available in the North American market. The majority of European vehicles are diesel, while the direct injection gasoline vehicle and the electric hybrid are both relatively new technologies to any market, and a useful addition to the study, allowing a comparison between all major technologies.

Light duty motor vehicle emissions are commonly tested on a dynamometer when dealing with the particulate mass or the composition of the exhaust. However, the particle number measurement instruments commonly used are designed for ambient air testing. This is a preliminary study attempting to merge these two testing methods in a lab environment. The dynamometer is used to drive the car and the particle measurement instruments take a sample from a diluter, which samples directly from the tailpipe of the vehicle. The study is designed to develop an understanding of what effects the data under the described conditions, and to determine the best lab conditions that can be set up to compare the different vehicle technologies to give results representative of what happens to exhaust under actual driving conditions.

The main objectives of this study are:

1. To compare the various engine technologies on the market today, and assign a relative ranking between them.
2. To determine the vehicle driving cycles and dilution method that can be used to accurately compare number concentrations between different vehicle technologies.

3. Investigating the capabilities of three different particle-counting instruments in their ability to measure the nanoparticles emitted from the vehicles in the study.

Chapter 2: Background

2.1 Particulate Matter

Most particle formation and losses in the engine and the sampling train are controlled by saturation ratio, temperature, dilution ratio, particle concentration (or surface area) and residence time in different combinations depending on the formation process or loss.

2.1.1 Particle Formation Mechanisms in Engine Exhaust

Engine exhaust particles can be divided into sulfates and organic particles. These are shown in figure 2, further divided into sulfuric acid aerosols, sulfate particles, hydrocarbon particles and carbonaceous agglomerates.

Figure 2: Typical Structure of Engine Exhaust Particles²³

The sulfur compounds are formed from sulfur rich fuel, which is oxidized to SO_2 or SO_3 .

The hydrocarbon particles result directly from unburned fuel and lube oil, while the carbonaceous particles (soot) result from the pyrolysis of the fuel and lube oil in fuel rich

areas. Although some soot forms from MPFI-SI engines, it originates primarily from DDI or GDI engines.

2.1.1.1 Coagulation

Coagulation is the process where particles interact and collide with one another and form new particles. This mechanism does not affect the total particle mass of an exhaust but it decreases the number of small particles and increases the number of larger particles in the exhaust. This process is controlled by the particle concentration and the dilution ratio in the sampling train. If the dilution ratio is high, and the dilution gas is clean then there are few particle collisions.²³

2.1.1.2 Adsorption

Adsorption is the process where molecules of a gas or vapour attach to the surface of a solid particle. It is governed by the saturation ratio (the ratio of the partial pressure of the condensing species to the local vapour pressure), so increasing the saturation ratio increases adsorption. Once the saturation ratio increases to a certain level, the continued increase of saturation ratio causes a slower increase in adsorption. At a saturation ratio of about 1.0, the adsorption turns into condensation. The reverse process is also possible, if the saturation ratio begins to decrease, the organics desorb from the particles and return to the gaseous state.

The two other controlling factors are the time required for adsorption to occur and the surface area available. If the sampling time is not enough for adsorption or there is not enough surface area, adsorption is minimized. In the case of vehicle exhaust, the adsorption is volatile organics onto exhaust particles, which affects the size and mass of

the particulate matter emissions, while decreasing the gaseous hydrocarbon content of the exhaust.²²

2.1.1.3 Nucleation

Nucleation is the formation of new particles from gaseous organic species. The precursor molecules of nucleation are polycyclic aromatic hydrocarbons.¹⁵ A high saturation ratio and a low particle surface area are optimal for the nucleation of new particles. Once a particle reaches a certain size and becomes stable it continues to grow by condensation.

The nucleation process occurs by two means: homogeneous nucleation and heterogeneous nucleation. Under high supersaturation values, homogeneous nucleation forms molecular clusters from vapour molecules and if the exhaust is supersaturated enough, the clusters become large enough that condensation takes over. This process leads to the production of large numbers of new particles. Heterogeneous nucleation is similar to homogeneous nucleation except there are nuclei already present in the exhaust, so it can occur at lower supersaturation levels.²³ Kittelson²¹ also discovered that a dilution ratio between 5:1 and 50:1 is likely to produce high saturation ratios, which maximize nucleation.

2.1.1.4 Condensation and Evaporation

Condensation is the process that takes over for both nucleation and adsorption when there are stable particles present and the saturation level is high. The condensation process can be reversed, and evaporation of the condensed gas can occur if the saturation level falls below 1.0.²² A decrease in the temperature in the sampling system causes gaseous molecules to turn into vapour, which increases the saturation ratio, and therefore

increases the chances of condensation. Condensation and evaporation can affect the size and the mass of the particulate matter.

2.1.2 Particle Losses in Engine and Sampling Train

2.1.2.1 Diffusion

Diffusion of particles occurs from the Brownian motion of the particles, which causes movement due to a concentration gradient. The loss of particles to the walls of the sampling system due to diffusion is governed by a particle's diffusion coefficient. This coefficient is inversely proportional to particle size, so the smaller particles diffuse more quickly than larger ones. Losses from diffusion occur more quickly in more turbulent flows. To reduce the effects of diffusion, short sampling lines should be used.²²

2.1.2.2 Inertial Impaction

Particles with large amounts of inertia cannot follow the fluid streamline and tend to collide with walls, removing them from the stream. This tends to remove only the largest particles, especially if isokinetic sampling is not performed. The particles that have been removed can rejoin the exhaust flow later, causing variability in the sampling results.²²

2.1.2.3 Electrostatic Deposition

Electrostatic deposition occurs when the sampling lines and the exhaust particles have opposite charges, causing the particles to move towards the sampling walls, removing them from the exhaust. Diesel exhaust particles often have a charge from the combustion process, so the sample lines must be carefully chosen to minimize this effect (metal is recommended, while Teflon should be avoided as it is easily charged). This mechanism removes the larger particles, since the electrical mobility increases with increased particle size.²²

2.1.2.4 Thermophoresis

Thermophoresis is similar to diffusion but the movement of the particles is due to a temperature gradient. As with diffusion, the effect of this mechanism is greatest on the smaller particles, but deposition of the larger particles is possible as well. Figure 3 illustrates the motion of a diesel particle from thermophoresis. The temperature gradient between the exhaust gas and the sampling train walls causes a thermal force that is stronger on the hot side of the particle, which pushes the particle to the colder region, near the sampling train walls. From here, the particles collide with the walls, and are lost from the exhaust.

Figure 3: Thermophoresis from a Temperature Gradient²²

Particles move towards the walls of the sampling train

It is also possible for re-entrainment of the particles to occur, which causes variability in the samples. Keeping the sampling line at a similar temperature to the exhaust gas minimizes thermophoresis.^{22, 23}

2.1.3 Particles of Concern

Particles less than 10 microns in diameter are the most harmful because they can penetrate the lungs. More specifically, although coarse particles are easily inhaled, the fine particle fraction can travel into the deepest areas of the lungs once inhaled, so these are an even greater concern. Once released into the air, fine particles can remain suspended for long periods, and can therefore be transported over large regions.¹⁰

Fine particles are further divided into accumulation mode (0.1-0.3 μm diameter), and nuclei mode (0.005-0.05 μm diameter). Carbonaceous agglomerates and adsorbed materials are usually the bulk of the accumulation mode, while the nuclei mode has volatile organic and sulfur compounds, as well as solid carbon and metals. When comparing the accumulation, and nuclei modes to the coarse fraction, the accumulation mode makes up the majority of the particle mass, with the nuclei and coarse areas only making up a maximum of 20% each, leaving over half to be present in accumulation mode. On the other hand, if the particle number is examined, 90% of the particles come from the nuclei fraction, and to further quantify, most of that percentage is in the nanoparticle ($D_p < 50\text{nm}$) range. This is shown in figure 4, which represents diesel engine exhaust, but gasoline exhaust shows a similar distribution.²⁰

Figure 4: Mass and Number Weighting of Diesel Engine Exhaust Particles²⁰

This is reasonable, since the size of a particle and its mass is related, so the mass of a particle increases by the cube of the radius. This is shown in the following example:

In general;

$$m = \frac{4}{3} \times \rho \times \pi \times r^3$$

So, for two particles with the same density, only varying in size, everything but the radius is eliminated:

$$\frac{m_1}{m_2} = \frac{r_1^3}{r_2^3}$$

If the radius of the second particle is 3 times the radius of the first:

$$\frac{m_1}{m_2} = \frac{1^3}{3^3}$$

$$\frac{m_1}{m_2} = \frac{1}{27}$$

$$m_2 = 27 \times m_1$$

Therefore, the mass of the larger particle is 27 times the mass of the smaller, although it is only 3 times as large in radius.

2.1.4 Health & Environmental Effects

Particulate matter shows effects on many different parts of life. There are known effects on human health, but there are also lesser known effects on a variety of items, including destruction of plant life and agriculture, decreased visibility, soiling of homes and clothing, and effects on climate.¹

2.1.4.1 Effects on Human Health

Particulate matter is known to effect human health in many ways. Evidence has shown that exposure to increased levels of PM cause respiratory distress, increased hospital visits, and can lead to death. Even though there have been many studies linking particulate matter with various health problems, there is still uncertainty about what aspect of particulate matter (mass, size, chemical composition, or some combination of these) is primarily responsible for the associated human health effects.¹⁰

Focusing on fine particulate matter, studies have linked these small particles to significant health problems (mentioned above) including death. As in all particulate matter studies, the effects are seen most often in the elderly, or children (those with weaker immune systems). Since children are still developing, their immune system is weaker, and they inhale up to 50% more air per pound of body weight than adults. “The

breathing of fine particles by children is believed to cause both acute and chronic respiratory problems such as asthma.”³⁷

New studies are now emerging which focus on the ultrafine and nanoparticle diameter range. It makes sense that the effects, which appear from exposure to fine particulate or particulate matter in general, would also appear from exposure to ultrafines and nanoparticles. Recent studies conclude that particles, which are safe in large diameters, become toxic in the ultrafine and nanoparticle range. As an example, a 1995 study showed that if rats were exposed to TiO_2 in the 0.25 and 0.02 μm diameter, they produced an inflammatory response to the 0.02 μm , but none with the 0.25 μm particles.²⁰

In 2000, the Ontario Medical Association produced a report titled ‘*The Illness Costs of Air Pollution*’, which attempted to give a monetary value to illnesses based on air pollution, focusing on ozone and particulate matter. The findings indicated that air pollution costs the people of Ontario \$1 billion a year in hospital admissions, emergency room visits, and absenteeism. The report also attempts to assign a cost to pain, suffering and death due to air pollution.²⁹

Based on the current levels of pollution, attributed mainly to PM_{10} , the study predicted for the year 2000: 1,900 premature deaths, 9,800 hospital admissions, 13,000 emergency room visits and 47 million minor illness days. In terms of costs, this is about \$600 million to the health care system, and another \$560 million to employers and employees, for a \$1 billion total. If pain and suffering, and loss of life are estimated, this adds another \$9 billion dollars to the total, which gives a cost of \$10 billion for the year

2000. Ozone accounts for about half of the hospital admissions and emergency room visits associated with air pollution, while PM_{10} accounts for the rest.²⁹

2.1.4.2 Environmental Effects

Engine exhaust has an environmental impact, the extent of which is influenced by particle size. A particle that remains in the atmosphere is given the opportunity to travel, reduce visibility and influence the population. Particles between 0.1 and 10 μm have the longest atmospheric residence time, which is about 1 week. This means, that not only are these small particles harmful, but they are the most likely to travel to reach something to harm. Larger particles settle out of the atmosphere and smaller ones are removed by diffusion and coagulation. Although it seems encouraging that the smallest particles are disappearing, the main mechanism for this removal is coagulation, which means they become larger particles and now fall into the 0.1-10 μm category.²⁰

The major environmental effects are on plants and agriculture, visibility effects, and effects on materials. Although less prominent, they are another reason to try to minimize particulate matter emissions. Damage to crops and vegetation are estimated at \$70 million dollars in Ontario.¹²

Visibility changes result from the particles either absorbing light or scattering it. The light absorption from these particles contributes to the decreased visibility that is experienced in many parts of the world. In the US, it is estimated that the reduction in visibility is up to 70%. Since the particles have long residence times, they travel to different cities, states or countries. For example, the haze over the Grand Canyon is attributed to the pollution generated in Southern California.³⁷

Since particulate matter is deposited everywhere, buildings, clothing, indoors, outdoors, all materials are effected. There are two major effects: corrosion and erosion (chemical or physical degradation) and loss of aesthetic value (soiling and discolouration).

Soiling and discolouration is an aesthetic problem on the surface, but an impact analysis shows that it also causes excessive cleaning and refinishing. In the case of clothing, this means more washing is needed, using more water, and shortening the life span of the clothing. In the case of building materials, this has a two-fold effect. Most exterior building materials are brick or stone, which are eroded by the particulate matter, and soiled by it as well.²

2.1.5 Current Regulations

2.1.5.1 Ambient Air Quality Regulations

In Canada, rather than outlining a standard that must be met, the National Ambient Air Quality Objectives (NAAQO) gives a reference level above which there are known effects.² The Federal/Provincial Working Group responsible for these objectives produced a report in 1999, which outlines the determining factors in this NAAQO. Reference levels were deemed unnecessary for plant effects, since the majority of the effects were based on composition rather than size. Visibility is affected by smaller particle sizes, so a PM_{10} reference level was not useful, and a $PM_{2.5}$ reference level was not easily defined due to the problem of determining an acceptable visibility level. The final major factor considered was human health effects, which indicates that reference levels are needed, and are set at $25 \mu\text{g}/\text{m}^3$ for PM_{10} averaged over 24 hours. This is supported by several mortality and hospitalization studies. The $PM_{2.5}$ reference level is

given as $15 \mu\text{g}/\text{m}^3$ averaged over 24 hours, also supported by mortality and hospitalization studies. This does not mean that there are no health effects below these levels. Since these types of studies do not include all particulate matter related health effects, the Working Group further indicates that at particulate matter concentrations across Canada, casual health effects (reduced lung function, school absenteeism, loss of work) are occurring.²

These objectives carry with them no repercussions if they are not met, since they are only recommended goals. The United States has an alternate approach to air quality, which allows them to enforce their air quality standards through the Clean Air Act. This act grants power to the U.S Environmental Protection Agency to outline and enforce National Ambient Air Quality Standards. These standards are as follows; $150 \mu\text{g}/\text{m}^3$ averaged over 24 hours for PM_{10} and $65 \mu\text{g}/\text{m}^3$ averaged over 24 hours for $\text{PM}_{2.5}$. Currently, only the PM_{10} standards can be enforced, the $\text{PM}_{2.5}$ standards are only for reference.³¹

The Clean Air Act also requires any state that does not meet the air quality standards to produce a State Implementation Plan, which details how they will comply with air quality standards. The EPA has the power to approve these plans or reject them and force the state to follow a federal implementation plan. The EPA can impose penalties for failure to comply with the Clean Air Act, such as cutting off federal highway funding.³¹¹

2.1.5.2 Motor Vehicle Emissions Regulations

In the case of light duty vehicles, the Canadian emission standards are set-up to be in alignment with the U.S standards. The PM emission standards are mass based, and until

recently, there were only standards for diesel vehicles, with none for gasoline vehicles. The current standard for light duty gasoline and diesel vehicles in Canada is 80 mg/mile. These standards are enforceable, a new vehicle is not allowed to be sold in Canada without approval, and therefore must meet the standards.¹³

2.1.6 Particle Size Distribution

Aerosols are suspended particles (either solid or liquid droplets), and are made up of particles of various sizes, often with a range of 2 or more orders of magnitude. Since the effects of aerosols are dependent on the size of the particles, the distribution of sizes must be accurately characterized. To accomplish this, the entire size range is divided into smaller groups, so that the number of particles can be counted for that group. Each group has an upper and a lower size limit, and the upper size limit of each group is the same as the lower interval for the next larger group. If a particle size is that of a limit, belongs in the larger size group.¹⁷

Once the particles are counted for each size group, graphing techniques are used to compare the different groupings with accuracy. The number of particles in an interval is dependant on the size of the interval. To overcome distortions from comparing different interval widths, the number of particles in the interval is divided by the width of the interval, which gives particles/ μm for the y-axis. This correction allows different size intervals to be compared, and a normalized histogram is created by plotting the number of particles/unit of size interval versus the particle diameter. In this way, the area of each rectangle of the histogram is the number of particles for that size group, and once all these are added together, the total number of particles is determined.

To allow comparisons between different sample sizes, the histogram is further standardized by dividing the number of particles per unit size interval by the total number of particles. The plot then becomes the fraction of particles per unit of size interval. The area of these rectangles represents the fraction of particles in a size group, and the sum of the areas should add to 1.0.

Aerosols are infrequently represented by a normal distribution because these aerosols skew the distribution. Empirical studies have shown that lognormal distribution represents single-source aerosols, although there is no theoretical reason why this is so. The empirical data also indicates that the lognormal distribution works best when the ratio of the largest to the smallest particle diameter is greater than 10.

The lognormal distribution follows the same principle as the histograms discussed previously. In this case, the plot becomes the number of particles divided by the log of the particle size interval ($dN/d(\log D_p)$) versus the log of particle diameter. The area under the curve remains the total number of particles.¹⁷

2.2 Review of Engine and Emission Control Technology Used in Motor Vehicles

“There has been debate about whether gasoline vehicles emit more particles, though less mass, than diesel vehicles, and whether new-technology direct-injection diesel engines emit more particles than their older technology counterparts.”²⁴

All vehicles have the same basic components, which power the car. If the airflow path is followed from its initial intake to the exhaust, it passes from the intake manifold to the engine where fuel is added, and from there it passes through the exhaust gas after-treatment to the tailpipe. The engine is also connected to the transmission, which takes the energy produced from the engine and translates it into the turning of the wheels.

These components directly influence the composition of the exhaust, so they are of the most concern when examining different vehicles.

2.2.1 Engines

Engine operating conditions can influence the particles emitted in motor vehicle engine exhaust. The air/fuel ratio (A/F) is the mass of air divided by the mass of fuel. In theory, if the actual A/F is equal to the stoichiometric A/F (giving an equivalence ratio ϕ of 1.0) then there is enough air for all the fuel to combust. There is no particle formation when all the fuel combusts, since all carbon is converted to CO_2 , all hydrogen to H_2O and all sulfur to SO_2 . This does not always occur as the theory indicates, since the air and the fuel are not always perfectly mixed when exposed to the heat. If there is not enough or too much oxygen in the combustion region, combustion cannot occur, which leads to unburned or partially burned fuel.

Engine design also affects all aspects of particulate matter emissions, including quantity, the size and the mass. The multi-port fuel injected spark ignition gasoline engine is known to emit less soot, on a mass basis, than compression ignition diesel engines, which explains why the diesel engine has been studied more extensively. Even though the multi-port fuel injected spark ignition engine emits less mass, this does not mean that they are better engines on a nanoparticle count basis. Engines that produce a large amount of volatile material, but low soot concentrations have been found to show more particle nucleation and growth than engines that produce the same amounts of volatile material and more soot. This is supported by figure 5, which shows the change in saturation ratio at different dilution ratios for high and low soot-producing engine. The saturation ratio increases much more when there is low soot, which is optimal for

nucleation to occur.²³ This conclusion was based on different diesel engines, but it is possible that the same conclusion can be extended to apply to gasoline engines.

Figure 5: Saturation Ratio vs. Dilution Ratio for High and Low Soot Engines²³

2.2.1.1 Multi-Port Fuel Injected Spark Ignition Gasoline

The air and fuel that enter the multi-port fuel injected spark ignition engine are mixed prior to entering the cylinder by a fuel injection system. Once the air and fuel enter the engine and follow the cycle to the compression stroke, a spark ignites the fuel, as in the basic four-cycle engine.

As discussed in section 2.1.1, organic particulates (including soot) and sulfates are the two main categories of particles emitted from the MPFI-SI engine. Sulfates are formed

from the sulfur present in the gasoline oxidizing to SO_2 and then SO_3 , which combines with water at low temperatures to form sulfuric acid aerosol. These emissions are higher with an oxidation catalyst than a three way catalyst because the former provides an oxidation mechanism for SO_2 (formed in the engine cylinder from sulfur) to convert to SO_3 .¹⁶

Since the fuel and the air are pre-mixed, the SI engine operates with an equivalence ratio of approximately 1.0, but there are still instances of the incomplete burning of the fuel. The main sources are bulk and wall quenching and crevices in the engine. From here, the organic particulates can form by any number of mechanisms discussed in section 2.1.1.

2.2.1.2 Direct Injection Diesel

Direct injection technology for diesel engines is well established. Air is injected into the engine and compressed and then fuel is injected into the compressed air, and ignites from the high temperature created by the compression, rather than using a spark.

The main particles from diesel engines are soot particles where some organic compounds have absorbed. Both the fuel and the lubrication oil can contribute to the organic component of the particulate matter, however, the concentration of soot particles from the engine is highest in the fuel spray, where the mixture is rich.⁹ Diesel engines tend to operate quite lean (excess oxygen) in an attempt to ensure complete combustion, which does not always work. During injection, regions develop that are fuel-rich and oxygen deficient, and the temperature and pressure is high so the fuel pyrolyzes, or starts to break down, before it has a chance to mix with air and burn properly. This pyrolysis leads to the formation of carbonaceous soot particles. Unburned or partially burned fuel

can condense onto the particles, or the particles can agglomerate, which increases their size and mass.³ Once injection has ceased and mixing occurs, the soot concentrations decrease.¹⁶

In previous years, the focus of diesel engine design was on reducing the mass of diesel particulate emitted. Now, studies are starting to indicate that the new designs have lower mass emissions, but have more particles that fall into the nanoparticle range.²⁰

2.2.1.3 Direct Injection Gasoline

For gasoline-fuelled engines, this technology is a recent development. The fuel is injected as a liquid under high pressure directly into the cylinder, but the engine requires a spark plug to ignite the air-fuel mixture. Since the fuel is injected directly into the cylinder, the engine can run leaner than possible with conventional fuel injected gasoline engines. Better control over fuelling is obtained, resulting in improved fuel economy.

The possibilities for particulate matter formation are similar to both the diesel and the gasoline engines.

2.2.1.4 Electric Hybrid Engines

Hybrid Electric Vehicles have two parts: an energy conversion section (which usually uses two or more technologies) and an energy storage part.⁴⁵ Most current models of hybrid electric vehicle consist of a heat engine and an electric motor. In the parallel hybrid, the electric motor and the heat engine are both connected to the transmission and both can contribute power to turn the wheels. In a series hybrid, the electric motor is used to power the transmission. The heat engine is used to turn a

generator to charge the batteries, which power the electric motor, or to power the electric motor directly.²⁷

The gasoline engine on the electric hybrid is a small version of the multi-port fuel injected spark ignition engine. The electric motor has the ability to draw energy from the batteries to power the car, or return energy to the batteries, and slow the car down.²⁷

The particulate matter emitted from the electric hybrid is a result of the use of the multi-port fuel injected spark ignition engine. This means they originate from the same areas as the traditional multi-port fuel injected spark ignition engine. By using the electric motor during the drive cycle where the emissions would otherwise be high, the particles should be reduced to concentrations that are present during the stable driving periods.

2.2.2 Emissions Controls

The different engines are not the only component that affects the tailpipe emissions. Each vehicle is also equipped with some form of emissions control technology.

2.2.2.1 Catalytic Converter

The catalytic converter is an important piece of emissions control technology. It is responsible for reducing the amounts of NO_x , hydrocarbons and carbon monoxide. The idea behind this involves the use of a catalyst to aid in converting these chemicals into their less harmful counterparts, N_2 , H_2O and CO_2 .

The three-way catalytic converter has two stages; the first is a reduction reaction, which converts the NO_x to N_2 . The second stage is an oxidation reaction, which converts the hydrocarbons and carbon monoxide to carbon dioxide. The oxidation catalytic

converter is similar to the second stage of the three-way catalytic converter. It only works on carbon monoxide and hydrocarbons, and is unable to reduce the NO_x concentrations. The oxidation catalytic converter also causes particle problems with the sulfur in fuel. The sulfur can be oxidized to SO_2 and SO_3 , which later combine with water vapour to form sulfuric acid aerosols.¹⁶

In the case of either catalytic converter, the oxidation of hydrocarbons reduces the possibility of the hydrocarbons nucleating, condensing or adsorbing, which lowers the particle concentration and mass.

2.2.2.2 Exhaust Gas Re-circulation

The exhaust gas re-circulation control is mainly used to reduce NO_x emissions, by taking 5% of exhaust gas and returning it to the intake manifold. NO_x forms at high temperatures in the presence of excess oxygen. By adding exhaust gas to the mixture, the peak temperature is reduced and there is less oxygen for the nitrogen to combine with. This also maintains the air/fuel ratio, so the hydrocarbon and carbon monoxide concentrations do not increase.

2.2.2.3 Particle Filters

Particle filters are emissions control devices used on diesel engines. They operate by removing particles through surface and deep bed filtration. The trapped particles are removed from the filters through thermal regeneration. This regeneration process is carefully balanced between the soot being captured and the soot being removed (through oxidation). This regeneration is induced by increasing the exhaust gas temperature or lowering the soot ignition temperature with a catalyst. The solid particles are easily controlled with this filter, but the non-solid particulate may not be affected.⁷

The optimum characteristics that a filter system requires are high filtration efficiency, high operating temperature, resistance to material effects from the high temperatures and possible presence of metal oxides in the particulate matter. Ceramics have emerged as a good material that satisfies these requirements fairly well. The two main uses of the ceramics are wall-flow monoliths force the gas through porous walls, made of ceramic, or ceramic as fibers, which are made into filter cartridges.⁷

The second concern with particulate filters is the regeneration method. There are two main methods of regeneration, either by reducing the soot combustion temperature with a catalyst, or increasing the temperature of the exhaust gas through heating. If a catalyst is used, the regeneration occurs during periods of high exhaust gas temperature. If the exhaust gas is heated, the regeneration occurs during these periods.⁷

2.3 Particle Size Measurement

Particle size and the distribution of particle sizes are measured with various instruments, depending on the size range of interest. The Electrical Low Pressure Impactor (ELPI) and the Scanning Mobility Particle Sizer (SMPS) have emerged as instrumental techniques capable of particle size discrimination in the size range of interest for motor vehicle exhaust emissions. The SMPS measures from 5 nm to 1000 nm while the ELPI measures from 29 nm to 10000 nm. By using both instruments, a range from 5 nm to 10 μm is reached, which covers most particles of concern from a human health perspective. The method used to separate the particles and determine the sizes is the main operational difference between these instruments. The ELPI separates the particles into size ranges based on aerodynamic diameter, while the SMPS separates them based on electrical mobility related diameter. While ELPI operates as both the size

discriminating device and counter in different size ranges, the SMPS requires a Condensation Particle Counter (CPC) to provide the counting capabilities. The operational principles of these 3 instruments are discussed below, while the specific details of their deployment in this study are presented in the next chapter.

2.3.1 Electrical Low Pressure Impactor (ELPI)

2.3.1.1 Theory

The ELPI measures airborne particle size distribution in the size range of 0.03 – 10 μm . The instrument, shown in figure 6, has three main components: a corona charger, a low-pressure cascade impactor and a multi-channel electrometer.

Figure 6: ELPI Unit⁵

The vacuum pump on the ELPI draws the sample in, which first passes through the charger, from which the particles exit with an electrical charge. The charge is created by a corona discharge that is controlled to ensure the particles gain a positive charge that is

high enough so that they are detected easily. The discharge is a high number of gas ions capable of transferring their charge to the particles. The corona also acts as a small electrostatic precipitator, and eliminates very large particles as well as those below 20 nm.

Next, the particles enter a cascade impactor, which classifies them according to their size. An impactor is a device with two plates, which are parallel to one another, with a small nozzle through one of the plates. The sample enters through the nozzle, and flows between the plates. Particles that are too large to make the turn hit the collection plate (the second plate), as in figure 7.

Figure 7: Impactor⁶

The cut diameter is the size of particles collected with 50% efficiency. The cascade impactor has 13 of these plates (called stages), so that various particle sizes are quantified at one time. The highest stage has a cut diameter of 10 μm and the lowest stage has a cut diameter of 0.03 μm . The stages of the impactor are insulated electrically and each stage is connected individually to an electrometer current amplifier. Once the particle hits the

collection plate of a stage, its charge produces an electrical current, which is amplified and measured. Each stage has its own channel, and the current value of a channel is directly proportional to the number of particles collected, therefore, a large current means a higher number of particles and thus, a larger particle concentration in the particular size range. The current values are converted to an aerodynamic size distribution using particle size dependent relations describing the properties of the charger and the impactor stages.⁶

Since the ELPI operates on the principle of charging particles to count, it is necessary for the particles to enter the ELPI with no charge. It is possible that the particles are exiting the vehicle already charged, so a neutralizer can be used between the diluter and the ELPI to return the aerosol to a Boltzman neutral charge distribution.³²

Figure 8: Model 3012 Aerosol Neutralizer³²

The Model 3012 Aerosol Neutralizer, shown in figure 8, uses 2 millicuries of Krypton-85 to produce positive and negative ions that collide with the oppositely charged particles, and neutralize them. Figure 9 shows the equilibrium values, that, given enough time, the neutralizer will reduce the charge level on the aerosol particles. Notably, not all of the particles end up neutral, there is still a small percentage with a charge, but this ensures that the exhaust is exiting with a known amount of charge.³²

It is especially important to neutralize particles that start with a positive polarity before entering the ELPI. If this is not done, the particles will have a higher than expected charge when the particles leave the charger. In addition, since the corona discharger also operates as an electrostatic precipitator, if the particles have an overly large positive charge, large numbers of particles will be precipitated out.⁶

Figure 9: Distribution of Charges on Aerosol Particles³²

The 90% of the 0.1 μm particles and 15% of the 1.0 μm particles are neutralized

2.3.1.2 Data Collection and Presentation

As the sampling occurs, the ELPI program sends instantaneous output of the collected data to an external computer. The program has the capability of displaying the data as it arrives, in various distributions specified by the operator, as well as the operation status of the ELPI. The distributions are current (fA), number (1/cm³),

diameter ($\mu\text{m}/\text{cm}^3$), area ($\mu\text{m}^2/\text{cm}^3$), volume ($\mu\text{m}^3/\text{cm}^3$), and mass (mg/m^3). The data is stored as current data, which is the raw data from the ELPI, all the other distributions are calculated from it. To calculate the other distributions, a conversion vector is used for each stage. The following equations were used in the ELPI program to calculate the number distribution for this study.

$$[dN] = [C_i] \times \left[\frac{1}{X_i \times D_i} \right]$$

where,

$[dN]$ = calculated number distribution ($1/\text{cm}^3$)

$[C_i]$ = current distribution collected from the ELPI (fA)

$\left[\frac{1}{X_i \times D_i} \right]$ = conversion vector

X_i = charger efficiency defined by the manufacturer

D_i = midpoint diameter

As discussed earlier in this chapter, aerosol distributions are often represented in the $(1/\log(D_p))$ mode, which divides the distribution by the logarithmic width of the stage.

$$\left[\frac{dN}{d \log(D_p)} \right] = [dN] \times \left[\frac{1}{d \log(D_p)} \right]$$

where,

$\left[\frac{1}{d \log(D_p)} \right]$ = inverse log width of stage

$\left[\frac{dN}{d \log(D_p)} \right]$ = number distribution $\left[\frac{1}{d \log(D_p)} \right]$ mode ($1/\text{cm}^3$)

The ELPI program also contains within it a data file filter program, which converts the stored data to a specified distribution, as well as formatting it for various database programs. This allows the operator to change the current data to a mass, number, diameter, area or volume distribution, calculated as discussed above.⁶

2.3.1.3 Errors and Maintenance

- Zeroing

The ELPI uses current electrometers to count the particles, and these need to be zeroed before each test. Initially, the ELPI should be turned on for about an hour to warm up, before it is zeroed. To zero, either initially, or between tests, the flush pump is turned on, which sends filtered air through the ELPI charger and impactor. Once the filtered air has had a chance to flush out any remaining particles, the instrument zero is turned on, and all channels are zeroed. If the instrument is zeroed properly, for any given range that the instrument is set at, the current values when nothing is running should appear as shown in table 2. These values are the background currents (noise) that appear because the instrument is very sensitive.⁶

Table 2: Current Values with the Flush Pump On⁶

Range (fA)	Current (fA)
10 000	1
40 000	2
100 000	5
400 000	5

- Impactor Loading

Long collection periods, or high particle concentration gases can cause the properties of the collection plate to alter as particles cover its surface. Particle bounce is one over-

load effect. Particles that normally impact on a collection plate bounce off, possibly leaving part of their charge behind or collecting more charge, and re-enter the gas flow to affect further stages.⁶

Another effect from particle over-load is particle filtration. This occurs when the gas penetrates the fluffy bed of particles present on an impactor stage, and some small particles are filtered out. This is the opposite effect of particle bounce, particles do not travel far enough, rather than traveling too far, and deposit their charge on the wrong stage.¹² There is also the problem of re-entrainment, meaning particles that have already impacted upon one stage may re-enter the gas stream from the impact of other particles hitting the stage. The ELPI has an alarm that is triggered if the set value for total collected mass is reached, as well as a display to indicate the percent reached at any given second.⁶

When the total collected mass is approaching the alarm value, the ELPI should be cleaned, to ensure all the particles that impact on the collection plate are counted once. To clean the ELPI, the stages are removed and put in a solution of isopropanol and water in an ultrasonic cleaner for 0.5 hours, while the Teflon insulators are rinsed with isopropanol and allowed to air-dry. Once the ELPI is re-assembled, the warning system is re-set.⁶

- Induced Current

An induced current is created from the image charge effect of small particles passing through the upper stages of the ELPI. As the charge approaches the conducting surface, the conductor produces an image of the object in front of it, which results in a positive peak. Once the particle leaves the stage, a negative peak is displayed. If the conditions

are ideal, the positive and negative peaks cancel each other out. Often, the aerosol concentration changes rapidly and the output does not display equal but opposite current peaks, shown in figure 10.⁶

This phenomenon is worsened if the small particles are overcharged, which happens if they leave the tailpipe with a charge. It is minimized by the use of the neutralizer discussed above.⁶

Figure 10: Induced Current Peaks⁶

Top: Ideal response of a stage to the small charged particles going through the stage

Bottom: Measurement of real induced currents

2.3.2 Condensation Particle Counter (CPC)

2.3.2.1 Theory

The CPC unit in figure 11, is a model 3025A continuous flow, condensation particle counter that measures ultrafine particles, with 50% detection at 3 nm and 90% detection at 5 nm.

Figure 11: Model 3025A CPC³⁴

The theory behind the CPC is based on heterogeneous condensation, so the particles are enlarged when vapor condenses on them to form easily detected particles. When the gas stream enters the CPC, it is divided into aerosol flow and sheath flow, with bypass flow if the CPC is operating in high flow mode. The pump in the CPC always pumps 1500 cm³/min, so during high flow mode, it draws the 1500 cm³/min into the inlet, and 1200 cm³/min becomes the bypass flow. During low flow mode only 300 cm³/min enter the inlet, the rest is from a second inlet, which draws in the rest of the 1500 cm³/min. The

sheath flow is filtered and passes over heated liquid, where it becomes saturated with vapor. The aerosol and sheath flows rejoin in a condenser where they are cooled by thermal diffusion and the vapor around the particles reach a point where they condense onto the particles in the aerosol flow. This point occurs when the vapor becomes supersaturated, as measured by the saturation ratio. The saturation ratio is defined as the actual vapor partial pressure divided by the saturation vapor partial pressure. The vapor does not condense randomly onto any particle; it only works for particles if they are large enough. The minimum particle size that acts as a condensation nucleus is inversely proportional to the saturation ratio (and is called the Kelvin diameter).³⁴

The droplets enter the next phase, consisting of a lighted volume and a photo-detector. When the particles interact with the light they scatter it, the photo-detector receives it and converts it into electrical pulses, which are counted. The intensity of the electrical pulses determines the particle concentration.

The CPC uses two methods to count particles, one for concentrations below 10,000/cm³, and one for concentrations between 10,000-100,000/cm³. There are two main counts to be concerned with from the CPC, the particle count and the time count. For low particle concentrations, the counter counts each individual particle pulse, and a continuous time (second by second). This means when one particle is in the viewing volume when another enters, the pulse extends and the counter is disabled (and therefore not counting particles), but the time is still counted. When the concentrations are between 10,000 – 100,000 particles/cm³, there are too many particles in the viewing volume at once, so the counter is often disabled. The difference in this scenario is the time counter also stops counting until the pulse exits the viewing volume. In this case,

the time counted is the time between particle pulses. The CPC also performs a total cumulative count of the number of particles, so long as the concentration remains below 100,000/cm³. If it exceeds this value, the display on the CPC flashes.³⁴

2.3.2.2 Data Collection and Presentation

The CPC unit has two storage possibilities for the collected data. It can store the data in the internal computer or it has the capability of linking to an external computer and storing the data as it is collected, in ASCII files. When an external computer is used, the CPC program presents the data collected as it changes each second.³⁴

2.3.2.3 Errors and Maintenance

- Coincidence

Since the electrical pulses created by the particles are counted one at a time, if a particle enters the lighted volume before the counter is done with the previous particles, it extends the pulse. This is called coincidence, and it causes the counter to take a longer amount of time to count the pulse and move on. Coincidence is one of the major problems with the CPC. At high concentrations (above 10,000/cm³) there is a good chance that two or more particles are in the viewing volume at once.³⁴

2.3.3 Scanning Mobility Particle Sizer (SMPS)

2.3.2.1 Theory

The SMPS consists of a model 3080 Classifier with a long differential mobility analyzer (DMA), shown in figure 12, and a model 3025A CPC, which measures the size distribution of sub-micrometer particles.

Figure 12: The Model 3080 Classifier with LDMA³³

As the aerosol progresses through the SMPS it passes several stages, the first of which is the impactor. The impactor operates the same way that the ELPI impactor works, and is present to keep the large particles out. Then the aerosol enters the electrostatic classifier, which contains an aerosol neutralizer that operates in the same manner as the neutralizer discussed with the ELPI. The particles mix and collide with bipolar ions, which give them the charge distribution shown in figure 9. Next, the aerosol enters the DMA, which is a cylinder with a collection rod inside. The aerosol enters at the top of the cylinder along with the sheath flow. The sheath flow makes up the inner core of the flow (flowing closest to the collection rod) and the aerosol makes the outer core (flowing closest to the

cylinder wall). Since the collector rod has a negative voltage, the positively charged particles are attracted to the rod and precipitate on it, based on their electrical mobility. Particles with a high electrical mobility precipitate high up on the collection rod, while those with low electrical mobility precipitate lower on the rod. To collect particles for counting, there is a slit in the rod, where particles within a narrow range of electrical mobility exit. To change the size range that is counted, the magnitude of the negative voltage on the collection rod changes, and therefore different sized particles are attracted to the rod where the exit hole is. Electrical mobility is inversely related to the diameter of the particles, so large particles have low electrical mobility, and they precipitate low on the collection rod. By increasing the voltage on the collection rod, it increases the attraction the particles have for the rod. This in turn, helps the large particles precipitate higher up on the rod, and the exiting particles increase in size. Once the particles leave the DMA they enter the CPC and are counted.³³

2.3.3.2 Data Collection and Presentation

All of the instruments used by the SMPS are hooked up to an external computer, which controls sample collection, storage and reporting. When a test begins, the CPC begins the sample. It counts the particles leaving the DMA and saves this data to the computer. It also controls the Differential Mobility Analyzer rod voltage, based on the scan parameters stored in the computer. During the up scan, the rod voltage is increasing and the CPC is counting particles leaving the DMA. The user enters boundaries for the size range the SMPS is measuring, the number of smaller groups (bins) that this size range is divided into, and the scan time. During the scan time for each bin the rod voltage remains constant, so the particles belonging to that bin exit the collection rod.

There is no particle counting during the down-scan, it allows time to bring the rod voltage back to its initial value, and for the sample in the DMA to return to initial conditions.

Once the raw counts are taken by the CPC, the computer divides the data into particle-size channels, based on their mobility and with the assumption that each particle has a single charge. Now the SMPS software is able to calculate the particle concentration in each size channel.³³

2.3.3.3 Errors and Maintenance

- Impactor Loading

Since the impactor nozzle on the SMPS operates in the same fashion as the impactor on the ELPI, it makes sense that the same losses, particle bounce, particle filtration and re-entrainment, can result in an impaction plate that is not clean. The recommended cleaning time for the impactor nozzle is after 5 –50 hours of operation to curb these effects.³³

Chapter 3: Experimental Methodology

The experimental part of this study was completed at Environment Canada's Emissions Research and Measurement Division laboratories, using the ELPI, SMPS and CPC, the first study at ERMD with these instruments. Eight vehicles were operated on a chassis dynamometer following common test cycles and the exhaust was sampled after dilution in a standard dilution tunnel or a mini-diluter set-up, which resembled work done by Maricq²⁴. This chapter presents the details of the procedures used in the testing program.

3.1 Vehicle Specifications

The vehicles tested were the Chrysler Intrepid, the Nissan Gloria, the Mercedes A170, the Mitsubishi Dion, the MicroCompact SmartCar, the Volkswagen Lupo, the Renault Megane, and the Toyota Prius. This selection gives a range of technologies with one gasoline multi-port fuel injected spark ignition vehicle, three direct injection gasoline vehicles, one electric hybrid and three direct injection diesel vehicles.

The Chrysler Intrepid was the gasoline multi-port fuel injected spark ignition engine used, and since it is available in the North American market, it has already met the standards set up for Canadian vehicles. In this study, it is used as a base to determine the proper test set-up and to examine to what degree different criteria affect the test results.

The other vehicle tested that is available in North America is the Toyota Prius, which is a parallel hybrid, with some series hybrid ideas incorporated. It uses the electric motor for light loads or when starting up from a stopped position. The electric motor is supplemented by battery power when the car is accelerating full-throttle. It uses the gasoline engine for normal, steady driving. When decelerating or breaking, the motor

recharges the batteries by acting as a generator, and the gasoline engine shuts off. This system works by using a transmission that either sends power to the wheels or to the electric generator, which controls the electric motor and re-charges the batteries.⁴

The remaining vehicles are European or Japanese vehicles, the Nissan Gloria, Mitsubishi Dion and the Renault Megane are direct injection gasoline vehicles, while the Mercedes A-170, MicroCompact SmartCar and Volkswagen Lupo are direct injection diesel vehicles.

A summary of vehicle specifications is shown in table 3.

Table 3: Vehicle Specifications

Vehicle	Curb Weight (kg)	Engine	Transmission	Fuel Economy (L/100 km)	Emissions Controls
Gasoline Pre-Mixed Spark Ignition					
Chrysler Intrepid	1563	~	4 speed automatic	Not available	EGR 3-way catalyst
Diesel Direct Injection					
2000 Mercedes A170	1095	1.7L turbocharged inline 4 cylinder 66 kW @ 4200 rpm 180 Nm @ 1600-3200 rpm	5 speed manual, automatic clutch	5.6 city 4.2 highway	Oxidation Catalyst
2000 MicroCompact SmartCar	730	0.8L turbocharged inline 3 cylinder 30 kW @ 4200 rpm 100 Nm @ 1800-2800 rpm	6 speed automatic, sequential gearbox	3.6 city 3.2 highway	Oxidation Catalyst
2000 Volkswagon Lupo		1.2L turbocharged inline 3 cylinder 45 kW @ 4000 rpm 140 Nm @ 1800-2400 rpm	5 speed automatic, sequential gearbox	3.4 city 2.7 highway	EGR Oxidation Catalyst
Gasoline Direct Injection					
2000 Nissan Gloria	1628	3.0L V6	4 speed automatic	Not available	3-way catalyst
2000 Renault Megane	1135	2.0L inline 4 cylinder 103kW @ 5500 rpm 200 Nm @ 4250 rpm	5 speed manual	8.7 city 6.1 highway	3-way catalyst
2000 Mitsubishi Dion	1390	2.0L inline 4 cylinder	4 speed automatic	Not available	3-way catalyst
Gasoline Pre-Mixed Spark Ignition - Electric Hybrid					
2000 Toyota Prius	1254	1.5L inline 4 cylinder 52 kW @ 4500 rpm 111 Nm @ 4200 rpm Electric Motor: Permanent magnet 33 kW @ 1040-5600 rpm 350 Nm @ 0-400 rpm Batteries: NiMH, 228 cells @ 1.2 V each	Electronically controlled continuously variable	4.5 city 4.6 highway	3-way catalyst

3.2 Fuels

Emissions Certification Diesel Fuel and Emissions Certification Gasoline (Indolene), are the two types of fuels used in this study. Both of these are low sulfur fuels, which are standard for use with the US Federal Test Procedure. The properties of the fuel are summarized in tables 4 and 5.

Table 4: Indolene Fuel Specifications

	Indolene
Octane (RON/MON)	99.3/90.5
Sulphur (ppm)	4
Lead (mg/L)	<1.0
Manganese (mg/L)	<0.5
RVP (psi)	9
Hydrocarbon Composition (vol %)	
Olefins	0.5
Aromatics	27
Saturates	72.5
Distillation (°C)	
IBP	33
10%	51.7
50%	106.6
90%	153.7
EP	196.7

Table 5: Certification Diesel Fuel Specifications

	Certification Diesel
Cetane Number	46.0
Sulphur (ppm)	380
Hydrocarbon Composition (vol %)	
Aromatics	26.9
Saturates	73.1
Distillation (°C)	
IBP	144
10%	175
50%	242
90%	276
EP	337

3.3 Experiment Set-up

Vehicle emissions are influenced by several factors: the driving pattern (the type of driving; city driving has a lot of stop and go driving, while highway driving is more steady state), the ambient conditions (such as the humidity or temperature outside), and

the vehicle specifications (such as the size of the vehicle, its age, the type of fuel it uses, the condition of the engine, and the maintenance of the emissions control equipment). This experiment was designed to test new vehicles (so the emissions control equipment should be at its peak) with different engine types and different fuels (since a specific engine type uses a specific fuel, they are dependent on one another, and neither were fixed), to see which technology emits the smallest amount of particulate matter.

In each test there are four main components to the set-up, the intake airflow rate measurement, the car, the dilution method, and the gas sampler and particle counting. This is shown in figure 13.

Figure 13: Main Components of Experimental Set-up

3.3.1 Vehicle Set-up

Each of the test vehicles was imported by Transport Canada for testing, prior to use with ERMD. All fuel remaining on-board from previous testing was removed and replaced with the proper test fuel, and at approximately 24 hours before testing, the vehicle was driven on a chassis dynamometer through the first two stages of the Federal Test Procedure, after which the vehicle was stored in the laboratory at 20 °C until testing. Each vehicle was installed on a chassis dynamometer and the exhaust was collected and analyzed as the vehicle was operated over the different test cycles.

3.3.2 Air Intake

The air intake flow rate was measured using a mass airflow sensor that contains a hot-wire anemometer. The mass airflow sensor was installed into the air intake of the vehicle by removing the air filter and inserting an intake tube that the airflow sensor was attached to. The lack of filter in the intake is compensated for by the laboratory itself, which uses filtered air and is therefore better than ambient air.

Figure 14: Hot Wire Anemometer⁹

The hot wire anemometer, shown in figure 14, is a common method of measuring fluid velocity. It is made of an exposed hot wire, which is heated by a constant current, or maintained at a constant temperature. The wire is placed in the fluid flow path, and the heat lost is measured, which is a function of the fluid velocity, based on convective theory. The volume flow rate of the fluid is also a function of this heat lost, if the area of flow remains constant.⁹

Before the vehicle tests began, the mass airflow sensor was calibrated at Environment Canada's ERMD. The calibration determined the equation that relates the voltage generated by the hot wire anemometer (measured by a voltmeter) and the fluid

flow rate, which is shown in appendix B. The voltage was logged by a computer using a data acquisition system, and the equation determined during calibration was applied to the data.

3.3.3 Chassis Dynamometer

The dynamometer allows for drive cycle simulation without the vehicle actually moving. The driver of the vehicle chooses a simulation to complete, and follows the trace on a video screen in-place in the vehicle. The video screen displays the selected test trace (speed versus time) as well as the changing speed of the vehicle, so that the driver can keep the vehicle speed that of the chosen test.

3.3.4 Test Cycles

There are several test cycles available for measuring vehicle emissions; the ones chosen best represent the different types of driving, because they include transient variations in speed and load. They are the cold start LA4, the hot start LA4, the highway fuel economy test, the New York City Cycle, the US06 and steady state driving at idle, 40 km/h, 60 km/h, and 100 km/h.

3.3.4.1 Cold Start and Hot Start LA4

The cold start and hot start, shown in figure 15, both follow the same driving cycle, with the only difference being the cold start allows the car to sit overnight before it is started and the hot start is started after the car is already warmed up.

Figure 15: Cold and Hot Start LA4 Driving Trace

The driving cycle represents city driving and the two cycles together give a picture of the excess emissions from a cold start. The cycle is 1370 seconds long and travels a total distance of 12 km with an average speed of 32 km/h⁸

The Federal Test Procedure (FTP) is made up of three phases that are a combination of the cold and hot start. The first 505 seconds of the cold start test corresponds to the cold transient phase of the FTP, while the last 865 seconds corresponds to the stabilized phase. The first 505 seconds of the hot start corresponds to the hot transient phase of the FTP.

3.3.4.2 Highway Fuel Economy Test

The Highway Fuel Economy Test (HWFET) shown in figure 16, represents highway driving conditions, and is generally used to determine the highway fuel economy of light duty vehicles. It is 765 s long and travels a total distance of 16.45 km with an average speed of 77.7 km/h.⁸

Figure 16: HWFET Driving Trace

3.3.4.3 New York City Cycle

Figure 17 shows the New York City Cycle, which represents city driving, simulating stop and go driving. It is a 600 s test, with a travel distance of 1.89 km, an average speed 11.4 km/h and a maximum speed of 44.6 km/h.⁸

Figure 17: NYCC Driving Trace

3.3.4.4 US06

The US06 (or Supplemental Federal Test Procedure: SFTP) is shown in figure 18. It represents aggressive driving at high speeds and rapid speed changes. The cycle is 600 s along a 12.8 km route with an average speed of 77.9 km/h and a maximum speed 129.2 km/h. The test was run with the trace clipped at 100 km/h due to the limitation of the dynamometer controller, meaning any speed above this is reduced down to 100 km/h.⁸

Figure 18: US06 Trace

3.3.4.5 Steady State

The steady state tests run for 20 minutes at a speed of either 40 km/h, 60 km/h, 100 km/h or idle. This test is used to compare different aspects of the experimental set-up. With the speed at a steady value, parameters such as temperature, dilution method, SMPS scan time and the quality of the dilution air, were varied to compare the changes in the output values.

3.3.5 Dilution Method

The tailpipe of each vehicle is connected to either a mini-diluter in series with a dilution tunnel (Constant Volume Sampler - CVS) or the dilution tunnel alone. The choice of dilution method is based on the expected raw exhaust PM concentration, since

the mini-diluter dilutes far less than the tunnel. Since the particle measurement instruments are sensitive to high particle concentrations and will overload, the diesel vehicles are sampled using the dilution tunnel, while the gasoline vehicles were tested with the mini-diluter.

Using either dilution method, the instruments take a sample of dilute exhaust from the dilution flow. However, in all cases, the gaseous emissions are determined based on CVS samples.

3.3.5.1 Tunnel Diluter

The intake air measurement is taken as the engine draws air in, which then passes through combustion chamber and is emitted at the tailpipe, along with combustion gases. The tailpipe emissions flow through a flexible hose, which is generally several meters in length, into the tunnel. The tunnel dilutes the sample to a constant volume of 750 scfm (which gives an average dilution ratio of approximately 50:1), by adding filtered ambient air into the mixture. A sample of diluted exhaust is taken by the instruments, while the rest is vented outside. The set-up of the tunnel is in figure 19.

Figure 19: Experiment Set-up with Tunnel Dilution

3.3.5.2 Mini-Diluter

The gasoline engines are sampled using the mini-diluter, since their particle emissions are much lower than the diesel engines. A similar set up is found in the study done in 2001 by Maricq²⁴, in which the exhaust gas is sampled from the tailpipe and diluted with either one or two Dekati diluters, using N₂. However, in Maricq's²⁴ set-up a second diluter is used (maintained at room temperature), for diesel vehicles, instead of the tunnel set-up previously discussed.

The air flows through the car to the tailpipe following the same method as the tunnel set-up. Once the exhaust gas exits the tailpipe, it flows through a short connection pipe (less than 0.5 m in length). From the connecting pipe, a sample is drawn into the mini-diluter from the suction the injection of dilution air causes, while the rest exits through the CVS where it is exhausted out the stack. So long as the sample pressure remains constant, the mini-diluter dilutes the exhaust in a constant 7 to 1 ratio, so for every volume of exhaust entering the mini-diluter, 7 volumes of gas leave the mini-diluter.

From the mini-diluter, the diluter exhaust is sampled by the particle counting instruments while the excess is directed back to the pipe leading to the tunnel, so that a constant pressure is maintained during sampling.

Figure 20: Experiment Set-up with Mini-Diluter

Although the manufacturer of the mini-diluter specifies the dilution ratio at 7:1, later studies at ERMD lead to the discovery that the actual dilution ratio is 7.8:1. The data in this study was not corrected using the 7.8:1 dilution ratio, so the actual concentrations using the mini-diluter are approximately 10% higher than the results discussed in the present work. For future studies, this problem was corrected by replacing the curved probes, used to equalize the pressure of the sample, to straight ones.

Rather than using ambient air as the diluter gas, either nitrogen or compressed air is used, since they are both 'cleaner', with no particles. The mini-diluter also has a heating element to allow it to be heated, thus eliminating water condensation inside the diluter.

Both the tunnel and the mini-diluter are valid methods of diluting the sample, but they each represent different conditions. The exhaust exits the tailpipe into a heated flex pipe (120 °C) where it travels for several seconds and is then diluted with ambient temperature air. The mini-diluter is representative of the particles as they are when they leave the tailpipe, before outside conditions play a role. The exhaust exits the tailpipe into the mini-diluter, which is heated to resemble the tailpipe. A portion of the exhaust goes immediately into each of the particle size measurement instruments previously discussed in Chapter 2.

3.3.6 Summary of Vehicles, Test Cycles and Dilution Methods

Each vehicle tested represents different vehicle design, mainly with the use of different engine technologies. To compare all of these, a set of tests were defined which give a full picture of each vehicles capabilities with respect to particulate matter emissions. Each vehicle was tested using the tests and dilution methods that best suited that particular vehicle, and these are outlined in Appendix C. The Chrysler Intrepid is a multi-port fuel injected spark ignition engine fueled with indolene, the only multi-port fuel injected spark ignition engine tested. As the only vehicle tested which is available for mass-market in North America, it is used as the standard for the testing. Using the Intrepid, the tunnel and the mini-diluter are compared, as well as dilution temperature, dilution air quality, and SMPS scan parameters. The results from the SMPS, the CPC

and the ELPI are also compared, to determine if the instruments are giving similar results.

Using the information gathered from the Intrepid, the rest of the vehicles are tested.

The test schedule designed allowed for each vehicle to be tested for a two-day period, so the vehicles were compared under a variety of driving conditions. Each day the following test cycles were completed: cold start LA4, hot start LA4, HWFET, NYCC, US06, Steady State (Idle), Steady State (60 km/h), and Steady state (100 km/h). All of the vehicles followed the test schedule, with the exception of a few.

The Mercedes A-Class is a diesel vehicle, which was tested with both the tunnel and the mini-diluter under all conditions, to determine whether the particle counting instruments could support the testing of diesel vehicles with the mini-diluter. The US06 was left out of testing since the ELPI overloaded and required cleaning during the test schedule using the mini-diluter. With the negative results of this test, the rest of the diesel vehicles were tested using only the tunnel.

The Nissan Gloria is a gasoline direct injection vehicle, which was tested with only three test cycles, due to the short time the vehicle was in the lab. The majority of driving conditions are represented by the cold start, hot start and HWFET, so the best possible information was gathered under this timeframe.

The Volkswagen Lupo is a diesel vehicle, which was tested under all test cycles using the dilution tunnel, but the intake air data was not gathered, without which correction for dilution volume is impossible, so the data is not used for any further purpose.

3.4 Particle Measuring Instrument Corrections

3.4.1 ELPI

In most of the tests, the ELPI data usually contains one, or possibly more stages that would not zero. This was noted during each test, and the resulting plot using these stages tends to have a high peak around whichever stage was not zeroed. If this stage remains in the plots, it overwhelms the other data points, since the concentration is so much higher, shown in figure 21.

Figure 21: ELPI data with all stages

In figure 21, the data presented is one of the scenarios studied later on for the effect of a neutralizer on the data. The actual test is not important, but the high concentration

point in the third stage is something to note. The point causes a large y-axis scale, which in turn makes all the other data points appear as zero. For this reason, stages were omitted from the plot if they did not zero. Figure 22 shows the difference in the appearance of the plot without stage 3.

Figure 22: ELPI Data without Stage 3

Following the study the ELPI was taken apart, and it was discovered that one of the Teflon insulators was carrying a static charge. Since the ELPI was cleaned each day, this insulator was moved from stage to stage, which caused different stages to have a zeroing problem. The static problem was corrected for future studies by implementing a revised cleaning and assembly procedure. There was also a problem specifically with stage 3 because the wiring for that stage was not attached properly, which caused the stage to

show constant errors. Since the third stage consistently did not zero throughout the entire testing period, it is eliminated from all further data analysis.

3.4.2 CPC

Reviewing the CPC data, there are many instances where there is a zero concentration value, followed by a very large concentration value, and another zero value, an example of which is in table 6. The time step usually shows a repeat of the same second over the three concentration values. There are also various instances when the time skips several minutes of data. This seems to indicate what the CPC manual terms a coincidence, shown in the following table. As discussed in chapter 2, coincidence occurs when a particle enters the viewing volume before the previous particle has exited, which paralyzes the counter.

Table 6: Coincidence in the CPC data

Time	Concentration (particles/cc)
14:08:16	246
14:08:17	193.2
14:08:18	201.4
14:08:19	209.4
14:10:13	0
14:10:13	28466.8
14:10:14	0
14:10:15	204.2
14:10:16	211.2
14:10:17	183

Plotting the CPC data from the Chrysler Intrepid at 60 km/h, with all the coincidence values present, the plot in figure 23 resembles a straight line with spikes at different intervals.

Figure 23: CPC data with Coincidence

The spikes range in value from 100 000 particles/cc to 250 000 particles/cc. This is out of range (the CPC has a particle concentration cap of 10^5 particles/cc) for either of the counting methods the CPC utilizes, which indicates that the spikes are coincidence occurrences. Eliminating this data, as invalid, the rest of the data is better represented in a plot, as in figure 24.

Figure 24: CPC Data After Coincidence was Eliminated

Figure 24 still shows incidences of spiking, although they are smaller, and remain within the range the CPC can count. For example, around the 600-second mark there are a series of spikes that decrease to zero and then spike to some average value. Since there should be no zero concentrations, the hypothesis is this data corresponds to areas where the inlet flow rate was out of range. The inlet flow rate is set to $5 \text{ cm}^3/\text{s}$, and when the inlet flow exceeds this by $\pm 0.5 \text{ cm}^3/\text{s}$, the data is unreliable. Removing this data shows the final CPC values that the counter could manage, shown in figure 25.

Figure 25: CPC Data with all Extraneous Spikes Removed

There is also a spike present around 500 seconds, which is much higher than any other value, but it is not preceded and followed by zero concentration values, and there is no skipped time, so there is no reason to remove this point. It is believed that these spikes are real, and although the vehicle is under steady state conditions, the concentrations emitted do not have to be. With these problems in mind, the CPC data is always represented without the values indicating coincidence or values that indicate the flow rate is out of range. Any other spikes, which show no pattern in the data, are retained.

After the testing involving the Chrysler Intrepid was complete, the CPC was not used for several vehicles, to allow time for flow rate re-calibration. The data collected with

the CPC after re-calibration shows an improvement in coincidence events, as there were few incidences of missing time steps.

3.4.3 SMPS

Since the SMPS uses the CPC as a particle counter, it is also under the influence of the effects of coincidence. This effect is controlled since only one size range is counted at once. This means the number of particles entering the CPC is much lower when attached to the SMPS, and therefore the probability of coincidence is reduced.

Another issue to consider with the SMPS is using it in scan mode during transient testing, where the speed of the vehicle, hence the dilute exhaust sample composition, is changing with time. Since scan mode operates by changing which particle size range the SMPS is counting with time, the data collected must be de-convoluted to determine the number of particles that are collected at any given speed. The desired output from this de-convolution would report the size range scanned, with the corresponding concentration measured, and the power of the vehicle.

Before testing, the user must decide on the aerosol flow, the sheath flow and the impactor nozzle diameter. These parameters determine the overall size range the SMPS is going to scan. Based on the choices made in this study, the SMPS range was between 5.7 and 239 nm. During the test, the SMPS data from each scan is collected and saved separately, and reports the concentration every 1/10 of a second. These files group the particles into bins based on a channel resolution of 64 channels per decade of particle size. This resolution can be changed to 4, 8, 16, 32, or 64 when the data is put through the data processor. To get equal counting time in size bins that get larger as the particles get larger, the voltage during each scan changes exponentially with time.

Using a channel resolution of 64, a particle size range is counted for approximately 1.5 seconds in each 160-second scan, and the best available power around this time is determined (using the equation for power outlined in appendix B). By repeating this calculation for each of the seven 160-second scan, seven data points are generated for each size bin, which are then plotted.

Without using any complex data analysis, the data can be examined for a pattern by creating and comparing graphs. The Chrysler Intrepid is used during cold start, with no neutralizer and the mini-diluter at approximately 180 °C, the results are shown in figure 26 and 27.

Based on all previous research on particle formation in engine exhaust, acceleration is directly linked to the concentrations observed. Other than during start-up conditions, the major emissions of particles are expected during rapid speed changes (meaning high acceleration periods). Since power and acceleration are directly related, as the vehicle power increases, so should the number of particles emitted.

Figure 26: Particle Number(dN) as a function of Particle Size(D_p)(nm) and Vehicle Power

Figure 26 shows concentrations 1-2 orders of magnitude higher in the smallest particle concentrations, which is due to the initial cold start. Since the smallest particles are sampled first, they are the ones that will show the effects of a cold start. Further study into de-convoluting the SMPS data should use one of the other transient tests for an initial analysis, so the cold start data does not influence the results. Once a de-convolution process is determined, it can be applied to the cold start to see how the cold start influences the results.

Figure 27: Particle Number(dN) as a function of Particle Size(D_p)(nm) and Vehicle Power, Particle Number scaled to show finer detail (between 0 and 500 particle)

Figure 27 shows three instances of high concentrations around 120- 150 nm, which correspond to low power episodes (in each of these cases the power is negative). A negative power indicates that the vehicle is decelerating, so the particle concentrations should not be increasing. This does not indicate that there is a strong correlation between the power and particle number.

Since only one test was used to attempt this de-convolution, and there are only 7 data points for each particle size range, more data is necessary to create an accurate picture of how the concentration fluctuates during transient conditions. The data collected for this study is not sufficient to make a concrete conclusion about the de-convolution, and therefore, only the steady state SMPS data is used for the remainder of this study.

Currently, the SMPS is used during transient testing by running the SMPS in a single size mode, meaning it only counts one particle size range for the entire test. This gives a direct way to gather transient data from the SMPS. To get a size distribution from a particular vehicle for a particular transient test, several tests are needed, each examining a different size range. The other option is to run the test once using several instruments set to different size ranges. These methods are currently under study at Ford, but they are either time consuming or expensive or both, so extensive resources are needed.⁵⁷ Given the preliminary observations from the de-convolution, further research into using one SMPS and developing a program to de-convolute it may result in a good method of using SMPS data during transient tests.

3.5 The Effect of Quality of Dilution Air in the Tunnel

During normal driving, as exhaust exits a vehicle it is not diluted with particle free air. Since the tunnel uses ambient air for dilution, it can be used to study how the quality of dilution air effects the resulting particle concentrations. Figure 28 shows the various changes in set-up used to study these effects.

Figure 1: Tunnel Set-up

Top: Scenario 1, Scenario 2 and Scenario 3

Bottom: Scenario 4 and Scenario 5

To determine the effect of dilution air quality on the exhaust, the tunnel was set up with no vehicle attached, and different scenarios were devised where ambient air was allowed into the tunnel. This gives an idea of what concentrations of particles are in the tunnel without the exhaust data, in other words, background concentrations.

The regular test set-up used for all tunnel-diluted vehicles has the car is attached to a flex pipe, which is in turn attached to the tunnel, which has a HEPA filter to filter the dilution air. The tunnel also has several sampling ports (used for collecting dilution air samples from the tunnel) that are capped off so no air can enter. The tests designed to examine the effect of dilution air quality are as follows:

- Scenario 1 – This test corresponds to #1 in figure 28. The tunnel is closed off where the flex-pipe normally attaches. The HEPA filter is in place and the sampling ports are capped off. All airflow through the tunnel is HEPA filtered.
- Scenario 2 – This test corresponds to #2 in figure 28. The flex-pipe is attached to the tunnel and capped off where the vehicle would normally be. The HEPA filter is in place and the sampling ports are capped off. Suction draws ambient air in through the flex pipe.
- Scenario 3 – This test corresponds to #3 in figure 28. The flex-pipe is attached to the tunnel and capped off where the vehicle would normally be. The HEPA filter is in place, but the sampling ports are not capped, which causes a small additional leak, and reduces the suction on the flex pipe.
- Scenario 4 – This test corresponds to #4 in figure 28. The tunnel is closed off where the flex-pipe normally attaches. The HEPA filter is removed, so the air is only filtered through pleated filters, and the sampling ports are capped off.

- Scenario 5 – This test corresponds to # 5 in figure 28. The flex-pipe is attached to the tunnel and capped off where the vehicle would normally be. The HEPA filter is removed, so the air is only filtered through pleated filters, and the sampling ports are capped off. Suction draws ambient air in through the flex pipe.

The results from these tests from the ELPI, the SMPS and the CPC are shown in figures 29, 30 and 31 respectively.

Figure 29: The Effect of Dilution Air Quality on ELPI Data

Figure 30: The Effect of Dilution Air Quality on SMPS Data

Figure 31: The Effect of Dilution Air Quality on CPC Data

By comparing scenario 1 and 2 (with and without the flex-pipe respectively, with HEPA installed and sampling ports capped) from figures 29, 30 and 31, the conclusion can be drawn that by removing the flex-pipe the quality of dilution air improves. Scenarios 1 and 2 from the SMPS graph (figure 30) show that the majority of the particles allowed in by the flex-pipe are those less than ~50 nm. This is supported by the ELPI data in figure 29, at the small diameter end of the scale scenario 2 has far more particles than scenario 1, but as the particle diameters get larger, the concentrations of the two scenarios get closer together. This stands to reason, since the flex pipe is made of metal pieces that link to hold one another together, meaning there are spaces where ambient air can enter. These spaces are large enough to allow the small nanoparticles through, but filter out the larger particles.

Comparing scenarios 1 and 4 or 2 and 5, the difference the HEPA filter makes is displayed. Scenario 4 is scenario 1 (flex-pipe installed, sampling ports capped) with no HEPA filter, and scenario 5 is scenario 2 (no flex-pipe, sampling ports capped) with no HEPA filter. In all 3 graphs, both of these combinations indicate that the HEPA filter removes approximately one third to one-half of the particles.

Since the HEPA filter was always used, only two of the scenarios may mimic the background concentrations of the tunnel. Scenario 1, with no flex-pipe is the best-case scenario. This assumes that the vehicle's exhaust flowing through the flex-pipe completely relieves the flex-pipe of the suction that draws air in from outside through its links. The worst-case is scenario 2, with the flex-pipe installed. This assumes the vehicle relieves none of the suction on the flex-pipe to draw air in from outside through its links. These two scenarios will be used in the next section to determine the proper correction for the tunnel data.

3.6 Correction for Particle Concentrations Measured with the Dilution Tunnel

As shown in the previous section, the exhaust gas particle concentration is changing with the addition of ambient air. Since the tunnel uses filtered ambient air as its dilution gas, the particle concentrations measured in dilute exhaust in the dilution tunnel can be corrected for the effect of dilution as well as for the concentration of particles in the dilution air. In contrast, the concentrations measured with the mini-diluter are not subject to the correction for particles in the dilution air, as the dilution medium used with the mini-diluter is bottled nitrogen gas, assumed free from any particles. The final scenarios decided upon for comparison with the mini-diluter are as follows:

- Scenario 1 – The mini-diluter is used and the sample is corrected only for the dilution volume used. This assumes that the N₂ used for dilution is particle free.
- Scenario 2 – The tunnel is used and the sample is corrected only for the dilution volume used. This assumes that the HEPA is 100% effective, and all particles are filtered from the ambient air before entering the tunnel, and there is no leakage through the flex-pipe.
- Scenario 3 – The tunnel is used and the sample is corrected for both the dilution volume and the particle concentration in the dilution gas. This scenario uses the best-case data from the dilution air quality tests, in which the flex-pipe is removed.
- Scenario 4 – The tunnel is used and the sample is corrected for both the dilution volume and the particle concentration in the dilution gas. This scenario uses the worst-case data from the dilution air quality tests, in which the flex-pipe is installed, the HEPA filter is in-place and the sampling ports are capped.

To determine the relative merit of the correction scenarios, it is useful to compare data from the mini-dilution tunnel to that from the dilution with different correction approaches.

Scenarios 2, 3 and 4 are the various corrections employed on the tunnel data. The ELPI graphs in figure 32 and 33 indicate that the correction using the best-case background concentrations (scenario 3) brings the concentrations down from scenario 2, which only corrects for the dilution volume. However, it does not align the tunnel data with the mini-diluter data, it under-corrects the data before approximately 980 nm, after which it begins to overcorrect. The correction using worst-case background

concentrations (scenario 4) overcorrects the data through all the stages. The resulting concentrations from the correction in scenario 4 (the condition with the flex-pipe installed), are below zero throughout all stages. If this were truly the case, then the car is removing particles from the combustion air, which is not likely. This indicates that the condition with no car and nothing running is unable to mimic the conditions that occur when the car is running and the tunnel is diluting the exhaust. Without the car delivering exhaust to the flex pipe, there is a much stronger vacuum in the tunnel, which has more pull on the ambient air through leaks in the flex pipe, thus increasing the particle concentrations in the tunnel dilution air.

Figure 32: Mini-Diluter and Tunnel Dilution Correction Comparisons for ELPI Data

Figure 33: Enlarged View of Mini-Diluter and Tunnel Dilution Correction Comparisons for ELPI Data from 1000 to 10000 nm

From the SMPS graph in figures 34, it appears that SMPS and ELPI data do not support the same conclusions. Each of the tunnel correction scenarios from the SMPS are overlapping, to the point where they are identical to each other, and neither of the concentration corrected graphs fall below zero. Upon examination of figure 35, it appears that scenarios 3 and 4 begin to deviate from scenario 2 around 10 nm. This, along with the ELPI data, indicates that the particles allowed in by the flex-pipe are from the lower half of the ELPI size range, and the upper half of the SMPS range.

Figure 34: Mini-Diluter and Tunnel Dilution Correction Comparisons for SMPS Data

Figure 35: Enlarged View of Mini-Diluter and Tunnel Dilution Correction Comparisons for SMPS Data

The CPC data in figure 36 shows the various tunnel corrections indistinguishable from one another. Since the CPC collects far more particles than either the SMPS or the ELPI, with its range starting at 3 nm, concentration differences become overwhelmed with the broad range of the CPC, so all 3 tunnel scenarios appear as one plot.

Figure 36: Mini-Diluter and Tunnel Dilution Correction Comparisons for CPC Data

Given the above observations, that there is no way to determine the contribution in the tunnel of particles from dilution air under the conditions in which the car is actually running. Without a vehicle, the system is under vacuum of approximately 3-5 inches of water, which draws the air into the flex pipe. Once the vehicle attached to the tunnel and running, its exhaust flow reduces the suction, and the flex pipe draws in fewer particles. Further, there is no way of aligning the tunnel concentrations with the mini-diluter concentrations given the data available. The best approach is to examine the tunnel data available without a correction for particle concentrations contributed by the dilution air.

3.7 The Effect of Dilution Method

Now that the two dilution correction methods have been finalized, a comparison can be made between the tunnel and the mini-diluter. Since the tunnel is not corrected for

particle concentration in the dilution air and the mini-diluter is assumed to have a dilution particle concentration of zero, they should result in different concentration profiles.

To compare the two methods, each was tested during a 20-minute steady state cycle, traveling at 60 km/h with a Chrysler Intrepid, as well as with the Mercedes A-Class under the same conditions. Since the tunnel has no heater, its temperature is assumed around ambient temperature. The mini-diluter was kept at 30 °C so the two methods are on the same basis. The mini-diluter had a neutralizer installed, since all the steady state testing on the Intrepid used the neutralizer.

3.7.1 Gasoline Engine (Chrysler Intrepid)

An initial comparison of the mini-diluter and the tunnel using the CPC data in figure 37 shows the basic differences between the dilution methods. The tunnel concentrations are always higher than the mini-diluter concentrations. The CPC figure is a good depiction of the magnitude of difference between the mini-diluter and the tunnel, indicating there are fundamental differences between the diluted exhaust from the two instruments.

Figure 37: Dilution Method Comparison for CPC

The possible factors contributing to the differences in particle concentrations are as follows:

- Dilution Gas. The mini-diluter has a better chance of providing consistently particle free air. The tunnel uses ambient air that relies on a HEPA filter, which is unlikely to be 100% effective, and the particle concentration in the ambient air depends on laboratory conditions at that time.
- Time. The mini-diluter is relatively compact, with the total length from tailpipe to measurement instruments at approximately 1 metre. The tunnel is much longer, with a total length of several metres. This means that the particle have a longer residence time in the tunnel, causing such effects as coagulation,

adsorption, nucleation, condensation and diffusion. These result in the formation of new particles or particle deposition in the tunnel.

- Flex pipe. The mini-diluter was connected to the vehicle with one metal pipe, with no leaks. The tunnel was connected to the vehicle by the flex pipe, which from the discussion in the previous section, is known to allow unfiltered ambient air into the tunnel.

A similar study was performed by Maricq²⁴ during which he compared the different particle size distributions (given by an SMPS) resulting from dilution with either a tunnel, or a mini-diluter. His results showed that the tunnel and the mini-diluter had similar concentration values (less than an order of magnitude difference between them), however, he also observed a nanoparticle peak that occurred from the tunnel data in the 10-20 nm size range, three orders of magnitude higher than the mini-diluter concentrations. Maricq²⁴ determined that the transfer hose from the tailpipe to the tunnel played a significant role in the nanoparticle peaks resulting in the tunnel distribution. The transfer hose used in Maricq's²⁴ study was a silicone rubber hose, which does not have the same problems that are associated with the flex-pipe used in this study, however, both studies show that the method of connecting the tailpipe to the diluter can have a significant effect on the resulting concentrations.

The mini-diluter attempts to represent the exhaust particle concentration as it leaves the vehicle. The tunnel does not provide the same information, however, the approach has its own value because it attempts to show what happens when the exhaust leaves the tailpipe in real driving conditions, i.e. dilution with ambient air. Since the scope of this

study includes a comparison of different vehicles, a standard dilution method is required to compare them on equal footing.

3.7.2 Diesel Engine (Mercedes A-Class)

Although a standard dilution method is desirable, the mini-diluter is not a reasonable dilution method for all the vehicles, since its dilution capabilities are low (only 7:1 dilution ratio), meaning the tunnel is necessary for diesel vehicles. To check this, the first diesel vehicle tested was run with the mini-diluter, but the diluter over-loaded in the first half of the test day. To clean the diluter several times in one day is not feasible, so the tunnel is used for all diesel vehicles. This means that direct numerical comparisons cannot be made between the mini-diluter and the tunnel data (and therefore gasoline and diesel vehicles), but qualitative observations can link the vehicles performance based on the Mercedes A-170. By comparing the Mercedes to the gasoline vehicles (when it was run with the mini-diluter), a general idea of the difference in the two technologies is gained. Also, by comparing to other diesel vehicles (with the data from the tunnel test), these other diesels are also indirectly compared to the gasoline vehicles. For instance, if the Mercedes is compared to the Nissan and has fewer particles of a particular size range (as reported by the ELPI) and it is also compared to the Volkswagen and the Mercedes has more particles in that same size range, then it is concluded that the Volkswagen also has fewer particles than the Nissan. This will be discussed further in Chapter 4.

3.8 The Effect of Mini-Diluter Temperature

To determine whether the temperature of the mini-diluter effects the number concentration results as reported from the CPC, three different temperatures were used on the Chrysler Intrepid at a steady state of 60 km/h: 30-32 °C, 50 °C, and 180-190 °C. The

three plots, shown in figure 38, all fluctuate around 1000 particles/cc, although the lower temperatures have more variation and coincidence. Since coincidence indicates CPC overloading, and there was little coincidence at higher temperatures, the concentration decreases as temperature increases.

Figure 38: Temperature Effects on CPC Data

The sudden fluctuations at lower temperatures and increased incidence of coincidence may be a result of nucleation from the exhaust pipe to the instruments. Since the CPC operates on a principle of counting particles that are formed into droplets, the extra condensation droplets may interfere with the count. For this reason, as well as the temperature related dilution problems discussed in Chapter 2, this study uses a mini-diluter temperature of approximately 190 °C in all testing. Despite the problems associated with unheated dilution, the tunnel is maintained at ambient temperature.

However, since the average dilution ratio from the tunnel is around 50:1, it falls outside the dilution ratio range that Kittleson²¹ reported has the most effect on gas-to-particle conversions.

3.9 The Effect of a Neutralizer

As discussed in Chapter 2, a neutralizer can be used to remove charge present on aerosol particles so they enter the particle measurement instruments with a Boltzman neutral distribution. To examine the effect of a neutralizer on the exhaust data, two tests were done with and without the neutralizer, on the Chrysler Intrepid at a steady state of 60-km/h. The ELPI data is presented earlier in the discussion regarding ELPI data corrections (figure 22), while the SMPS and CPC graphs are in figures 39 and 40 respectively. The ELPI data shows a general trend of higher particle concentration when there is a neutralizer installed. This indicates that the particles are leaving the car with a charge, so when they enter the ELPI, their charge is neutralized and they are not all counted.

Figure 39: The Effect of a neutralizer on SMPS Data

The SMPS graph also indicates that the particles are leaving the vehicle with a charge. Since the SMPS has a neutralizer installed in it, the external neutralizer should not have much of an effect. However, the results with the neutralizer are 3 times the results without a neutralizer. It is possible that the diluted exhaust does not have a long enough residence time in the internal SMPS neutralizer, and therefore is still charged when it enters the classifier. The internal neutralizer in the SMPS is much smaller than the one used externally, so the external neutralizer allows for a longer residence time, giving the sample exhaust the expected Boltzman neutral distribution.

Figure 40: The Effect of a Neutralizer on CPC Data

In general, the CPC graph of particles/cc against time shows very similar overall concentrations for the two cases. The neutralizer has fewer large peaks, but both cases fluctuate around 1000 particles/cc. Since the CPC does not depend on the charge of the particles, the total number of particles counted in both cases is relatively equal, and there is no loss of particles.

The ELPI manual suggests the use of a neutralizer, and the data from this study supports this recommendation. However, due to the scheduling constraints of the instruments and the availability of the cars, analysis of the testing parameters (from the Intrepid data) was not complete when the cars were available, and so the assumption was made that the neutralizer was unnecessary for the tests, since it was not being used in other studies reported.

3.10 The Effect of SMPS Instrument Parameters

The length of time that the SMPS scans the particle range can be set to any chosen value. To test the different concentration values measured by changing the scan time, tests were run on an Intrepid at 60-km/h steady state for 20 minutes. Four scan times were studied: 160 seconds up and 20 seconds down, 140 seconds upscan, 40 seconds downscan, 110 seconds upscan, 10 seconds downscan and 50 seconds upscan, 10 seconds down scan.

The graph shown in figure 41, shows all of the plots remained in the same range, with similar shapes. Generally, the scan generating the highest values was the 110-second up and 10 second down scan and the lowest from the 50 second up and 10 second down scan. The 50 second up and 10 second down scan seems to miss the particle peak that occurs between 10 and 50 nm in all the other scans. Although the SMPS can accommodate a scan time as short as 30 seconds, Kittelson suggests that distortion occurs if the scan time is too short, and the optimal time lies between 2 and 4 minutes.²¹

In general, the longer the actual sampling time, the more accurate the results are, so the manufacturer of the SMPS recommends a minimum down-scan time of 10 seconds and a minimum up-scan time of 50 seconds. A longer scan allows more time to get a representative sample, while a short scan might only get the peak values. For instance, if a sudden burst of particles was released, the longer scan collects the particles from the burst, but also the low points surrounding it. On the other hand, if the scan is too long, it does not give a good representation of the number of particles in each size range over time. If one scan is stretched over an entire drive cycle, the first particle range only represents the beginning of the cycle, since no data is collected after its turn in the scan.

Figure 41: The Effect of Scan Parameters on SMPS Data

The down-scan time is also important, although no counting is taking place. It is the time that allows the voltage to return to its base value. A longer scan time ensures that the voltage has had enough time to return, as well as giving any stray particles time to exit before the next scan. If the down scan time is too long, time is wasted with the analyzer waiting to take its next sample.

The results of this test were not available when the testing parameters were chosen for the rest of the study. The 160 second up scan and 20 second down scan lies in the range suggested by the manufacturer and by Kittelson²¹, so it became the standard used in the study.

3.11 A Comparison of Data from the ELPI and the CPC

The ELPI, along with counting particles in each size range, also counts the total number of particles per unit volume. This is used to compare the data from the ELPI to the CPC, for both the tunnel and the mini-diluter. The comparisons were made with the Chrysler Intrepid at 60-km/h steady state, for 20 minutes.

To compare these two instruments on a relevant level, the ELPI data file filter program was used to remove the third stage from the total. Once completed, the total particle concentrations from the ELPI and the CPC are in the same range, shown in figures 42 and 43. The ELPI fluctuates more, while the CPC is consistent around a single concentration.

Figure 42: ELPI vs. CPC using the Mini-Diluter (Chrysler Intrepid at 60 km/h)

Figure 43: ELPI vs. CPC using the Tunnel (Chrysler Intrepid at 60 km/h)

The graphs show ELPI values below the CPC counts, which can be accounted for by several factors:

- The ELPI does not measure particles between 3 and 30 nm or over 10 μm , while the CPC does, therefore the ELPI data should fall below the CPC totals, since the CPC counts a larger range of particles.
- The ELPI does not have a neutralizer installed, which, according to the neutralizer discussion indicates that the ELPI is missing a large fraction of the particles passing through it. The test shown in figure 42 above was repeated with a neutralizer and the results are below in figure 44. The ELPI data falls in line with the CPC data, and the average concentration for each of these is approximately 900 particles/cc.

Figure 44: CPC vs. ELPI with a Mini-Diluter and a Neutralizer

The discrepancies are more noticeable with the tunnel data, the mini-diluter shows ELPI concentrations close to those from the CPC. There are two possible explanations for the discrepancies in the tunnel data:

- Temperature. The low temperature of the tunnel can cause nucleation, while the higher temperature of the mini-diluter minimizes it. If condensation occurs, and the water droplets that enter the ELPI and the CPC fall into the 3 and 20 nm range, the ELPI does not detect them but the CPC does. The mini-diluter has less condensation so there are fewer particles between 3 nm and 20 nm, bringing the CPC and the ELPI data closer together.

- Flex-pipe. Although the low temperature of the tunnel causes condensation, the high dilution ratio prevents it. However, the flex-pipe is known to draw in nanoparticles, and since the CPC covers a larger range of nanoparticles than the ELPI, it should show higher concentrations.

3.12 A Comparison of Data from the ELPI and the SMPS

Since the lower end of the ELPI size range overlaps with the higher end of the SMPS size range, the concentrations from the two instruments can be compared. This was done for both the tunnel and the mini-diluter with the Intrepid at 60-km/h steady state, for 20 minutes.

One concern in comparing the raw exhaust frequency from the ELPI and the SMPS is the effective diameter used to obtain the size distribution in each instrument. The ELPI divides particles based on aerodynamic diameter, while the SMPS operates using electrical mobility based diameter. A study by Maricq²⁵ shows similar result by comparing the concentrations from the ELPI using the aerodynamic diameter and the particle mobility for the SMPS. However, if the aerodynamic diameter from the ELPI is converted to electrical mobility, the concentration results are further apart. For the comparison purposes of this study, no corrections will be made to the diameters. The comparison will use aerodynamic diameter for the ELPI and electrical mobility based diameter for the SMPS.

Since the volume passing through the particle counter on both the ELPI and the SMPS influences the number of particles counted, it is necessary to ensure the flow rates through both instruments are equal. The flow rate used through the ELPI is 10 L/min

while the flow rate through the SMPS is only 1.5 L/min. Changing the flow rate on the instruments is not an option since testing has been completed, so to correct this the SMPS data is scaled to a concentration that would result from a 10 L/min flow rate.

With these difficulties in mind, the ELPI and the SMPS operate on similar principles in that they each divide the particle stream into size ranges (referred to as stages by the ELPI and bins by the SMPS). The ELPI stages are much broader than the SMPS bins, they encompass a larger particle size range. For instance, the smallest stage of the ELPI has a range of particle sizes from 20 nm to 44 nm, while there are 5 SMPS bins that cover this same range. There are two ways to compare these data sets on the same basis: the ELPI data can be divided into SMPS bins, or the SMPS data can be grouped into ELPI stages. By dividing the ELPI stages, an assumption must be made that the total number of particles collected can be evenly distributed over each of the SMPS bins. Using the SMPS data grouped together requires no such assumption, and is therefore a more accurate representation. As an example (using fictional data), figure 45 shows how the two data sets can be compared, by grouping the SMPS bins into one ELPI stage.

Figure 45: One Stage from the ELPI and its corresponding SMPS Bins

The first bar represents 5 SMPS bins with the number of particles per micron collected indicated for each bin. The total number of particles for each bin is determined

by multiplying the number of particle per micron for each bin by the size of that bin. Summing these up gives the total number of particles collected for all five bins. These five bins correspond to one ELPI stage, which is represented by the second bar. For this bar, the total number of particles from the SMPS (15 particles) is divided by the entire size range (12 μm) of the stage giving 1.25 particles/micron, so that it can be compared to the data collected by the ELPI for this size range.

Figure 45 and the resulting example assume that the ELPI and the SMPS data are both represented by a number of particles per micron. However, this is not the case, the ELPI diameters are in microns and the SMPS diameters are in nanometers. The data for both are represented by $dN/d(\log D_p)$, in other words, the base of this is the difference in the logarithm of the diameters rather than the diameters themselves. This still means that the concentrations reported are normalized for the size of the bin, so to find the total number of particles in a particular bin, the SMPS data can be multiplied by the difference in the logarithm of the diameters, with the diameters in nanometers. Then, to put it on the same level as the ELPI data, this total is divided by the difference in the logarithm of the diameters for the ELPI stage, with these diameters in microns.

A further problem with the SMPS and ELPI data arises because the bins from the SMPS do not line up with the ELPI stages, as assumed in figure 45. Figure 46 shows how the first two ELPI stages align with the corresponding SMPS bins.

If an SMPS bin covers two ELPI stages, the bin is divided up by determining the percentage of the bin that covers each stage. For instance, the first ELPI stage has a range from 20 to 44 nm, while the SMPS bin with a diameter of 45.3 nm has a range from 42.28 nm to 48.82 nm. Therefore the percentage of the SMPS bin that is in the first

ELPI stage is $(44 \text{ nm} - 42.28 \text{ nm}) / (48.82 \text{ nm} - 42.28 \text{ nm})$ or 26 %. The remainder of the bin (74%) falls into the second ELPI stage. These percentages are applied to the number of particles from the SMPS bin, to divide them into each ELPI stage. This assumption may not be correct, but it is a simple method, which is sufficient for the purposes of this study.

Figure 46: SMPS Bins versus ELPI Stages

The data from the Chrysler Intrepid testing at a steady state of 60 km/h (mini-diluter with no neutralizer at a temperature of approximately 180 °C, and tunnel at ambient temperature) is used for the comparison, with the results shown in figures 47 and 48.

Figure 47: ELPI versus SMPS Comparison for the Mini-Diluter

Figure 48: ELPI versus SMPS Comparison for the Tunnel

In both cases, the SMPS has higher concentrations than the ELPI, which can be at least partially explained by the fact that the SMPS has a neutralizer and the ELPI does not. According to the discussion on the effects of a neutralizer, the neutralizer increases the number of particles detected by the instrument, which indicates the SMPS should have higher concentrations than the ELPI.

Maricq's²⁵ study used a steady state test at 60 km/h with a tunnel diluter, and showed much closer agreement between the ELPI and the SMPS, with the largest difference a factor of 2. However, Maricq's²⁵ study used a larger data sample for comparison, while this study uses only one day of data. Also, Maricq's²⁵ study is the first to observe that a comparison can be made using different effective diameters. Others have shown that

using electrical mobility based diameter and aerodynamic diameter does not given a good comparison.²¹

Both the ELPI and the SMPS have their strengths, the SMPS can sample very small nanoparticles, and the ELPI provides representative samples for both transient and steady state testing. The ELPI collects data for each particle size range every second giving 1200 seconds of data, while the SMPS collects several seconds of data for each particle size range every 180 seconds, giving between 10 and 60 seconds of data for each size range. Therefore, with more data points, the ELPI delivers a more accurate sampling of the concentrations resulting from the overall drive cycle.

3.13 Finalized Experiment Parameters

The instrument parameters investigated must be finalized before reviewing the data from other vehicles, so that a common plateau is used to compare all the vehicles. The following summary in table 7 shows the suggested parameters used for further study.

Table 7: Recommended Parameters for Further Study

Experimental Variable	Diesel or Gasoline
Dilution Method	Tunnel with no flex pipe or two Mini-Diluters
SMPS Scan Time	2-4 minutes
Neutralizer	Required
Diluter Temperature	Heating Required

Although these are the recommended parameters, the analysis of these parameters was not available when the decision was made for this study. The parameters in table 8 are those used in this study, and are based on other studies, which have used similar experimental designs.

Table 8: Experimental Parameters used in this Study

Experimental Variable	Diesel	Gasoline
Dilution Method	Tunnel with flex-pipe	Mini-Diluter
SMPS Scan Time	160s up 20s down	160s up 20s down
Neutralizer	None	None
Diluter Temperature	~20 °C	200 °C

Chapter 4: Vehicle Emissions Results

4.1 Mass Emission Rates

4.1.1 Filter Samples

Since the vehicles were on loan for short periods, testing time needed to be fully used. During testing, filters were set up to collect mass emissions and bags to collect gaseous emissions for chemical analysis, so a more complete picture of each vehicle was obtained.

The total particulate matter mass emissions with a cut point diameter less than 2.5 microns were collected from the dilute exhaust over each test. Once the dilute exhaust from the constant volume sampler (CVS), it entered a probe that collected the samples isokinetically and isoaxially. Following this, it entered a cyclone to remove particles greater than 2.5 microns in diameter, and then a manifold, which directed the exhaust to one of four filter holders. The first filter holder had a Teflon membrane filter collecting particulate matter for determining mass emissions, while the others were collecting data to analyze semi-volatile organic carbon, organic and elemental carbon, and detailed organic analysis. A dilution air sample was also collected each day, and analyzed for the same things.¹³

Mass emission rates of fine particulate matter ($PM_{2.5}$) were determined for each vehicle over each test, and are shown in figure 49. Vehicles are compared for the effects of driving cycle on emissions and different vehicle technologies are compared.¹³

Figure 49: $PM_{2.5}$ Mass Emission Rates¹³

Tier 1 Light Duty Vehicle Standards in Canada currently require a $PM_{2.5}$ level of 80 mg/mile, for both diesel and gasoline vehicles. Compliance to this emission rate is determined using the Federal Test Procedure (FTP). The FTP procedure is divided into three sections, or bags, which are weighted to get a composite emission rate. It consists of the cold start LA4 driving cycle as the cold transient period (bag 1 - first 505 seconds) and the stabilized period (bag 2 - last 865 seconds) of the FTP 75. The hot start LA4 repeats this same cycle after a soak of approximately 10 minutes. The hot transient of the FTP is the first 505 seconds of the hot start LA4 (bag 3). By using the results from the

cold start and the first 505 seconds of the hot start, the FTP results can be determined.

Table 9 compares the vehicles tested to the Canadian standards.¹³

Table 9: PM_{2.5} Mass Emission Rates (mg/mile, FTP) and Canadian LDV Standards¹³

Tier 1 LDV Standard	80.0
Diesel Vehicles	
Mercedes A170	111.0
MicroCompact SmartCar	39.0
Volkswagon Lupo	60.0
Gasoline Vehicles	
Mitsubishi Dion	25.0
Renault Megane	13.0
Nissan Gloria	9.0
Toyota Prius	5.7

These data show the general trend that diesel vehicles have higher PM mass emission rates followed by direct injection gasoline, and then the electric hybrid. Testing was not done on the Chrysler Intrepid for this, and therefore the multi-port fuel injected spark ignition gasoline engine cannot be included in this comparison.¹³

4.1.2 Particulate Matter Measurement Instruments

The particulate matter mass emissions can also be calculated from the data collected from the size instruments. By making some general assumptions of the properties of the particles, the number concentration data can be converted to mass data.

Difficulties arise in trying to compare this data to the mass emission rates from the filter samples. The ELPI and the CPC do not sample PM_{2.5} specifically, and the SMPS does not sample each size range continuously over the entire drive cycle. The CPC counts all the particles emitted that are larger than 3 nm, and the ELPI counts particles between 30 nm and 10 microns. The CPC data can best be used to estimate the total suspended particulate (TSP) concentrations, which cannot be compared with the filter

samples. The ELPI on the other hand, can estimate $PM_{2.5}$ by only using the results from certain stages, but the stages do not collect particles under 0.020 microns. Since it is the smallest particles that are missing, they do not affect the overall mass substantially, and this is the closest estimation to $PM_{2.5}$.

The ELPI data program filtered the 0.059-micron stage, the 0.102-micron stage and the 0.249-micron stage. The third stage was left out of the analysis for reasons already discussed in this thesis. The equations used to calculate the mass emission rate from the ELPI data are presented in appendix B, and the results are in table 10.

Table 10: $PM_{2.5}$ Mass Emission Rates (mg/mile) Determined using the Filters and ELPI

	Filters	ELPI
Diesel Vehicles		
Mercedes A170	111.0	54.8*
MicroCompact SmartCar	39.0	14.8*
Volkswagon Lupo	60.0	~
Gasoline Vehicles		
Mitsubishi Dion	25.0	5.96
Renault Megane	13.0	1.71
Nissan Gloria	9.0	~
Toyota Prius	5.7	0.007

* from tunnel diluter

Since the filter samples are collected for dilute exhaust, the dilution method plays a role in the mass of particles collected. Both the ELPI data and the filter samples were collected after dilution, so the influences of the diluter on the particles are the same for both methods. There are several possible reasons that the values obtained from the filters are very different from those obtained from the ELPI. First, the ELPI does not collect particles under 0.020 microns, so some particles are not accounted for in the mass

emission rate. However, since it is the nanoparticles that the ELPI does not collect, this accounts for very little of the total particle mass.

The ELPI also makes assumptions about some particle characteristics: the diameter and density of the particles. The particle density is assumed constant and equal to 1.0 for all particles collected. The diameter used for the calculations of mass emissions for each stage is the cut point diameter of that stage. It is possible that another diameter (such as the Stokes diameter) would better represent the majority of the particles present in each stage. The largest issue that affects the ELPI data is the lack of information about stage 3. Only four of the stages fall in the $PM_{2.5}$ category, so 25 % of the data is invalid, so only three stages were used.

The ELPI data supports the conclusion that the cars all fall under the Tier I light duty vehicle standard. However, with all of the errors and assumptions made, the values calculated from the ELPI data cannot be relied upon to reflect the mass of particles emitted from any vehicle.

4.2 Assessment of Test Methods

4.2.1 Dilution Methods

Since there are only two vehicles that were tested using both the tunnel and the mini-diluter, our data sample is small. In the case of the Mercedes A-170, the tunnel and the mini-diluter are not used at the same temperature, so the Chrysler Intrepid is the only vehicle that had a set of tests where all the variables were equal except for the diluter used. The mini-diluter and the tunnel were each tested once using a steady state drive cycle with a speed of 60 km/h, no neutralizer at ambient temperature, so there is nothing to measure whether the data from each of these is repeatable over a period of time.

Although all the conditions were the same, the mini-diluter and the tunnel are far apart in terms of number of particles, as shown in Chapter 3 in the comparison of the two diluters. Earlier studies²⁴ have shown that the tunnel data and the mini-diluter data do not coincide, reinforcing the conclusions reached here. “The details of the dilution and cooling process determine the relative amounts of material that adsorb or condense onto existing particles and nucleate to form new particles.”²⁰

Variables known to affect the particles collected include the material the sampling lines are constructed of, the dilution ratio, and the temperature of the dilution air.⁵³ Since the saturation ratio is a driving force behind many of the gas to particle conversions, there are several different critical saturation ratios in which some particle formation, growth, or loss will occur. If the temperature of the dilution air is much cooler than the exhaust air, the saturation ratio will rise because the gaseous particles will turn to vapour, and nucleation, condensation and thermophoresis can occur.

The dilution ratio can influence the mechanisms that are dependent on the particle surface area present. If the dilution ratio is large, and there are few particles present in the dilution air, adsorption, coagulation and condensation are minimized. However, the dilution ratio can also be linked to saturation ratio. Kittelson²¹ discovered that there is a range of critical dilution ratios between 5:1 and 50:1 that have the highest potential to cause a high saturation ratio, and therefore encourage nucleation when there are few particles present.

The construction of the diluter and the sampling lines can cause particles to be removed from the exhaust stream because of electrostatic deposition if the walls are made

of a material that is easily charged, such as Teflon. To reduce this, metal is suggested for connection lines.²³

In general, during sampling, the mechanisms that effect aerosol behaviour are condensed into two groups, particle-to-particle interactions and gas to particle conversion.²³ Both of these are visible to different extents in the dilution methods used in this study. The tunnel is a metal construction, so electrostatic deposition is minimized, but the connection pipe between the tailpipe and the tunnel is a flexible hose that allows unknown amounts of ambient air into the sample. Also, the exhaust exiting the tailpipe travels several meters, and is diluted by room temperature ambient air before reaching the PM measurement instruments. This means there is a long residence time in the tunnel, and a large temperature change, so any number of the mechanisms discussed in section 2.1.1 have the means to occur. Since the tunnel dilution ratio is high (approximately 50:1), the saturation ratio should be low, which should minimize these effects, however, the unknown amounts of particle filled ambient air allowed in through the flex pipe increases the particle concentration.

The exhaust traveling through the mini-diluter has a different path, it travels through a very short metal connection pipe (approximately 0.3 metres long), then enters the mini-diluter, which is held at a temperature of 200 °C, where it is diluted and flows immediately into the PM measurement instruments. The entire set-up from tailpipe to PM measurement is about 1 metre long. There is still a short travel time between the two ends, but it is significantly reduced, as is evident by the reduced particle concentrations with the mini-diluter.

Neither the tunnel nor the mini-diluter can represent what happens to the exhaust once it leaves the tailpipe under actual driving conditions, so they must be used to try to capture the emissions as they exit the tailpipe. There are two tasks for a diluter: provide sufficient dilution so the particle measurement instruments are not over-loaded and minimize the mechanisms that effect aerosol behaviour (gas to particle conversions and particle-to-particle interactions). Both of the cases presented here are unable to fulfill both criteria for all vehicles, so further study is necessary to determine a set-up that can.

4.2.2 Particulate Matter Measurement Instruments

The PM measurement instruments require some analysis to prove repeatability of the tests. The unfortunate problem with analyzing the data comes with the fact that there was no standard test run at certain intervals to allow for ease of analyzing the repeatability of the data. It is possible to analyze whether the instrument was able to repeat its measurements between day 1 and day 2 of each car, since the same tests were run for two days. However, it is not possible to analyze data at either end of the test schedule to determine whether the instrument is still producing the same quality of data.

4.2.2.1 ELPI

To make a repeatability comparison of the ELPI data, the average particle size distribution is compared for each drive cycle, for day 1 and day 2. The steady state 100 km/h test on the Mitsubishi Dion is presented in figure 50, as the best case, while the 60 km/h test on the Renault Megane is presented as the worst case, with the rest of the vehicle data found in appendix D.

To compare the repeatability from day to day the difference between the two maximum values from each day are compared. The difference between the two

maximum values for the Mitsubishi Dion is approximately 10%. A large difference between the two values do not indicate lack of repeatability, since a steady state driving cycle relies on the driver or a cruise control option to maintain a constant speed. In either case, steady state does not mean the resulting concentrations are uniform in time.

Figure 50: Mitsubishi Dion Total Particle Concentration for 100 km/h, ELPI

Not all the graphs are as consistent the Mitsubishi Dion shown. The Renault Megane data in figure 51, at 60 km/h showed a difference of 90% (or put another way, a tenfold difference) between maximum values observed on two consecutive days. The variability within the day also shows different patterns, with Day 1 distinguished by four very large peaks while Day 2 shows relatively uniform behaviour during the entire test.

Figure 51: Renault Megane Total Particle Concentration for 60 km/h, ELPI

Although there are several vehicles used to compare, each only has two sets of data, so a better measure of the repeatability might be the average difference between the maximum values from all the vehicles, which is approximately 50% for the ELPI.

4.2.2.2 SMPS

The repeatability of the SMPS data can be analyzed in similar fashion to the ELPI, by determining the total particle concentration for each size range. The 100-km/h test with the Mitsubishi Dion is presented in figure 52, with the others in appendix D.

Figure 52: Total Particle Concentration for Mitsubishi Dion, SMPS

The maximum difference in concentration is 95% for the Mitsubishi Dion data shown here. A minimum difference 18% also occurred using the Mitsubishi Dion, at idle, while the average difference from all vehicles was 54%.

4.2.2.3 CPC

The CPC counts the total number of particles per second, which is converted to a number concentration per volume since the volumetric flow rate through the instrument is also known. The behaviour of this number concentration with time can be used to compare repeatability from day to day. It can also serve to verify that the total particle counts do not remain constant during a steady state test. The graph presented in figure 53 uses the 100 km/h steady state test on the Mitsubishi Dion, and is representative of the results from all the vehicles.

Figure 53: Mitsubishi Dion Total Particle Concentration for 100 km/h

In graph in figure 52, it is difficult to see the differences between day 1 and 2, since they both follow the same distinct base concentration around which the fluctuations occur. The difference between maximum values is approximately 20%.

The three particle measurement instruments used in this study are highly sensitive pieces of equipment. This means any slight variation in the test procedure shows large differences in the particle concentration detected. Therefore, proving the instruments are repeatable with the limited amount of data available is difficult, and the variations between data sets may be 100% or more. The test conditions depend on the operator of the vehicle and the lab conditions from day to day, which can account for at least part of the variations.

4.3 Driving Conditions and Vehicles

4.3.1 Test Cycle Comparisons

To determine how the different test cycles affect the particulate emissions from each of the vehicles, the total or average number of particles was counted for each size range and plotted for the different test cycles. Since the Mitsubishi Dion has data for all the test cycles, it will be used in figures 54, 55 and 56, as the example for the discussion, while the rest of the vehicle results are in appendix E.

Figure 54: Steady State Tests on the Mitsubishi Dion with ELPI Data

The steady state ELPI data indicates that the number of particles generally decrease as the size of the particles increases, starting at 44 nm, the smallest particle size range the ELPI reports. There are some cases where a peak is observed at 100 nm.

Figure 55: Steady State Tests on the Mitsubishi Dion with SMPS Data

The SMPS data, which covers the 6- 200 nm range, shows the number of particles increasing to a peak around 60 nm range, after which it continues to decrease as the size gets larger.

The transient ELPI data in figure 56 also indicates that the number of particles generally decrease as the size of the particles increases, starting at 44 nm, the smallest particle size range the ELPI reports. There are some cases where a peak is observed at 100 nm.

Figure 56: Transient State Tests on the Mitsubishi Dion with ELPI Data

All of the data from each vehicle tends to support the same observations:

1. The particle size distribution from motor vehicle exhaust increases to a peak value around 10-100 nm, after which it begins to decrease.

Additional observations pertaining to the driving speed and cycle are:

1. The steady state comparisons indicate that the particle concentration is lowest under idle conditions. However, in one case, the Toyota Prius, the idle test showed higher concentrations than the 60 km/h test. Since the vehicle turns off after a few seconds of idling, this is probably due to the added suction on the flex-pipe from having no vehicle running. With the other vehicles, the 60 km/h and 100 km/h tests alternated which had the highest concentrations.

2. The transient comparisons show that a cold start results in significantly higher number of particles than the other test cycles. While this observation holds true for all but one of the vehicles, the relative ranking of the other test cycles depends on the vehicle.

Specifically, the ranking of drive cycles is shown in table 11.

Table 11: Drive Cycle Ranking for Various Vehicles

Vehicle	1	2	3	4	5
Mitsubishi Dion	CSLA4	HSLA4/HWFET/NYCC			US06
Renault Megane	CSLA4	HWFET	HSLA4		
Chrysler Intrepid	CSLA4	HSLA4			
Toyota Prius	CSLA4	NYCC	HSLA4	US06	HWFET
Nissan Gloria	HWFET	CSLA4	HSLA4		

(1 highest emission of particles, 5 lowest emission of particles)

4.3.2 Vehicle Comparisons

Since each car has its own technology, it also can have different scenarios during which it performs the best. To determine the best technology for particulate matter emissions under different conditions, a variety of tests were completed. All of the data are divided into tunnel and mini-diluter tests since a comparison cannot be made directly between them.

To compare the cars for each test cycle, a ranking of the vehicles based on their average number concentrations was developed. The method used to determine these ranks is discussed in appendix F. The ranking uses numbers from 1 to 6, with 1 representing the highest average number of particles, and 6 the lowest average number of particles. Since not all vehicles were tested using all drive cycles, there are not always

six ranks, if 3 cars were tested on a particular cycle, then 3 represents the lowest average number of particles. The overall vehicle rankings are shown in table 12.

Table 12: Overall Ranking of Each Vehicle from Average Number Concentrations

	Rank	Cold Start	Hot Start	HWFET	NYCC	US06	Idle	60 km/h	100 km/h
Mini-Diluter	1	Mercedes	Mercedes	Mercedes	Mercedes	Dion	Mercedes	Mercedes	Mercedes
	2	Megane	Dion	Megane	Dion	Megane	Dion	Dion	Dion
	3	Dion	Gloria	Dion	Megane	Prius	Megane	Megane	Megane
	4	Gloria	Megane	Gloria	Prius		Prius	Prius	Prius
	5	Intrepid	Intrepid	Prius				Intrepid	Intrepid
	6	Prius	Prius						
Tunnel	1	Mercedes	Mercedes	Mercedes					
	2	SmartCar	SmartCar	SmartCar					

From this table it is easy to see that the Mercedes A-170 shows the highest average number of particles in any driving conditions. The Renault Megane and the Mitsubishi Dion have a similar average number of particles so they fluctuate between position two and three, with the Nissan Gloria following behind. The Chrysler Intrepid and the Toyota Prius are similar in concentration and both show up with the lowest average number of particles. However, the Chrysler Intrepid and the Nissan Gloria were tested on so few drive cycles, their complete pictures are hard to determine, and their final positions could be quite different than shown here.

Since the Mercedes has data for both the tunnel and the mini-diluter, it can be used to compare the diesel vehicles to the gasoline and hybrid vehicles. The Mercedes consistently showed a higher average number of particles than the MicroCompact SmartCar. However, the concentrations from the SmartCar were fairly close to the Mercedes when both were tested with the tunnel, so most likely, it had worse

concentrations than any of the other vehicles tested with the mini-diluter, although this is uncertain.

Table 13: 2.5 μm Ranking of Each Vehicle from Average Number Concentrations

	Rank	Cold Start	Hot Start	HWFET	NYCC	US06	Idle	60 km/h	100 km/h
Mini-Diluter	1	Mercedes	Mercedes	Mercedes	Mercedes	Dion	Mercedes	Mercedes	Mercedes
	2	Dion*	Dion	Megane	Dion	Megane	Dion	Dion	Dion
	3	Megane*	Gloria	Dion	Megane	Prius	Megane	Megane	Megane
	4	Gloria	Megane	Gloria	Prius		Prius	Intrepid	Prius
	5	Intrepid	Intrepid	Prius				Prius	Intrepid
	6	Prius	Prius						
Tunnel	1	Mercedes	Mercedes	Mercedes					
	2	SmartCar	SmartCar	SmartCar					

The Dion and the Megane each appeared the same number of times in the second and third ranking. The Dion is ranked second because it ranked second with the smallest particles.

Since the smallest particles are the true concern of this study, the vehicles were ranked once more, using only the size ranges that were below 2.5 microns. These results do not change much from the overall ranking, as the only vehicles that change position are the Renault Megane and the Mitsubishi Dion and only in one instance, highlighted in table 13. This is expected, since they are the two vehicles with the closest concentrations.

Although the sample size is small, the general conclusion can be made that diesel direct injection vehicles have the highest particle number emission rates followed by gasoline direct injection vehicles, multi-port fuel injected spark ignition vehicles and electric hybrid vehicles. Lower fuel consumption and higher output are the major characteristics of the Gasoline Direct Injection (GDI) engine, making them attractive replacements for current multi-port fuel injected spark ignition vehicles. However, in

light of the above ranking, some of the benefits of fuel economy and power may be offset by higher particulate matter emissions. The electric hybrid provides a good alternative solution, since the particle concentrations are lower than the multi-port fuel injected spark ignition vehicle, and the fuel economy is better. If gasoline direct injection technology were to be used, to replace the direct injection diesel engine, it would provide a significant reduction in vehicle related particulate matter emissions.

4.4 Particle Concentrations vs. Drive Cycles

To examine how the drive cycle effects the particle concentration, number of total particles calculated from the ELPI was plotted against the drive cycle. This shows how the number concentrations vary under start-up conditions, sudden changes in speed, stopping and re-starting.

Figure 57 is a plot of the total particle concentration with the Nissan Gloria on the Cold Start LA4 drive cycle with the tunnel as a dilution method. It is the clearest example of the direct effects the drive cycle has on the particle concentration. Further examples of the other drive cycles are found in appendix G.

Figure 57: Total Number of Particles from the Nissan Gloria during Cold Start, ELPI

From the figure and appendix G, some general observations can be made about how driving conditions affect the total number of particles.

1. When the vehicle is initially started and running at idle, there is a sudden concentration spike.
2. When the speed becomes steady, the concentrations also become steady and drop to low values, even at high speeds.
3. When the speed suddenly increases the concentration also increases suddenly.

These observations support previous knowledge, which suggest the highest particle concentrations are emitted during start-up, particularly a cold start, and changes in speed cause changes in particle concentration.

Chapter 5: Conclusion and Recommendations

The conclusions for this study can be divided into two sections: conclusions from the experimental set-up and conclusions based on vehicle performance.

5.1 Experimental Set-up

The following conclusions are derived from the studies on the set-up of the experiment and various parameters examined during the first section of the study.

1. The temperature controlled mini-diluter minimizes the particle-to-particle or gas-to-particle reactions that can occur in the sampling train. This provides an accurate way of diluting from the tailpipe of a vehicle so that the particle concentrations measured reflect the size and concentration that are exhausted from the vehicle (although not representative of actual driving conditions).
2. The tunnel in this set-up has a high dilution ratio, which should minimize gas to particle conversion. However, the flex-pipe used distorts the particle concentrations by allowing unknown amounts of ambient air into the dilution tunnel. A more accurate method is required to connect the tailpipe of the vehicle to the tunnel before the tunnel measurements will reflect the size and concentrations of particles that are exhausted from the vehicle.
3. A set-up similar to the study performed by Marciq²⁴ would be beneficial for this type of work. The set-up adds a second mini-diluter immediately after the first to be used with diesel vehicles. This allows the dilution to occur immediately once the exhaust exits the tailpipe, as well as controls the diluter temperature. It gives the necessary dilution for comparisons between all fuel types, on one basis.

4. A 'real-world' simulation would provide a better understanding of what humans are actually exposed to, since particles from the exhaust can change with reactions in the atmosphere. This could be done with a wind tunnel, as has been previously studied by Marciq²⁴, or a set-up to study on-road emissions.
5. The SMPS is a very useful tool when dealing with steady state driving, as it can measure the nanoparticles that are of the most concern. The several options that currently allow it to be used under transient conditions (using several instruments scanning one bin each or using one instrument and running several tests with different bins scanned each test) are time consuming and costly. The proposed alternative requires further testing and study to provide the information necessary to determine whether de-convolution is a valid option. Positive results from this testing would mean one test and one SMPS would provide enough information to determine the particle size distribution under transient conditions.
6. The ELPI is able to reflect concentrations during any driving condition, making it useful for the type of study done here, and which makes it a likely choice for simulation of actual driving conditions. However, the size range that it is capable of dealing with is not small enough to provide a complete picture of the vehicle emissions. This requires a second instrument, either an SMPS or an ELPI designed with a broader sampling range.
7. The CPC often had flow rates that exceeded the allowed values and incidence of coincidence was common which makes CPC use limited in this study. Given the high concentrations that are sometimes detected from vehicle exhaust, the CPC is

best used to verify the results given by other instruments, rather than providing concrete data of its own.

8. To ensure the quality of the measurements made by the ELPI, the SMPS and the CPC, a standard steady state idle test on a specified vehicle should be performed at various time intervals during the testing schedule, so that the repeatability of the data is easily analyzed. This makes certain that the quality of the data is constant, and all the vehicles are being compared on the same basis. The use of the steady state idle test minimizes the effects of driver error.
9. The various drive cycles used in this study are good simulations of actual driving, but there is no way to reflect actual driving conditions in the lab in terms of the dilution history experienced by exhaust particles, and none of the instruments used can reflect the entire nanoparticle range under transient conditions. As an alternative to actual driving conditions, a series of steady state tests, using the SMPS as the main particle measurement instrument would provide the tailpipe concentrations for different vehicles and allow a comparison on that basis.
10. A neutralizer, although not used in this study with the ELPI, is necessary to ensure that the particles are not exiting the tailpipe with a charge, which influences the ELPI concentrations. This conclusion is supported by previous studies.⁴¹

The results of this study indicate that some simple modifications of the current study design would increase the accuracy of the results. A neutralizer should be used in conjunction with the ELPI to ensure the exhaust gas is neutral upon entering the instrument, and thereby ensuring that the exhaust particle concentration is correct. If a

mini-diluter is used for dilution, a second mini-diluter should be used for diesel vehicles, to provide adequate dilution, and to ensure all vehicles are compared on the same basis. In addition, the mini-diluter should be maintained at a temperature approaching that of the exhaust temperature, to minimize particle formation and losses in the sampling train. If the tunnel is used for dilution, the flex pipe should be replaced with a transfer hose constructed so as not to allow unknown amounts of ambient air into the exhaust.

Both the steady state and the transient drive cycles provide valuable information and are useful for this type of study, however, the choice of drive cycle is dependant on the capabilities of the particle measurement instruments. The ELPI can collect data equally well from all drive cycles, but cannot focus on the smallest nanoparticles. The SMPS can also be used for any of the drive cycles, but using the SMPS on the transient state cycles require considerable amounts of work to collect meaningful data.

5.2 Vehicle and Driving Cycle Study

The following conclusions reflect the second section of the study, focusing on several different engine technologies and how they relate to particulate matter emissions. This also includes general comments about driving cycles and particle concentrations.

1. The highest particle concentrations are found in the 10 to 100 nm range. Higher than 100 nm, the number of particles decreased as the particle size increased, in all driving conditions. In the highest size ranges, there were often very few particles present, and the instruments gave zero values.
2. The particle number profile tended to follow the shape of the driving cycle, so if the car accelerated, the particle count increased as well, and as the speed became steady, the concentration became steady. During a vehicle start, the number

concentration increased suddenly, and then leveled out, with the cold start as the worst start conditions.

3. The general ranking of the vehicles in terms of their nanoparticle emissions, from worst to best is: Mercedes A-170, MicroCompact SmartCar, Renault Megane = Mitsubishi Dion, Nissan Gloria, Chrysler Intrepid, and Toyota Prius. This relates to an engine comparison with the diesel engine as the worst, followed by the direct injection gasoline then the premixed multi-port fuel injected spark ignition gasoline and the electric hybrid. This reflects what is known of how the particle concentrations of diesel engines compare to gasoline engines.
4. From the remarks in 3, it can further be said that replacing the direct injection diesel engine with the electric hybrid engine would provide a significant decrease in vehicle related air pollution. Using the electric hybrid to replace the multi-port fuel injected spark ignition engine would provide a further reduction in air pollution. Since the particle concentrations from multi-port fuel injected spark ignition and electric hybrid were in the same range, and there was only one of each of these, further study is appropriate.

The results from the second section of this study serve to reinforce many observations made in previous studies regarding the size range in which the highest particle number concentrations are found, how driving conditions affect these particle number concentrations, and which engine types produce the highest particle number concentrations.

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Appendix A: Definitions

- **Accumulation Mode:** particles in the 0.1-0.3 μm diameter range.²⁰
- **Aerosol:** suspension of solid or liquid particles in air, although it is sometimes used to refer to the particles only.³⁰
- **Air-Fuel Ratio:** mass of air over the mass of fuel in the engine.
- **Ambient air:** that portion of the atmosphere, external to buildings, to which the general public has access.¹
- **Cetane Number:** measure of the how easily diesel fuel ignites (a high cetane number indicates a short time between fuel injection and ignition, meaning smoother combustion).
- **Coarse Particles:** Those particles that fall in the 2.5-10 μm diameter range.²⁰
- **Combustion:** the rapid oxidation of a gas or vapor at an elevated temperature.¹
- **Electrical Mobility:** the velocity of a particle with a given charge in an electric field.¹⁷
- **Exhaust Gas Re-circulation (EGR):** returns ~5% of the exhaust to the intake manifold, which displaces the A/F charge without affecting ratio, mainly reduces NO_x emissions.¹⁸
- **Fine Particles:** Particles with a diameter less than 2.5 μm .
- **Fly ash:** inorganic particles in a waste gas stream, which cannot be combusted.⁵
- **Inhalable Particles:** those with the potential of entering the respiratory tract including the head airways region.³⁰

- **Isoaxial Sampling:** a condition of sampling in which the direction of the airflow into the sampling probe inlet is the same as that of the unidirectional airflow being sampled.
- **Isokinetic Sampling:** a procedure to ensure that a representative sample of aerosol enters the inlet of a sampling tube when sampling from a moving aerosol stream.¹⁷
The condition of isoaxial sampling in which the mean velocity of the air entering the probe inlet is the same as the mean velocity of the unidirectional airflow at that location.
- **Motor Octane Number:** octane number determined under high speed, high load and high temperature situations.
- **Nanoparticles:** Particles that are less than 0.05 μm (50 nm) in diameter.²⁰
- **National Ambient Air Quality Standard (NAAQS):** The ambient air quality standard set by the EPA in order to safeguard human health (primary standards), and welfare (secondary standards).¹
- **Nuclei Mode:** particles in the 0.005-0.05 μm diameter range.²⁰
- **Octane Number:** measure of the resistance of gasoline to premature detonation (knock) when exposed to heat and pressure in a combustion engine.
- **Oxidation Catalyst:** oxidizes HC and CO (little effect on NO_x) with ~90% efficiency using platinum and/or palladium as a catalyst.¹⁸
- **PM₁₀:** a general term for airborne particles ten microns or less.
- **PM_{2.5}:** a general term for airborne particles 2.5 microns or less.
- **Primary Pollutant:** pollutant directly emitted from a source.

- **Regenerative Braking:** instead of just using the brakes to slow the car, the electric motor (in the hybrid) acts as a generator and charges the batteries while the car is slowing down.²⁷
- **Research Octane Number:** octane number determined under low speed and low engine load
- **Respirable Particles:** those with the potential of entering the gas-exchange region.³⁰
- **Secondary Pollutant:** pollutant formed in the atmosphere from reactions among other pollutants.
- **t-test:** assesses whether the means of two groups are statistically different from each other.
- **Thoracic Particles:** those with the potential of entering the tracheobronchial region (the lower respiratory tract, including the trachea, bronchi, and gas-exchange region)³⁰
- **Three-Way Catalyst:** oxidizes HC and CO and reduces NO_x at the same time.¹⁸
- **Total Suspended Particulate Matter:** solid or liquid particles that are of a size and configuration such that they remain suspended in the air.¹¹
- **Ultrafine Particles:** those with a diameter less than 0.1 μm.²⁰

Appendix B: Formulas and Derivations

- Dilution Correction:

Once the exhaust gas exits the tailpipe it travels through either a mini-diluter or a tunnel, to dilute the concentrations to those that are appropriate for the instruments to analyze. The data stored by the instruments are corrected for this dilution factor so that the final values represent the exhaust from the vehicle. To determine the particle concentration of the exhaust before dilution, a mass balance is performed on the diluter.

Figure 58: Mass Balance On the Diluter

Where C_e represents the particle number concentration from the tailpipe before dilution, C_s represents the particle number concentration that the instrument calculated after dilution, C_d is the particle number concentration in the dilution air, V_e is the volume of gas exiting the tailpipe, V_s is the sample volume, V_d is the dilution air volume, and $\#_e$ is the number of particles exiting the tailpipe. From this mass balance, several equations are formed;

$$V_s = V_e + V_d \quad (1)$$

Therefore,

$$V_d = V_s - V_e \quad (2)$$

Also,

$$\#_s = \#_e + \#_d \quad (3)$$

Since;

$$C_e = \frac{\#_e}{V_e} \quad (4a)$$

$$C_s = \frac{\#_s}{V_s} \quad (4b)$$

$$C_d = \frac{\#_d}{V_d} \quad (4c)$$

Equations 4a, b and c are rearranged and substituted into equation 3, which gives:

$$C_s \times V_s = C_e \times V_e + C_d \times V_d \quad (5)$$

Now, substitute equation 2 into equation 5:

$$C_s \times V_s = C_e \times V_e + (V_s - V_e) \times C_d \quad (6)$$

Solve equation 6 for C_e :

$$C_e = \frac{C_s \times V_s - (V_s - V_e) \times C_d}{V_e} \quad (7)$$

Finally,

$$C_e = \frac{V_s}{V_e} \times (C_s - C_d) + C_d \quad (8)$$

Since the mini-diluter has a 7:1 dilution ratio, each volume of raw exhaust is diluted to produce 7 volumes of dilute exhaust. It uses N_2 as its diluter gas, so there are no particles coming from the dilution air, this means:

$$C_d = 0$$

And,

$$\frac{V_s}{V_e} = \frac{7}{1}$$

So, equation 7 becomes:

$$C_e = 7C_s \quad (9)$$

So, to obtain the number concentration of the gas stream exiting the tailpipe, multiply the sample concentration in the dilute exhaust by 7.

On the other hand, the tunnel has a constant flow output of 750 scfm, which means V_s is constant, but V_s/V_e changes with time. Assuming the dilution air from the tunnel is filtered so no particles remain ($C_d = 0$), the correction equation becomes:

$$C_e = \frac{V_s \times C_s}{V_e} \quad (10)$$

$$C_e = \frac{750 \times C_s}{V_e} \quad (11)$$

The mini-diluter uses N_2 or compressed air to dilute the exhaust, so it is assumed that this does not add any particles to the gas stream, the correction for dilution air is sufficient. The tunnel uses ambient air that passes through a HEPA filter. Since the HEPA filter is not 100% efficient, assuming there are no particles is not an accurate assumption. The measured data for the tunnel includes some particles that came from the dilution stream, so equation 8 applies and becomes:

$$C_e = \frac{750}{V_e} \times (C_s - C_d) + C_d \quad (12)$$

To make the correction in equation 12, the particle concentration in the dilution air (C_d) is required. A study of the dilution air, and which dilution air measurement accurately reflects the testing, is needed to determine C_d .

- Weighted Composite Emission Rate from FTP:

$$W = \frac{0.43 \times m_1 + m_2 + 0.57 \times m_3}{D_1 + D_2}$$

W = Weighted Mass Emission Rate (mg/mile)

m_1 = Total Particle Mass from Phase 1 of FTP (mg)

m_2 = Total Particle Mass from Phase 2 of FTP (mg)

m_3 = Total Particle Mass from Phase 3 of FTP (mg)

D_1 = distance traveled during cold transient phase (bag 1)

= distance traveled during hot transient phase (bag 3)

D_2 = distance traveled during stabilized period (bag 2)

- Mass Emission Rate from ELPI:

The data from the ELPI can be converted to mg/m^3 by using the ELPI data file filter. The ELPI assumes a constant density of 1 g/cm^3 . To obtain a weighted composite mass emission rate to compare to the values from the FTP test, the cold start data from the ELPI was divided into two sections: the first 505 seconds and the last 865 seconds. The total mass from the first 505 seconds corresponds to bag 1 (cold transient phase) in the FTP calculations, while the last 865 seconds corresponds to bag 2 (stabilized phase). The first 505 seconds of the hot start corresponds to bag 3 (hot transient phase). From here, the weighted composite emission rate formula is used:

$$W = \frac{0.43 \times m_1 + m_2 + 0.57 \times m_3}{D_1 + D_2}$$

$D_1 + D_2$ = distance traveled = 7.5 miles

There are two separate ways to determine the total particle mass used in the weighted composite emission rate formula. For the mini-diluter the raw exhaust particle concentration and the intake air is measured every second, so the total particle mass is calculated as follows:

$$m_i = \sum_{t=0}^{t=T} (C_{raw})_t \times (V_{air})_t$$

m_i = total particle mass from phase i (mg)

$(C_{raw})_t$ = raw exhaust particle concentration at time t (mg/m³)

$(V_{air})_t$ = measured intake air at time t (m³)

Since the tunnel dilutes the raw exhaust to a constant volume of 750 scfm, the average dilute exhaust concentration can be used to calculate the total particle mass as follows:

$$m_i = V_T \times C_{dilute}$$

m_i = total particle mass from phase i (mg)

C_{dilute} = average dilute exhaust particle concentration (mg/m³)

V_T = total exhaust volume (m³)

where;

$$V_T = Q \times t_i \times k$$

Q = diluted exhaust flow = 750 scfm

t_i = length of phase i (min)

$k = \text{conversion factor} = 28.316 \times 10^{-3} \text{ m}^3/\text{scf}$

- Mass Air Flow Sensor Conversion from Voltage to Flow:

$$y = 3.1035 \times x^3 + 3.7121 \times x^2 + 7.709 \times x + 0.5248$$

$y = \text{Flow (scfm)}$

$x = \text{Voltage (volts)}$

This equation had an R^2 value of 0.9996, meaning 99.96% of the variation in the flow can be explained by the change in voltage, which indicates the equation is a good fit.

- Vehicle Power (P):

$$P = V_{avg} \times M_{gr.veh.} \times a$$

V_{avg} = average velocity of vehicle

$M_{gr.veh.}$ = gross vehicle mass

a = acceleration

Appendix C: Combinations of Vehicles, Test Cycles, Instruments and Dilution

Methods Used

Table 14: Chrysler Intrepid Data

		Diluter	Neutralizer	Temperature	ELPI	CPC	SMPS	Diluter	Neutralizer	Temperature	ELPI	CPC	SMPS
	Test	Chrysler Intrepid						Chrysler Intrepid					
Day 1	Cold Start LA4	M		190	Y	Y	Y	M	Y	50	*	*	*
	Hot Start LA 4	M		190	Y	*	*	M	Y	50	Y	Y	Y
	HWFET												
	NYCC												
	US06												
	Steady State (40 km/h)	M		190	Y	Y	Y						
	Steady State (60 km/h)	M	Y	190	Y	Y	Y	M	Y	30	Y	Y	Y
	Steady State (60 km/h)	M	Y	190	Y	Y	Y	M	Y	50	Y	Y	Y
Day 2	Cold Start LA4	M	Y	190	Y	Y	Y	M	Y	25	Y	Y	Y
	Hot Start LA 4	M	Y	190	Y	Y	Y	M	Y	25	Y	Y	Y
	HWFET												
	NYCC												
	US06												
	Steady State (40 km/h)												
	Steady State (60 km/h)	M	Y	190	Y	Y	Y	M		150	Y	Y	Y
	Steady State (60 km/h)	M	Y	190	Y	Y	Y	M	Y	190	Y	Y	Y

Table 15: Renault Megane and Further Chrysler Intrepid Data

		Diluter	Neutralizer	Temperature	ELPI	CPC	SMPS	Diluter	Neutralizer	Temperature	ELPI	CPC	SMPS
	Test	Chrysler Intrepid						Renault Megane					
Day 1	Cold Start LA4							M		190	Y	Y	Y
	Hot Start LA 4							M		190	Y	Y	Y
	HWFET							M		190	Y	Y	Y
	NYCC							M		190	Y	Y	Y
	US06							M		190	Y	Y	Y
	Steady State (Idle)							M		190	**	**	**
	Steady State (60 km/h)	T		25	Y	Y	Y	M		190	Y	Y	Y
	Steady State (100 km/h)							M		190	Y	Y	Y
Day 2	Cold Start LA4							M		190	Y	Y	Y
	Hot Start LA 4							M		190	Y	Y	Y
	HWFET							M		190	**	**	**
	NYCC							M		190	Y	Y	Y
	US06							M		190	Y	Y	Y
	Steady State (Idle)							M		190	Y	Y	Y
	Steady State (60 km/h)							M		190	Y	Y	Y
	Steady State (100 km/h)							M		190	Y	Y	Y

Table 16: Mitsubishi Dion and Microcompact SmartCar Data

		Diluter	Neutralizer	Temperature	ELPI	CPC	SMPS	Diluter	Neutralizer	Temperature	ELPI	CPC	SMPS
	Test	Mitsubishi Dion					MicroCompact SmartCar						
Day 1	Cold Start LA4	M		190	Y	Y	Y	T		25	Y		Y
	Hot Start LA 4	M		190	Y	**	Y	T		25	Y		Y
	HWFET	M		190	Y	Y	Y	T		25	Y		Y
	NYCC	M		190	Y	Y	Y	T		25	Y		Y
	US06	M		190	Y	Y	Y	T		25	*		*
	Steady State (Idle)	M		190	Y	Y	Y	T		25	Y		Y
	Steady State (60 km/h)	M		190	Y	Y	Y	T		25	Y		Y
	Steady State (100 km/h)	M		190	Y	Y	Y	T		25	Y		Y
Day 2	Cold Start LA4	M		190	Y	Y	Y	T		25	Y		Y
	Hot Start LA 4	M		190	Y	Y	Y	T		25	Y		Y
	HWFET	M		190	Y	Y	Y	T		25	Y		Y
	NYCC	M		190	Y	Y	Y	T		25	Y		Y
	US06	M		190	Y	Y	Y	T		25	*		*
	Steady State (Idle)	M		190	Y	Y	Y	T		25	Y		Y
	Steady State (60 km/h)	M		190	*	*	*	T		25	Y		Y
	Steady State (100 km/h)	M		190	Y	Y	Y	T		25	Y		Y

Table 17: Volkswagen Lupo and Mercedes A-170 Data

		Diluter	Neutralizer	Temperature	ELPI	CPC	SMPS	Diluter	Neutralizer	Temperature	ELPI	CPC	SMPS
	Test	Volkswagon Lupo						Mercedes A-170					
Day 1	Cold Start LA4	T		25	*	*	*	M		190	Y		Y
	Hot Start LA 4	T		25	*	*	*	M		190	Y		Y
	HWFET	T		25	*	*	*	M		190	Y		Y
	NYCC	T		25	*	*	*	M		190	Y		Y
	US06	T		25	*	*	*						
	Steady State (Idle)	T		25	*	*	*	M		190	**		**
	Steady State (60 km/h)	T		25	*	*	*	M		190	Y		Y
	Steady State (100 km/h)	T		25	*	*	*	M		190	Y		Y
Day 2	Cold Start LA4	T		25	*	*	*	T		25	Y		Y
	Hot Start LA 4	T		25	*	*	*	T		25	Y		Y
	HWFET	T		25	*	*	*	T		25	Y		Y
	NYCC	T		25	*	*	*	T		25	Y		Y
	US06	T		25	*	*	*	T		25	Y		Y
	Steady State (Idle)	T		25	*	*	*	T		25	Y		Y
	Steady State (60 km/h)	T		25	*	*	*	T		25	Y		Y
	Steady State (100 km/h)	T		25	*	*	*	T		25	**		**

Table 18: Nissan Gloria and Toyota Prius Data

		Diluter	Neutralizer	Temperature	ELPI	CPC	SMPS	Diluter	Neutralizer	Temperature	ELPI	CPC	SMPS
	Test	Nissan Gloria						Toyota Prius					
Day 1	Cold Start LA4	M		190	Y	Y	Y	M		190	Y	Y	Y
	Hot Start LA 4	M		190	Y	Y	Y	M		190	Y	Y	Y
	HWFET	M		190	Y	Y	Y	M		190	Y	Y	Y
	NYCC							M		190	Y	Y	Y
	US06							M		190	Y	Y	Y
	Steady State (Idle)							M		190	*	*	*
	Steady State (60 km/h)							M		190	Y	Y	Y
	Steady State (100 km/h)							M		190	**	**	**
Day 2	Cold Start LA4	M		190	Y	Y	Y	M		190	Y	Y	Y
	Hot Start LA 4	M		190	Y	Y	Y	M		190	Y	Y	Y
	HWFET	M		190	Y	Y	Y	M		190	Y	Y	Y
	NYCC							M		190	Y	Y	Y
	US06							M		190	Y	Y	Y
	Steady State (Idle)												
	Steady State (60 km/h)							M		190	Y	Y	Y
	Steady State (100 km/h)							M		190	Y	Y	Y

Legend:

- T Tunnel
- M Mini-Diluter
- Y Instrument used
- * Testing done, data not used
- ** Data used, possibly compromised

Appendix D: Repeatability of PM Measurement Data

This appendix is intended to give a better understanding of the procedure used for the study of the repeatability of the PM measurement data, and to present the data not appearing in the final report. If a graph is missing for a particular vehicle for certain tests, there was data missing from one of the two days. The Mercedes A-170 is not analyzed because different dilution is used from one day to the next. The Nissan Gloria is not analyzed because there was no steady state testing was done. The MicroCompact SmartCar was missing its steady state data, so no analysis is done on it.

- ELPI

Figure 59: Mitsubishi Dion Total Particle Concentration for Idle, ELPI

There is a 69% difference between the maximum values from day 1 and day 2

Figure 60: Mitsubishi Dion Total Particle Concentration for 60 km/h, ELPI

There is a 25% difference between the maximum values from day 1 and day 2

Figure 61: Chrysler Intrepid Total Particle Concentration for 100 km/h

There is a 20% difference between the maximum values from day 1 and day 2

Figure 62: Chrysler Intrepid Total Particle Concentration for 60 km/h

There is a 74% difference between the maximum values from day 1 and day 2

Figure 63: Renault Megane Total Particle Concentration for Idle

There is a 43% difference between the maximum values from day 1 and day 2

Figure 64: Toyota Prius Total Particle Concentration for 60 km/h

There is an 81% difference between the maximum values from day 1 and day 2

Figure 65: Toyota Prius Total Particle Concentration for 100 km/h

There is a 61% difference between the maximum values from day 1 and day 2

- SMPS

Figure 66: Total Particle Concentration vs. Particle Diameter (Mitsubishi Dion Idle)

There is an 18% difference between the maximum values from day 1 and day 2

Figure 67: Total Particle Concentration vs. Particle Diameter (Chrysler Intrepid 100km/h)

There is a 40% difference between the maximum values from day 1 and day 2

Figure 68: Total Particle Concentration vs. Particle Diameter (Chrysler Intrepid 60 km/h)

There is a 63% difference between the maximum values from day 1 and day 2

Figure 69: Total Particle Concentration vs. Particle Diameter (Renault Megane 100 km/h)

The difference between maximum values from day 1 and day 2 is 96%

Figure 70: Total Particle Concentration vs. Particle Diameter (Renault Megane 60 km/h)

There is a 55% difference between the maximum values from day 1 and day 2

Figure 71: Total Particle Concentration vs. Particle Diameter (Renault Megane Idle)

There is a 24% difference between the maximum values from day 1 and day 2

Figure 72: Total Particle Concentration vs. Particle Diameter (Toyota Prius 100 km/h)

There is a 45% difference between maximum values from day 1 and day 2

Figure 73: Total Particle Concentration vs. Particle Diameter (Toyota Prius 60 km/h)

There is a 46% difference between maximum values from day 1 and day 2

Appendix E: Particle Size Distributions

- Chrysler Intrepid

Figure 74: Steady State Test Cycle Comparisons for Chrysler Intrepid (ELPI)

Figure 75: Steady State Test Cycle Comparisons for Chrysler Intrepid (SMPS)

Figure 76: Transient Test Cycle Comparisons for Chrysler Intrepid (ELPI)

- Renault Megane

Figure 77: Steady State Comparisons for Renault Megane (ELPI)

Figure 78: Steady State Comparisons for Renault Megane (SMPS)

Figure 79: Transient Comparisons for Renault Megane (ELPI)

- Nissan Gloria

Figure 80: Transient Comparisons for Nissan Gloria (ELPI)

- Toyota Prius

Figure 81: Steady State Comparisons for Toyota Prius (ELPI)

Figure 82: Steady State Comparisons for Toyota Prius (SMPS)

Figure 83: Transient Comparisons for Toyota Prius (ELPI)

- Mercedes A-170

Figure 84: Steady State Comparisons for Mercedes A-170 with Mini-Diluter (ELPI)

Figure 85: Steady State Comparisons for Mercedes A-170 with Tunnel (ELPI)

Figure 86: Transient Comparisons for Mercedes A-170 with Mini-Diluter (ELPI)

Figure 87: Transient Comparisons for Mercedes A-170 with Tunnel (ELPI)

- MicroCompact SmartCar

Figure 88: Transient Comparisons for MicroCompact SmartCar (ELPI)

Appendix F: Vehicle Comparisons

This appendix is intended to explain how the vehicle rankings discussed in section 4.4 were determined. In theory, if the technologies perform equally, then the particle number concentrations in each drive cycle are equal. Since this is not the case, the maximum and average concentrations were determined using all available data, to attempt to rank the differences. For any particular vehicle, and within each driving cycle, the average number of particles collected in each size range should be equal, as well as the maximum number of particles in each size range. Table 19 shows the average concentration for the cold start LA4, for each size range.

Table 19: Average Raw Exhaust Particle Frequency from the Cold Start

Dp (μm)	Mini-Diluter						Tunnel	
	Chrysler Intrepid	Mitsubishi Dion	Nissan Gloria	Renault Megane	Mercedes A-170	Toyota Prius	MicroCompact SmartCar	Mercedes A-170
0.059	9.86E+05	8.89E+06	5.59E+06	6.01E+06	3.74E+07	1.58E+05	7.61E+07	1.09E+08
0.102	5.78E+05	1.11E+07	4.48E+06	1.08E+07	7.54E+07	5.63E+04	9.88E+07	1.82E+08
0.249	1.14E+05	4.01E+06	4.93E+05	3.06E+06	1.39E+07	6.04E+03	1.07E+07	1.45E+07
0.386	1.56E+04	9.74E+05	1.06E+05	8.57E+05	2.70E+06	1.55E+03	1.34E+06	2.87E+06
0.627	3.53E+03	1.91E+05	1.65E+04	2.09E+05	6.57E+05	3.94E+02	2.66E+05	1.29E+06
0.98	1.53E+03	4.99E+04	4.15E+03	6.12E+04	2.00E+05	1.86E+02	8.12E+04	2.19E+05
1.58	7.71E+02	1.34E+04	1.88E+03	2.09E+04	7.52E+04	6.46E+01	3.39E+04	7.45E+04
2.42	4.56E+02	7.13E+03	1.10E+03	1.13E+04	4.07E+04	3.64E+01	1.98E+04	3.75E+04
3.92	4.26E+02	7.24E+03	9.63E+02	1.09E+04	2.70E+04	2.37E+01	1.72E+04	2.99E+04
6.59	1.47E+02	4.27E+02	2.60E+02	3.06E+03	2.43E+04	9.80E-03	5.16E+03	1.11E+04
10.01	4.32E+02	7.34E+03	1.07E+03	1.14E+04	3.55E+04	2.41E+01	1.88E+04	3.35E+04

Within each particle size range, the vehicles can be ranked according to the average number of particles from this test. In comparing these values for each vehicle, a general idea of the best and worst vehicles (particle number wise) is developed. The ranking

system used in table 20 starts with 1 having the highest average number of particles, and ending with 6 as the lowest average number of particles. Since some of the test cycles were not performed on all vehicles, there are not always 6 ranks, if only 3 cars were tested then 3 is the lowest number of average particles.

Table 20: Ranking of Vehicles based on Average Raw Exhaust Particle Frequency from a Cold Start

Dp	Mini-Diluter						Tunnel	
	1	2	3	4	5	6	1	2
0.059	Mercedes	Dion	Megane	Gloria	Intrepid	Prius	Mercedes	SmartCar
0.102	Mercedes	Dion	Megane	Gloria	Intrepid	Prius	Mercedes	SmartCar
0.249	Mercedes	Dion	Megane	Gloria	Intrepid	Prius	Mercedes	SmartCar
0.386	Mercedes	Dion	Megane	Gloria	Intrepid	Prius	Mercedes	SmartCar
0.627	Mercedes	Megane	Dion	Gloria	Intrepid	Prius	Mercedes	SmartCar
0.98	Mercedes	Megane	Dion	Gloria	Intrepid	Prius	Mercedes	SmartCar
1.58	Mercedes	Megane	Dion	Gloria	Intrepid	Prius	Mercedes	SmartCar
2.42	Mercedes	Megane	Dion	Gloria	Intrepid	Prius	Mercedes	SmartCar
3.92	Mercedes	Megane	Dion	Gloria	Intrepid	Prius	Mercedes	SmartCar
6.59	Mercedes	Megane	Dion	Gloria	Intrepid	Prius	Mercedes	SmartCar
10.01	Mercedes	Megane	Dion	Gloria	Intrepid	Prius	Mercedes	SmartCar
Overall	Mercedes	Megane	Dion	Gloria	Intrepid	Prius	Mercedes	SmartCar

The overall ranking in this table is determined by giving the vehicle that appears most often in that column the rank for that column. Once the overall rank is collected, they can be compared for the different test cycles, shown in section 4.4.

Appendix G: Particle Concentration vs. Drive Cycles

- Cold Start LA4

Figure 89: Cold Start on the Chrysler Intrepid

Figure 90: Cold Start on the Mitsubishi Dion

Figures 89 and 90 show the high concentration spike resulting from the initial cold start of the Chrysler Intrepid and the Mitsubishi Dion respectively. In comparison, the hot start for the Mitsubishi Dion is shown in figure 91. Both graphs follow the driving trace, however, the hot start has approximately 1/3 the number of particles that the cold start has at start-up. The hot start for the Mercedes is also shown in figure 92. It has less of a spike during start-up, but its concentrations are higher throughout.

- Hot Start LA4

Figure 91: Hot Start on the Mitsubishi Dion

Figure 92: Hot Start on the Mercedes A-170

- HWFET

Figure 93: HWFET on the Mitsubishi Dion

Figure 94: HWFET on the Renault Megane

- NYCC

Figure 95: NYCC on the Mitsubishi Dion

Figure 96: NYCC on the Renault Megane

- US06

Figure 97: US06 on the Renault Megane

Figure 98: US06 on the Toyota Prius