Design and Characterization of a Diesel-aerosol Generating System

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Abstract

Airborne particles are considered to have significant effects on the human health and the concerns about the effects from ultrafine particles have risen during the latest years. The ultrafine particles in the atmosphere are considered to have their origin in combustion processes and dominantly from the traffic. This work has lead to the design and construction of a diesel aerosol generating system that can be used in human exposure studies and studies within the subject of aerosol aging. The system can be used to extract and dilute exhaust from light-duty vehicles, operating at idle mode, and lead the diluted exhausts to an exposure chamber.

The extraction and dilution system is a two stage dilution system that dilutes only a small part of the generated exhausts. The system has proven to give reproducible results and the dilution conditions were chosen in a way which is believed to resemble the dilution of exhausts in real world environments. Two cars were tested, a Volkswagen Passat and a Peugeot 307. The Peugeot was equipped with a diesel particulate filter. Because of the idling mode of the car a nucleation mode was not observed, only an accumulation mode. The number geometric mean particle diameters of this mode were within 93-96 nm for the VW Passat and about 71 nm for the Peugeot. These relatively large geometric mean values are explained by the idling condition of the car and the extra distance that the exhaust needs to be transported between the tail pipe and the primary dilution stage. Due to the low mass emissions from the Peugeot it could be clarified that a DPF-equipped car not suitable to use within health studies. The particle concentrations are too low. The VW Passat turned out to give high enough levels of particles and low enough levels of hazardous gases, such as CO and NOx.

During the future exposure studies it is desired to have a particle mass concentration that varies with time and where the mean concentration should be around 300 µg/m³. This level could be achieved with the system, together with the VW Passat, by turning the car on and off in pulses. However this method was assumed to result in smelly exhausts inside the chamber. During idling, and especially during the start, the engine may emit higher amounts of unburned fuel and other hydrocarbons. This could explain the smell. The smell turned out to be one of the major issues and could not be solved during the time period of this work.
**Abbreviations and symbols**

- Ø - Diameter
- µ - Deposition parameter
- C - Concentration
- CC - Cunningham factor
- C_{da} - Concentration of trace gas in ambient air
- C_{out} - Concentration out
- CPC - Condensation particle counter
- CVS - Constant volume sampler
- C_{w} - Concentration inside the chamber
- D - Diffusion coefficient
- d_{g} - Geometric mean diameter
- DMA - Differential mobility analyzer
- D_{p} - Particle diameter
- DPF - Diesel particulate filter
- DR - Dilution ratio
- F - Flow rate
- FEFD - Full exhaust flow dilution tunnel
- g - Gravity constant
- GMD - Geometric mean diameter
- GSD - Geometric standard deviation
- L - Tube length
- M - Molar mass
- N - Total number of particles
- n_{i} - Number of particles of size i
- P - Penetration ratio
\( P_d \) - Partial pressure

PDF - Primary dilution flow rate

PDR - Primary dilution ratio

PEFD - Partial exhaust dilution tunnel

POA - Primary organic aerosol

\( P_s \) - Saturation pressure

Q - Flow rate

\( Q_{tot} \) - Total flow rate

RH - Relative humidity

SI-engine - Spark ignition engine

SMPS - Scanning mobility particle sizer

SOA - Secondary organic aerosol

T - Temperature

t - Time needed to fill the chamber to a certain concentration

TEOM - Tapered elemental oscillating microbalance

ULPA - Ultra low penetration air filter

\( v_{ts} \) - Terminal settling velocity

\( \gamma \) - Surface tension

\( \eta \) - Viscosity

\( \lambda \) - Mean free path

\( \sigma \) - Geometric standard deviation

\( \rho \) - Density
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\section*{1. Introduction}

In recent years concerns about the health effects from the exposure of fine and ultrafine particles in the air have grown (Pope, 2002). The major sources of these particles are combustion processes and fine particles are therefore at the highest concentration near roadways and in cities. Recent technology has led to a significant decrease of particle emissions and new rules have been compiled to further decrease the emissions. The rules however, only limit the particle mass emissions and such rules do not exist for the emissions of particle numbers. When the particle mass concentrations in the ambient air decrease the particle size and number concentrations may be of more importance. It is believed that fine and ultrafine particles have different effects on the health than larger particles and size and number concentrations should maybe also be legislated.

Another impact from the airborne particles is the cooling effect on the earth. Particles in the atmosphere reflect some of the incoming sunlight back into the space. The importance of this effect is not well understood and research within the subject is performed worldwide. This research is necessary if accurate predictions regarding the future climate are to be done. To understand this matter it will also be important to understand the transformation processes that the airborne particles and gas components may be subjected to. The atmosphere does not only consist of particles emitted directly from different sources but also of particles that are formed from volatile and semivolatile material that undergo gas to particle conversions. This process is a part of the “aging” of an aerosol and is also under investigation.

This work has lead to the design and construction of a system for generation of diesel-aerosols that can be used in pilot studies within health effects and aerosol aging processes. The main objectives have been the following:

1. Do a literature study regarding the characteristics of diesel particle emissions from vehicles. This study is found within the theoretical section.
2. Design and build a diesel aerosol generating system and connect it to the available exposure chamber.
3. Characterize and evaluate the system and describe how it can be used in human health studies and particle aging processes.
Theoretical section
2. Aerosols, the basics

The definition of an aerosol is any solid or liquid particles suspended in a gas. The most important and common aerosol is the ambient air we breathe. It consists of primary particles that are emitted directly from a source into the atmosphere, and secondary particles that are formed in the air by gas to particle conversion. The ambient air is a polydisperse aerosol, meaning that it contains a wide range of particle sizes. The opposite, a monodisperse aerosol, contain particles with one particular size and can only be produced in laboratories or by special biological processes.

2.1 Formation and growth of airborne particles

2.1.1 Condensation and evaporation

To prevent evaporation the partial pressure, $p$, for a given gas needs to be equal or higher than the saturation pressure, $p_s$. If the two are equal the system is in equilibrium and the mass flow rate to and from the solid or liquid particles are the same. When considering liquid droplets the partial pressure required to prevent evaporation is higher than if the surface would have been flat. This is due to the curvature of the droplets and is called the Kelvin effect. It means that a supersaturation, called the Kelvin ratio ($K_R$), is required for equilibrium. This supersaturation is given by the Kelvin equation,

$$K_R = \frac{p_d}{p_s} = \exp\left(\frac{-\gamma M}{\rho R T d}\right)$$

(2.1)

where $\gamma$ is the surface tension, $M$ is the molecular weight, $\rho$ is the density, $d$ is the particle size, $R$ is the gas constant and $T$ is the temperature expressed in Kelvins. $P_d$ is the partial pressure required to reach equilibrium for the given particle size $d$. For water droplets, this effect is only significant for particles smaller than 0.1 µm.

The most common processes in nature for formation of aerosol particles are nucleation and condensation (Hinds 1999). New particles are formed by molecular conversion from the gas phase to the particulate phase. If this conversion occurs without any pre-existing nuclei or ion present it is called homogeneous nucleation or self-nucleation. If a condensation nuclei or ions are present, the more likely process for condensation is heterogeneous nucleation. Compared to the homogeneous nucleation, the heterogeneous nucleation requires much less supersaturation to occur. If the condensing liquid is soluble in the nuclei, the heterogeneous condensation might even take place in unsaturated conditions. Once a stable droplet is formed, and as long as the supersaturation is high enough, the particles will grow by continued condensation. The growth rate, or the radius increase, depends mainly on the saturation ratio and the particle size.

2.1.2 Coagulation

Due to the relative motion between particles they can collide and adhere to one another. Because of this process, referred to as coagulation, larger particles are formed and the total particle number concentration decreases with time. The relative motion between particles is mostly a result of Brownian motion, so called thermal coagulation. If other external forces are present, like gravitational and electrical forces, the process is called kinematic coagulation.

The effect of coagulation can be studied with two different cases. The first case is a monodisperse aerosol. With time this type of aerosol will evolve into a polydisperse aerosol because some particles will
become larger than other. The larger particles will due to their larger surface area be subjected to more collisions and will therefore grow faster. If two monodisperse aerosols are present, the larger particles will serve as deposition surface for the smaller ones and the coagulation rate will increase. The second case is an aerosol with a broad size-distribution. Once again the smaller particles will adhere to the larger ones. The number of smaller particles will decrease rapidly while the number of the large particles will be about the same, thus leading to a narrower distribution. The conclusion is that a wide size distribution of an aerosol will, due to coagulation, become narrower and a narrow distribution will become wider. The time scale for this to occur is highly dependent on the particle number concentration. The time to reach half the number concentration in a monodisperse aerosol, with an initial concentration of $10^{12}$ cm$^{-3}$, is 2 ms. The time required to decrease the number from an initial of $10^9$ cm$^{-3}$ is 33 minutes (Akselsson R 1994) and the time to reach half the initial concentration at ambient levels ($\sim 10^4$ cm$^{-3}$) is in the time scale of several days. In a polydisperse aerosol the time scale for this to occur is shorter and the coagulation is more complicated.

### 2.2 Particle deposition and losses

Particles, both in ambient environments and in laboratory equipment, are deposited on macroscopic surfaces. For larger particles (>1 µm) sedimentation is the dominant deposition mechanism. Due to gravitational forces the particles are falling through the gas with a certain velocity. This terminal settling velocity, $v_{TS}$, is given by

$$v_{TS} = \frac{\rho D_p^2 g C_c}{18 \eta}$$

(2.2)

where, $g$ is the gravitational constant, $\eta$ is the viscosity of the gas (air), $D_p$ is the particle diameter, $\rho$ is the particle density and $C_c$ is the slip correction factor (Cunningham factor) given by

$$C_c = 1 + \frac{\lambda}{D_p} \left[ 2.34 + 1.05 \exp \left( -0.39 \frac{D_p}{\lambda} \right) \right]$$

(2.3)

where $\lambda$ is the mean free path. From eq. 2.2 it can be seen that the settling velocity increases rapidly with particle size, confirming the above statement that sedimentation is important for large particles. The Cunningham factor can be set to 1, if dealing with particles larger than a few µm (Hinds 1999).

During measurements losses due to settling occurs if the aerosol is to be transported through a horizontal pipe. To minimize the losses the pipe should be as short as possible and the volume flow rate should be as high as possible. Generally, losses due to sedimentation can be neglected if the particles are smaller than 1 µm (Akselsson R 1994).

When the particle size is decreased (<0.1 µm) diffusion becomes the more important deposition mechanism. These smaller particles have high Brownian motion and can diffuse to the walls. It is important to note that the losses due to diffusion are independent of the tube diameter. When increasing the tube diameter the longer distance that the particles need to diffuse is compensated with the lower volume flow rate and longer residence time in the tube.

Impaction occurs when the particles, due to their inertia, are unable to follow the gas stream lines and adhere to a surface. This occurs for instance in sharp bends where the particles are transported to the outer
wall where the flow velocity is higher. Deposition due to *interception* occurs when the particles are able to follow the gas streamlines but are deposited on the surface because it is still within the particle radius.

Other common losses are due to *thermophoresis* or *electrical forces*. Thermophoresis arises when a temperature gradient is present. In the warmer area the particles are given a higher momentum and are experiencing a force in the direction to the colder area. This mechanism is important in combustion processes and losses are reduced by letting the temperature on the walls be higher than the aerosol temperature. It is also important to have the same temperature on all surfaces to avoid temperature gradients. To minimize losses due to electrical forces all pipes should be in metal or other conducting material.

### 2.3 Particle size and size distribution

#### 2.3.1 Equivalent particle diameters

Particle size is the property that largely determines the behavior of an aerosol and is therefore one of the more important parameters to know. Liquid particles can always be assumed to be spherical. However, solid particles do not consist of symmetrical and regular shapes but are very complex. This makes it necessary to introduce an *equivalent diameter* that is the diameter of a sphere that has the same given property as the irregular particle. The *aerodynamic diameter* is the diameter of the sphere with the density of 1000 kg/m³ that has the same settling velocity as the particle in question. A second common diameter is the *volume equivalent diameter* which is the diameter of the sphere with the same volume as the particle.

Within this work the *electrical mobility diameter* has been used. This diameter is the diameter of a sphere with the same electrical mobility as the particle in question.

#### 2.3.2 Size distributions

Size distributions are obtained by dividing the measured diameter range into small intervals (D_{n+1}–D_n) and plot it against the frequency (dN). If the intervals are sufficiently small a smooth curve can be constructed. Because the intervals can vary in size, the measured frequency (dN) is normalized by dividing it with the logarithm of the interval (dN/(\log D_{n+1} – \log D_n)). The logarithm is used because many aerosols consist of one or several log-normal distributions and because it is convenient to present the particle diameters on a logarithmic scale.

### 2.4 Atmospheric aerosols

The atmospheric aerosol consists of particles from many different sources. The particle size distribution is therefore often described with three different log-normal distributions. These three distributions, or modes, are depicted in *figure 2.1*. The *nucleation mode* is found in the size range of about 10 nm. This mode consists mainly of particles from combustion processes, both primary and secondary particles. This mode is especially found near combustion sources and during homogeneous nucleation in the atmosphere. The second mode is called the *accumulation mode* and is found at 0.1-1 µm. This mode contains larger combustion particles, like soot, and nuclei mode particles that have grown by condensation or coagulated due to high concentrations. The third, and last mode, is the *coarse mode* and consist of larger particles from natural sources, such as dust and sea salt, and particles generated due to mechanical wear. Because
of the many different sources to the atmospheric aerosol it is often very hard to distinguish between the different modes.

Figure 2.1. Typical atmospheric particle size distributions Top: Number weighted distribution. Bottom: Mass weighting distribution. The nucleation mode contains most of the particle numbers while the accumulation and coarse mode contains most of the particle mass. (Hinds, 1999)
2.4.1 Secondary formation and growth of particles in the atmosphere

A major component of the fine particle mass in the atmosphere consists of organic aerosols. As with the overall aerosol the organic part can be divided into primary and secondary species. The primary organic aerosols (POA) are emitted directly from the source and the secondary organic aerosols (SOA) are formed in the atmosphere due to oxidation of gas phase species. This is a part of the so-called aging of the aerosol and is due to the presence of oxidants, such as ozone, in the atmosphere and OH radicals formed by the UV light emitted from the sun. So far it has been suggested that the POA dominates the urban organic aerosols. But recent measurements indicate SOA dominance, even in heavily urbanized areas. This dominance of the SOA cannot be explained by the oxidation of known precursors. Robinson et al. (2007) exposed diluted diesel exhaust to ultraviolet light inside an environmental chamber at aerosol concentrations near typical ambient levels. After 3 hours of aging, the SOA had almost doubled the initial aerosol mass. This may imply that, except people living close to sources, the majority of the population is exposed to mostly SOA and not POA. However, the mechanisms of the aging of the atmospheric aerosols are not well understood and further research is needed.

3. Combustion aerosols

The two most widely used combustion engines are the spark ignition engine (SI-engine) that uses gasoline and the diesel engine. The main difference between the two is the way the fuel is ignited inside the combustion chamber. In a SI-engine the fuel is first mixed with air, the mixture is compressed by pistons and is finally ignited with an electrical spark produced by a spark plug. In a diesel engine the fuel is injected after that the air has been compressed. The generated heat from the compression makes the diesel fuel self-ignite and no spark plugs are therefore needed. This type of ignition system is called direct injection. Because of the self ignition, and the higher energy content of the diesel fuel, the efficiency of a diesel engine becomes higher compared to the SI-engines. A side effect is that a diesel engine forms higher levels of particulate mass. Particle mass emissions from diesel engines can be up to 10-100 times higher than from SI-engines (Kittelson 1997). This is the reason why environmental studies, regarding particle emissions from combustion engines into the atmosphere, almost always are based on diesel engines. However, new engines and exhaust aftertreatment with particulate filters have significantly decreased the particle mass emissions from modern diesel vehicles.

3.1 Diesel exhaust

Diesel exhaust is a complex mixture of different species, but the primary constituents are N₂, O₂, H₂O (g), CO₂, CO, hydrocarbons (in the gas-phase), NOₓ and particulate matter. The particles consist mainly of agglomerated solid carbonaceous materials, ash, low-volatile organics and sulfur components. Diesel engines are associated with higher soot formation compared to the SI-engines which is due to the injection system. As the diesel fuel is injected into the combustion chamber the fuel to air ratio at some locations is considerably higher than stoichiometric. This favors the formation of soot (Bernemyr 2007). The higher soot formation can further be explained by the higher concentration of aromatic compounds and the higher boiling point of the diesel fuel.

A small amount of the fuel and evaporated lube oil may escape complete oxidation to CO₂ and appear in the exhaust as volatile or organic compounds. These components reach the highest levels at light engine loads when the temperature in the engine is low. The organic fraction may contain polycyclic aromatic compounds that are classified as hazardous. Most of the sulfur, which is present in the fuel and lube oils,
is oxidized to SO$_2$ but some amount is further oxidized to SO$_3$. This further oxidation leads to the formation of sulfuric acid and sulfates in the exhaust particles. Without an oxidation catalyst the amount of sulfuric acid and sulfates is roughly proportional to the fuel sulfur content (Kittelson 1997). With a catalyst the conversion of sulfuric acid may increase when the engine is highly loaded. The diesel exhaust may also contain small amount of inorganic ash. This has its origin in trace additives or impurities of metal compounds in the fuel and lube oil.

In the tailpipe the temperature is high enough to keep the volatile materials in the gas phase, at least when the engine is operating under load. As the exhaust exits the tailpipe it cools and dilute with the ambient air. Nucleation, condensation and adsorption start to transform the volatile materials into solid or liquid particulate matter. Therefore, the final exhaust does not only consist of particles formed in the combustion, but also of secondary particles, formed during cooling and dilution. However, a majority of the organic compounds have such high vapor pressure that they remain in the gas phase upon dilution. Most of these compounds will eventually undergo oxidation in the atmosphere. Each step of oxidation typically leads to a reduced vapor pressure and most of these compounds will therefore eventually end up in the particle phase through gas to particle conversion, thus contributing to the ambient particle load. The time-scales of these processes are not fully known.

### 3.1.1 Diesel particle size distribution

A typical diesel particle size distribution is seen in figure 3.1. Most of the particle mass is found in the accumulation mode in the 0.1-0.3 µm diameter range. This is where the carbonaceous agglomerates and other adsorbed materials are found (Kittelson 1997). Depending on the fuel, lubricants and operating and sampling conditions, a nucleation mode may appear. This mode often consists of volatile organic and sulfur components that are formed during dilution and cooling of the exhaust. Nucleation occurs when the partial pressure is much greater than the saturation pressure for the nucleating species (Zhang M 2004). Sulphuric acid has a particularly low vapor pressure in the presence of water vapour and is therefore expected to be an important component in initiating nucleation. The nuclei mode contains only about 1-20 % of the particle mass but more than 90 % of the particle number. As will be described in section 3.1.4, the size of the nuclei mode is dependent on the fuel sulfur content. (D.B. Kittelson 2006a). A coarse mode may exist because of the release of accumulation mode particles that have been deposited on the exhaust system surfaces.

A diesel engine emits more particle mass, that is higher numbers of accumulation mode particles, than a gasoline engine. However gasoline engines are considered to emit more particle numbers in the nucleation mode than in the accumulation mode (Kittelson D B 2006). Health studies that focus on the particle number concentrations and not the mass concentrations should be interesting and during such experiment the gasoline vehicles might be of more importance than the diesel vehicles.
3.1.2 Influence of engine speed and load on particle size

Higher speeds and loads increase the total emissions (g km⁻¹) of particles from a vehicle. However, the concentrations do not change in orders of magnitude. Giechaskiel et al. (2005) have measured the particle size distribution of a diesel Euro III passenger car operating at different speeds and loads. At three different speeds, 50, 100 and 120 km h⁻¹, they found no significant effect on the accumulation mode particles. The geometric mean diameter of the accumulation mode was in the range of 55-62 nm and the used fuel had a sulfur content of 280 ppm. Vogt et al. (2003) found the same small sensitivity on the accumulation mode.

Particle number concentrations in the exhausts can be significantly higher directly after a load-increase compared to a stable load (Kittelson D 1999). When a vehicle is slowing down, the temperature of the exhaust decreases. Once the vehicle is idling, the temperature is at the lowest level and volatile particle-precursors can be deposited on the surfaces of the exhaust system. When the vehicle accelerates, the temperature increases and the volatile material is released. This strongly enhances the formation of a nucleation mode during the acceleration face. In the studies performed by Kittelson et al. (1999), a time period of 20 minutes was needed to eliminate all the stored material. The particle number concentration immediately after the acceleration was ten times higher compared to a stable driving. This change in particle concentration took place in the nucleation mode while the accumulation mode was unaffected. Another explanation for the concentration increase at acceleration is that there is a certain time needed for the oil consumption to stabilize. Lubricating oil is assumed to be an important contributor to the volatile particle material in diesel exhaust, especially when dealing with heavy engines (Kittelson D 1999).

Different speeds and loads may change the composition and shape of the particles. Park et al. (2003) studied the relationship between particle mass and mobility diameter for diesel exhaust particles and found that the effective density of the particles increased when the engine load was decreased. This can be explained by the higher amount of condensed fuel and lubricating oil that is present in the exhaust from

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Figure 3.1. Typical and schematic particle mass and number size distributions of diesel engine exhausts. Note that there are no definite definitions of nanoparticles and fine particles (Kittelson 1997).
an engine at low load. The volatile organic fraction decreases with increased load and the emissions of such species often reach its maximum when the engine is idling. The effective density is defined in section 8.4. Further, Park et al. (2003), show that the smaller particles (~50 nm) are more compact than the bigger particles (~100 nm). This is due to that the bigger particles are more agglomerated and are therefore more irregular and porous. It means that the effective density is lower for the bigger particles and that the difference between mobility diameter and aerodynamic diameter increases with bigger particle sizes. For 50 nm particles the aerodynamic diameter is about equal to the mobility diameter, because the effective density as ~1 g/cm³. However, particles with a mobility diameter of 300 nm correspond to an aerodynamic diameter of only about 120 nm.

3.1.3 Influence of exhaust aftertreatment devices on particle size
The two main methods for aftertreatment of diesel engine exhaust are with oxidation catalysts and diesel particulate filters (DPF). Today’s technology allows very high filtration efficiencies and more than 99% of the mass can be trapped (Vaaraslahti K 2004). New diesel vehicles might even emit lower mass concentrations than SI-engines. Without a particle trap most of the particles exists in the accumulation mode and most of the volatile material condenses on the solid particles (figure 3.2). When a particle trap is introduced the solid surface to condense on is removed and the probability of nucleation of the volatile material becomes much larger. The health effects of these smaller, nucleated particles are assumed to be different than the larger ones (Burtscher 2005). Oxidation catalysts are used to oxidize hydrocarbons and CO into water and CO₂. A side effect of this is that large amounts of the NO and SO₂ are oxidized to NO₂ and SO₃ (Fridell E 2006).

![Figure 3.2. Typical size distributions from a heavy diesel engine with and without a particle trap. As the accumulation mode particles are removed by the trap the volatile material nucleate and form new and smaller particle. The total particle mass is decreased but the number concentration could be increased (Burtscher 2005).]
3.1.4 Influence of fuel sulfur content on particle size

The formation of a nucleation mode is believed to be highly dependent on the sulfur content of the fuel, especially when dealing with light duty vehicles. Mariq et al. (2002) showed that the combination of high sulfur fuel (~350 ppm) and an oxidation catalyst will result in a nucleation mode but that neither alone does. This is explained by the conversion of SO$_2$ to SO$_3$ in the oxidation catalyst. SO$_3$ forms, together with water, sulfuric acid. As the exhaust cools down, the sulfuric acid may nucleate and act as condensation sites. This promotes the formation of a nucleation mode (Vogt R 2003). Figure 3.3 shows the particle size obtained in on-road measurement$^1$ of particle emissions in the exhaust plume from a passenger car (EURO III). The car was running on a 360 ppm sulfur content fuel, with an oxidation catalyst installed. At high speeds and loads the exhaust temperature is high enough for the catalyst to work efficiently. At lower speeds and loads the exhaust temperature is low and the efficiency of the catalyst is low. That is why the nucleation mode is found only at high speeds. No nucleation mode is observed when the catalyst is removed.

Figure 3.3. On-road measurements with a passenger car equipped with an oxidation catalyst. The nucleation mode can only be seen at high speed when the exhaust temperature is high. The nucleation mode disappears at all speeds when the catalyst is removed. Fuel sulfur content: 360 ppm (Vogt et al. 2003).

Figure 3.4 show the results obtained in on-road measurements at 120 km h$^{-1}$ with a high sulfur content fuel (360 ppm) and a low sulfur content fuel (10 ppm). No nucleation mode is observed with the low sulfur content fuel.

$^1$ On-road measurements mean that the test car is followed by a mobile laboratory on a test track. Air samples are taken directly from the exhaust plume and at a certain distance behind the test car.
Figure 3.4. On road measurements at 120 km/h with low (10 ppm) and high (360 ppm) sulfur content fuel. No nucleation mode is observed with the low sulfur content fuel (Vogt et al. 2003).

3.1.5 Influence of ambient air temperature and humidity

There are rather few studies on this matter but generally the particulate emissions are considered to increase at low ambient temperatures. Ristimäki et al. (2005) measured the semivolatile versus solid particle emissions at cold temperatures. They found that for light vehicles, the relative amounts between these two emissions are independent of the ambient air temperature once the engine warmed up. However the ambient temperature influences the formation of the nuclei mode, once the exhaust exits the tailpipe (Casati R 2007). In figure 3.5 the effect of dilution air-temperature and relative humidity (RH) can be seen. Between 20 °C and 10 °C there are no significant differences while at 50 °C the nucleation is strongly reduced (Casati R 2007). A higher temperature leads to a lower supersaturation of the volatile material and thus is the nucleation halted. The relative humidity has little effect at 10 and 20 °C. At 50 °C the relative humidity has a larger effect. An increase of RH from 0% to 8% leads to 10 times higher concentration of nucleation mode particles. This is explained by the fact that the vapor pressure of sulfuric acid increases rapidly below a RH level of 5 %. No nucleation mode was observed when a low sulfur content fuel (<10 ppm) was used.
3.1.6 Differences between light- and heavy-duty diesel engines

The most obvious difference between light and heavy engines is that bigger engines emit more particles. The heavy engines also use more lubrication oil which is suggested to affect the particle formation (Vaaraslahti K 2004). With a light duty engine, and if a low sulfur content fuel is used, the nucleation mode is expected to decrease or even disappear. This is independent on the engine load. However, this may not be true when dealing with heavy-duty engines. Because of the larger amount of lube oil in larger engines the composition of the lube oil will be more important. The sulfur content in the lube oil may for instance be significantly higher than in the fuel. Therefore it is reasonable to think that the lube oil has an important role in the formation of a nucleation mode. Kittelson et al. (2006) performed measurements on a heavy-duty engine running on fuels with different sulfur content. They found that at idle, the nucleation mode contained non-volatile material, which they supposed had its origin in metallic components in the lubrication oil. Vaaraslahti et al. (2004) were able to get a nucleation mode with a heavy engine running on low sulfur fuel (2 ppm). Due do this low concentration they suggested that the major part of the nucleation mode consisted of hydrocarbons.

Another important difference between heavy and light duty vehicles is the temperature of the generated exhaust. With a light diesel engine operating under a heavy load the exhaust temperature can reach levels of about 250 °C (N. L. Giechaskiel B 2005). The exhausts from a heavy engine may reach considerably higher temperatures. The higher temperatures in the engine and the exhaust system of a heavy vehicle contribute to higher conversions of sulfuric acid. This is why catalysts, which further promote the formation of oxidized sulphur compounds, are not efficient aftertreatment systems in heavy duty vehicles (Bernemyr 2007). Higher temperatures may also lead to more evaporation of lubricating oil, thus enhancing the importance of the oil composition.
4. Dilution of diesel engine exhausts in the laboratory

The design of the sampling and dilution systems determines what will be measured. The main reasons to dilute the exhausts are 1) to reduce the concentration to appropriate levels 2) to reduce the temperature to an adequate level 3) to control the condensation and nucleation processes and 4) to quench chemical reactions. The system also needs to be designed such that no significant losses will occur. Cooling the exhaust with no dilution will cause strong condensation and most of the volatile material will be found in the particle phase, adsorbed on the larger accumulation mode particles.

4.2 Dilution tunnels

The most frequently used dilution systems are the full exhaust flow dilution tunnel (FEFD-tunnel), also called constant volume sampler (CVS), and the partial exhaust flow dilution tunnel (PEFD-tunnel). The CVS system dilutes the entire engine exhaust and has therefore to be operated at very high flow rates. This system usually operates at a dilution ratio of about 1:10 and favors therefore the nucleation of particles (Burtscher 2005).

To reduce cost and occupied space, partial flow dilution tunnels may be used. This system uses only a defined percentage of the exhausts. If exact emission values are to be obtained this means that the exhaust flow has to be measured and the flow in the dilution tunnel has to be adjusted. At transient operating conditions this is a difficult task and requires very fast flow control systems (Maricq 2007).

4.3 Ejector diluters

Ejectors are widely used in automotive exhaust particle measurements thanks to their simplicity and absent of moving parts. An ejector operates by homogeneously mixing a finite amount of raw exhaust with a fine amount of dilution gas, often filtered ambient air. Figure 4.1 shows a typical ejector diluter.

![Ejector diluter diagram](image)

Figure 4.1. A typical ejector diluter and its parts (N. L. Giechaskiel B 2004)

Dilution gas, which is pressurized, flows through a ring orifice in the periphery of a nozzle. The developed underpressure, sucks in a sample that flows through the nozzle and the dilution occurs. Typical ejector diluters operate at a dilution ratio of about 10:1 (Giechaskiel, 2004). Higher dilution ratios can easily be obtained by connecting several ejectors in series. The dilution ratio depends on the inlet pressure. The drawback of this dilution system is that the orifice tends to clogg and needs to be cleaned frequently.
4.4 Measuring dilution ratios

The dilution ratio may be determined in two different ways. The first way is to use flowmeters and measure the raw and diluted exhaust flowrates. The dilution ratio, $DR$, is then defined as

$$ DR = \frac{Q_{tot}}{Q_s} $$

where $Q_{tot}$ is the total diluted sample flow rate and $Q_s$ is the raw exhaust flow rate. Another way is to measure the concentration of a trace gas, for instance CO$_2$ or NO$_x$, before and after the dilution. Then the dilution ratio is defined as

$$ DR = \frac{C_t - C_{da}}{C_{out} - C_{da}} $$

where $C_t$ is the trace gas concentration in the raw exhaust, $C_{da}$ is the trace gas concentration in dilution air and $C_{out}$ is the trace gas concentration in the diluted sample.

4.5 Laboratory dilution conditions

As the road-generated exhaust exits the tailpipe the dilution process starts. According to Zhang et al. (2004) this on-road dilution is a two stage process. In the first stage the dilution is induced by turbulence, generated by the traffic. The dilution ratio is about 1000:1 and this level is reached within 1-5s. The second stage is slower, 3-10 min, and depends on atmospheric turbulence. The dilution ratio in this second phase is about 10:1. Shi et al. (2002) found that the dilution ratio could reach 1000-4000 just 2-3m away from the passing vehicles. These large dilution ratios mean that the primary nucleation and particle growth processes, on and near roadways, are complete directly after the emission. However, secondary particles may still be formed, see section 2.4.1 aging of aerosols in the atmosphere.

The optimal dilution system depends strongly on the purpose of the system. Comparisons between on-road and lab measurements show that laboratory dilution systems tend to underestimate the nucleation mode (Casati R 2007). The most common way to dilute the exhausts, when not using a CVS tunnel, is to dilute a small part of the exhaust in two different steps. In the first and primary dilution step, the dilution ratio should be kept in the range of 1:5-1:30 and the residence time should be 1-3s (D.B. Kittelson 2006a). Because of the supersaturation that is needed for homogeneous nucleation, and because only a small amount of the exhaust is extracted, it is necessary to have high enough concentrations and temperature drops in the exhaust. High dilution ratios lead to larger temperature drops and the supersaturation is greatly increased. At the same time the particle concentration will become lower and the heterogeneous condensation is suppressed. A primary dilution ratio of 1:5-1:30 have shown to balance the concentration and temperature drop to give a particle size distribution that reflects the real world conditions. In principally it balance the homogeneous nucleation and the heterogeneous condensation at a relevant level. Figure 4.2 explains two different ways to get from the warm raw exhaust to the cold diluted exhaust. The second dilution stage has no or very small effect on the resulting particle size distributions and is more or less only used to decrease the concentrations to desired levels and to freeze coagulation.
The accumulation mode is not affected at any primary dilution ratios, meaning that this mode is independent on the dilution. Measurements performed by Kittelson et al. (2006) show that at low engine speeds, such as idle, the dilution of the exhaust becomes less important. This may be explained by the low exhaust temperatures (<100 °C) and the relative long residence time in the exhaust system. Low temperature and longer residence time makes it likely that significant particle growth occur in the exhaust system before the dilution take place.

![Figure 4.2. Two ways to get from the warm raw exhaust to the cold diluted exhaust. The figure show the total volatile mass concentration vs. temperature. The white area correspond to conditions without supersaturation and the shaded area represent conditions where condensation and nucleation will take place. The dashed line is so-called hot dilution. The volatile concentration is reduced with dilution at high temperature. After this dilution the exhaust are cooled and no nucleation or condensation has occurred. The solid line is a two stage dilution. In the first dilution step both the concentration and temperature deceases to a supersaturated level. Nucleation and condensation occur. Even if the second dilution mean that the exhausts reach an unsaturated level, the nucleated and condensed material may remain in the particle phase.](image-url)
*Methods*
5. Diesel-aerosol generation set up

5.1 Cars and driving mode
In this work 2 different diesel cars were used. A Volkswagen Passat, model year 1998, and a Peugeot 307, from 2003 equipped with a DPF. The diesel fuel used was Swedish MK1 diesel fuel with a sulfur content of < 10 ppm. All experiments were performed with the car engine running on idle mode. Before every experiment the car was allowed to warm up during about 15 min. This time was enough to give a stable exhaust temperature of about 70-80 °C. This temperature, measured with a thermocouple, is relatively low. But under the outdoor conditions, and the engine mode used, a higher temperature was not expected.

The Volkswagen Passat was used to study the reproducibility of the dilution system. These experiments are denoted VW1 and VW2 and the method was to fill the exposure chamber to a constant mass concentration and then perform several scans with the SMPS. The car was running continuously during these measurements. The Volkswagen has also been used to show how the dilution system can be used in human exposure studies. This was done by varying the mass concentration inside the chamber by turning the car on and off. This experiment is denoted VW3b. The Peugeot was used to study if a car with a particle filter can be used in the exposure studies. The method was the same as for the VW1 and VW2.

5.2 Exhaust extraction and dilution
The exhaust extraction and dilution system is depicted in figure 5.1. In principally it is designed to work as a partial exhaust flow dilution tunnel and a short description of how to set up the system is given in appendix A. The connection to the car tailpipe was done with a galvanized joining pipe (A). Two joining pipes with different diameters, φ=60.5 mm or φ=64.5 mm, could be used in order to be able to connect to exhaust pipes of different sizes. The different sizes and shapes of exhaust pipes are as many as there are car models and it exist no universal solution that fits with all types of exhaust pipes. The used diameters were chosen because they seem to represent most of the tail pipes on cars older than a few years.

Another problem was the presence of double tailpipes on some cars. Due to the low engine speed used this problem could be solved by simply plugging one of the tailpipes and connect the dilution device to the other. This works only if the two tailpipes are connected to the same exhaust silencer and if the extra tailpipe exists only because of cosmetic reasons. If the tailpipes follow different paths towards the engine this method cannot be used.
Figure 5.1. The exhaust extraction and dilution system. A) Connection for the tailpipe, B) Valve to discard most of the exhausts, C) Primary dilution stage, D) Secondary dilution stage E) Primary dilution air flow, F) Secondary dilution air flow, G) Outlet air from the chamber. The orifices were used to determine flow rates by measuring the pressure drop over the orifice. Samples for analysis were taken through holes on the chamber wall.

The tail pipe was connected to a flexible stainless steel tube, $\varnothing=60$ mm. The length of this tube was 1 meter, which was necessary to be able to connect it to the car tailpipe in an easier way. The tailpipes on diesel cars are almost always directed downwards and a straight tube would make any connection impossible. At the other end of the flexible tube the exhausts were divided into two flows. The main flow exited the tube, through a valve (B), into the ambient air. About 90% of the exhausts were discarded in this section. This was however not measured but is only an estimate. The remaining part of the exhaust was flowing through a 60 cm long copper pipe, $\varnothing=16$ mm. This pipe led the undiluted exhaust indoors, through the building-wall, to the first dilution stage (C).

During this work it has not been possible to measure the total exhaust flow rate from the car. This makes it impossible to fully define the residence time inside the extraction system. But, considering the length and diameters, it is reasonable to think that the residence time for the raw exhaust in undiluted condition is about 50% longer, compared to when the exhaust would be emitted directly from the car tail pipe.

The whole length of the extraction system, from the car exhaust pipe to the first dilution stage, was heated with two heating wires. The wires were tested up to 90 °C which is enough for the idling condition. The temperature was checked with thermocouples at three different positions. One was located a few centimeters from the exhaust pipe, the second was located at the T cross section and the final one was located on the middle of the copper pipe, inside the building wall. In order to avoid any big temperature gradients all three thermocouples should show about the same temperature ($70\pm10$ °C). However no
accurate control unit was available for this purpose. In order to be able to reach the desired temperature the pipes were insulated and wrapped around with plastic sheets to avoid rain and moisture. The exhaust extraction system can be seen in figure 5.2.

![Figure 5.2. The exhaust extraction system.](image)

### 5.2.1 Dilution system

The dilution of the exhaust was done in two stages and the air used was supplied by an air conditioning unit placed in the same room as the chamber. The unit made it possible to adjust the temperature and relative humidity of the air entering the chamber. The maximum total flow from the air conditioning unit, ~2 m³/min, was split into two flows, one for the primary dilution (E) and one for the second dilution (F). The primary flow was adjusted with a valve. If the primary dilution flow was increased, the secondary dilution flow decreased and vice versa. This meant that even if the primary flow rate was changed the total flow to the chamber was constant and an air exchange rate of ~5 h⁻¹ was always achieved. All the tubing of the dilution system was constructed in galvanized steel.

The first dilution stage can be seen in figure 5.3. The pipe, coming from the outdoors, was connected to a T cross section, Ø=100 mm. This was where the first dilution took place. An iris (orifice) was placed just after the mixing point in order to get higher turbulence and better mixing. The residence time between the injection point of the exhaust and the orifice was, depending on the dilution ratio, about 100-200 ms. The primary dilution ratio was varied between 1:7 and 1:27. By measuring the flow rate, before and after that the car tail pipe had been connected, this orifice could also be used as a secondary method to determine the dilution ratio. As mentioned later in section 7.5, the primary method to determine the primary dilution factor was by measuring the NOₓ concentration before and after the dilution stage. This was done with two special connection devices designed for this system and to fit the measuring probe of the combustion gas analyzer.
Figure 5.3. The primary dilution stage is shown by the arrow. The box in the lower left corner is the air conditioning unit that provided the dilution air.

Directly after the iris, the diameter of the pipe was reduced (from $\Theta=100$ mm) to 63 mm. This reduction in cross-area was necessary to lower the residence time between the first and second dilution stages. The residence times for two different flow rates, which both are within the recommended limits from section 4.5, are shown in table 5.2. The 63 mm pipe was about 490 cm long and was necessary to transport the diluted exhaust to the chamber and the second dilution stage. This long pipe is denoted the transport pipe. Above the exposure chamber the primary flow (E) met the secondary flow (F) in a new T cross section. The total flow was allowed to enter the chamber and the flow rate was measured with an orifice. As mentioned earlier this total flow rate gave an air exchange of \( \sim 5 \text{ h}^{-1} \) inside the chamber.

Both the primary and secondary flow had on its way to respective dilution stage passed through an activated carbon filter and an ULPA filter. This ensured that the dilution air was particle free.

<table>
<thead>
<tr>
<th>Primary dilution flow rate (l/min)</th>
<th>Residence time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 (PDR≈8)</td>
<td>2.8</td>
</tr>
<tr>
<td>790 (PDR≈27)</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table 5.2 Residence time between primary and secondary dilution stages. 400 and 790 l/min are used because these were the lowest and highest flow rates used. The time is within the recommended range, 1-3 sec, given in section 4.5. For higher flow rates the residence time is possible to increase by adding sections of larger diameter tubes.
6. Exposure chamber
The exposure chamber that has been used is a 21.6 m³ stainless steel chamber with a 0.8 m² large glass window on one of the walls. The ventilation air to the chamber is supplied by an external air conditioning system that uses air from the surrounding room. Within this conditioning system the air temperature and relative humidity can be controlled. Before the air enters the chamber it passes through an activated carbon filter and an ultra low penetration air (ULPA) filter. This assures that the air entering the chamber is as free from particles as possible. The minimum particle concentration that can be reached is about < 1 cm³. The air-outlet is situated in the diagonally opposite corner of the air-inlet and is controlled by an exhaust fan. The pressure inside the chamber is easily controlled by lowering or increasing the speed of this fan. To avoid penetration of the surrounding room-air into the chamber an overpressure of about 5-10 Pa is desired. If the chamber needs to be emptied quickly an express fan may be used. This fan makes it possible to reach 1 % of the initial concentration within 15-20 minutes. A detailed evaluation of the chamber has been done by Isaxon C. (2008).

To enter the chamber one must pass through an antechamber of 3.1 m³ in size. This small chamber is equipped with air tight doors both to the chamber and to the surrounding laboratory. The air supplied to this chamber is the exhaust air from the main chamber. This assures that the contamination of the main chamber air is as small as possible when entering and leaving the chamber. The aerosol samples for analysis are taken through small holes (of a few mm in diameter) on the chamber walls. A short description of the used measurement methods are given in the following section.

7. Measurement instrumentations
Within this work the main analysis methods have been SMPS and TEOM measurements. These instruments, and the settings used, are described below. A SMPS system combines two different instruments, a DMA and a CPC, and descriptions of these are therefore also presented.

7.1 Differential mobility analyzer
A differential mobility analyzer (DMA) is used to separate particles of different sizes. This is done by using the fact that electrically charged particles change their course when they are subjected to an electrical field. At a first stage, the inlet aerosol is neutralized to the Boltzmann equilibrium charge distribution by letting it pass through a bi-polar charger, also called a neutralizer. The bi-polar charger consist of a radioactive substrate, in this case ⁶³Ni. After the neutralizer the aerosol is introduced into a cylinder (the DMA) through a small annular hole that is situated at the top and at the cylinder wall. At the center of the cylinder a central rod is placed. Between the center rod and the aerosol flow a second flow, containing clean air, is introduced. This makes the cross section of the cylinder, from the center to the walls, look like: central rod, air flow, aerosol flow and cylinder wall.

When the central rod is connected to a negative voltage source and the cylinder wall is grounded an electrical field is formed. The particles with a positive charge will begin to move through the clean air and towards the negative central rod. Particles with different charges will bend differently in a certain electrical field. That is, particles of different sizes will have their trajectories bent differently compared to each other. At the bottom of the cylinder, and close to the central rod, there is a small gap that allows a small airflow to leave the cylinder. Only particles with a narrow range of electrical mobilities can enter the gap. Particles with a greater electrical mobility will bend too much and be deposited on the cylinder wall.
wall. Particles with smaller electrical mobility do not bend enough to be able to pass through the bottom gap. By varying the voltage on the central rod, for instance between 20 and 10 000 V, particles of different sizes can be allowed to pass through the exiting aerosol.

### 7.2 Condensation particle counter

The condensation particle counter (CPC) is an optical instrument that makes it possible to count the particles in an aerosol. A problem with optical measurement techniques is that they only allow detection of particles larger than about 0.1 µm. This problem is solved within the CPC by saturating the aerosol with water or an alcohol. After the saturation stage the aerosol is cooled and the particles start to grow by condensation. The final particle size is about 10 µm and is more or less independent on the original particle size. In this work butanol has been used as the condensation liquid. With this method it is possible to detect particles down to about 3 nm. The detection of the particles is done by measuring the scattered light from the droplets. When a particle enters the light from a laser, the light is scattered and the scattered light is detected. When the particle concentration becomes too high the CPC is unable to count the particles because several particles might contribute to the scattered light at the same time. The highest concentration that can be measured is about 10 000 cm⁻³.

### 7.3 Scanning mobility particle sizer

A scanning mobility particle sizer (SMPS) is an instrument that combines a DMA and a CPC. By varying the voltage to the DMA the number of particles of a certain size can be counted by a CPC. With the help of a computer a particle size distribution can be constructed. The DMA and CPC used within this work were a Long DMA and a CPC 3010, both from TSI Inc.

#### 7.3.1 Settings for the SMPS during this work

- Sheath flow: 5 lpm
- Aerosol flow: 1 lpm
- DMA dimensions: 
  - R1 2.50 cm
  - R2 3.35 cm
  - L 28.00 cm
- Min diameter: 10 nm
- Max diameter: 600 nm
- Inet flow rate: 0.5 lpm
- Inlet tube length: 1.5 m

### 7.4 Tapered elemental oscillating microbalance

The tapered elemental oscillating microbalance (TEOM, model 1400a, R&P Inc.) is an on-line instrument that measures the total particle mass concentration. The instrument measures the frequency of an oscillating tapered element. On top of the tapered element a filter is placed. When an aerosol passes
through the filter the particles are deposited on it and the oscillation frequency of the element decreases. The decrease of the frequency is proportional to the increase of the filter mass. To avoid water condensation on the filter the sample aerosol is preheated. During this work this temperature was set to 30 °C and the aerosol flow rate was 1 lpm. Before the TEOM sampling inlet a cyclone and a nafion drier was placed. This was done to get better ability to compare the SMPS data with the TEOM data, especially during calibration. The drier makes sure that no water, or very small amounts of water, is present in the aerosol. The cut-off of the cyclone was 1 µm, well above the particle sizes of a diesel aerosol and should not have affected the results.

7.5 Determination of dilution ratios
A portable flue gas analyzer (Nordtec Testo 350XL) was used to measure the NOx concentrations before and after the dilution. As explained in section 4.4 these values were used to calculate the dilution ratios. This instrument was also used to measure the levels of CO, NO and NO2 in both primary diluted and undiluted exhausts.

The volumetric flow inside the dilution system was measured with irises using pressure drop theory. With equation 7.1, provided by the iris manufacturer, the volumetric flow can be calculated. The irises were also used as a secondary method for the determination of the dilution ratio as described in section 4.4.

\[ Q = k\sqrt{\Delta P} \] (7.1)

Q is the flow in l/s, \( \Delta P \) is the pressure drop over the iris and k is a constant governed by the iris set up.

7.6 Sampling errors
The air inside the chamber can be assumed to be fully mixed. Measurements performed by Isaxson (2008) have shown that the concentration inside the chamber may only differ within 10 % between different locations. During sampling, losses due to settling have to be considered. When the sampling probe is directed upwards the particle number concentration may be overestimated. The opposite occurs when the sampling probe is directed downwards. During this work the sampling probe has been positioned in a horizontal position, thus minimizing the settling losses. Also, as described in section 2.2, settling losses for particles smaller than 1 µm can be neglected.

Another factor to consider when sampling from still air is the velocity of the probe inlet flow. If the flow is high particles with a large diameter may be unable to follow the gas stream lines. This will lead to an underestimation of larger particles. The particles used in this work can be estimated to be smaller than 1 µm. Thus sampling errors can be neglected.

8. Calculations

8.1 Time to fill the chamber to a constant concentration
To be able to do estimates of time that is needed to reach a certain concentration inside the chamber a simple mass balance can be put together. The mass balance results in a differential equation. In its solved state this equation gives the time, \( t \), needed to reach a certain concentration, \( C_n \), inside the chamber.
\[ t = -\frac{V}{F} \ln \left( \frac{C_{w}V + C_{in}}{C_{\text{start}} - C_{\text{in}} + V} \right) \]  \hspace{1cm} (8.1)

\( V \) - Chamber volume \([\text{cm}^3]\)

\( C_{w} \) - Wanted concentration inside the chamber \([\#/\text{cm}^3]\)

\( C_{\text{in}} \) - Concentration in the inlet flow \([\#/\text{cm}^3]\)

\( C_{\text{start}} \) - Starting concentration inside the chamber \([\#/\text{cm}^3]\)

\( F \) - Outlet flow rate \([\text{cm}^3/\text{min}]\)

\( t \) - Time to reach concentration \( C_{w} \) in the chamber \([\text{min}]\)

The derivation of the above equation is found in appendix B.

### 8.2 Deposition losses

The diesel particles are well below 1 µm and settling losses can therefore be neglected (see section 2.2). Losses due to thermoporesis inside the exhaust extraction pipes are possible. This was minimized by avoiding large temperature gradients and by allowing an adequate temperature of the tube walls. The temperature used during this work, ~60-70°C, was about the same as the exhaust temperature and losses due to thermoporesis should have been small.

Because of the small particle sizes and the long transport distances the most likely deposition mechanism inside the dilution system is by diffusion. The residence time is longest in the transport pipe between the primary and secondary dilution and deposition due to diffusion is therefore most likely to take place there. Calculations are also performed for the copper pipe, through the building wall, where the flow is lower and the temperature is high (~50-60°C). The calculations, found in appendix C, show that losses due to diffusion are small. This should mean that the overall losses are very small. Even if the losses are not expected to affect the results it might be necessary to clean the tubing once and a while. This is most easily controlled by checking the irisises, and see if there are any soot on them. However, this was never the case during this work. It is confirmed that losses due to turbulence and impaction are significant in the extraction system at the tail pipe connection. Due to the downward direction of the tail pipe the flow hits the flexible tube wall in almost a perpendicular angle. These losses are confirmed by the presence of soot inside the pipe but they are not characterized.

### 8.3 Geometric mean diameter

For a lognormal size distribution the mean, mode and median will all have the same value. This is not the case for an asymmetrical distribution. Because the fact that most aerosol size distributions, like diesel aerosols, are lognormal it is common to use the geometric mean diameter (GMD), \( d_{g} \). This diameter is defined by

\[ \ln d_{g} = \frac{\sum n_{i} \ln d_{i}}{N} \]  \hspace{1cm} (8.2)

where \( n_{i} \) is the number of particles of size \( i \), \( d_{i} \) is the midpoint of a characteristic diameter and \( N \) is the total number of particles. The geometric standard deviation (GSD), \( \sigma_{g} \), is given by
Using effective density to obtain mass concentrations from the SMPS

To be able to compare the results from the SMPS and the TEOM it is necessary to know the effective density of the particles. Because smaller diesel particles are more compact and more spherical than bigger particles the effective density will change with particle size. Equations 8.4 and 8.5 are taken from the work of Park et al. (2003). The effective density, $\rho_{\text{eff}}$, is calculated with

$$\rho_{\text{eff}} = k D^{D_f - 3}$$ (8.4)

where $k$ is a constant, set to $8.24 \times 10^{-4}$, $D$ is the particle diameter and $D_f$ is the mass fractal dimension. For spherical particles the $D_f$ factor has a value of 3, while for non-spherical particles this value is below 3. Diesel particles, produced at low engine load, have shown to have a $D_f$ of 2.4 (Park K 2003).

To be able to calculate the total mass, $m$, from the SMPS data following equation is applied:

$$m = \sum \frac{\pi}{6} D^3 N \rho_{\text{eff}}$$ (8.5)

$N$ is the number of particles of size $D$. 

\[\begin{align*}
\text{ln} \sigma_g &= \left(\frac{\sum n_i (ln d_i - ln d_p)^2}{N-1}\right)^{1/2} \\
\text{8.4 Using effective density to obtain mass concentrations from the SMPS} \\
\text{To be able to compare the results from the SMPS and the TEOM it is necessary to know the effective density of the particles. Because smaller diesel particles are more compact and more spherical than bigger particles the effective density will change with particle size. Equations 8.4 and 8.5 are taken from the work of Park et al. (2003). The effective density, } \rho_{\text{eff}}, \text{ is calculated with} \\
\rho_{\text{eff}} &= k D^{D_f - 3} \\
\text{where } k \text{ is a constant, set to } 8.24 \times 10^{-4}, \text{ } D \text{ is the particle diameter and } D_f \text{ is the mass fractal dimension. For spherical particles the } D_f \text{ factor has a value of 3, while for non-spherical particles this value is below 3. Diesel particles, produced at low engine load, have shown to have a } D_f \text{ of 2.4 (Park K 2003).} \\
\text{To be able to calculate the total mass, } m, \text{ from the SMPS data following equation is applied:} \\
m &= \sum \frac{\pi}{6} D^3 N \rho_{\text{eff}} \\
N \text{ is the number of particles of size } D.
\end{align*}\]
Results and conclusions
9. Results

Due to the idling condition of the cars and the low sulfur content fuel used, the results, regarding particle size distributions, were not expected to show a nucleation mode, only an accumulation mode. However, dilution conditions, such as dilution ratio, air temperature and relative humidity were still chosen in a way to simulate real world conditions. The dilution air temperature was at all measurements set to 18 °C and the relative humidity to 40-50 %. The fact that the accumulation mode is not strongly affected by the dilution conditions made it reasonable to think that the dilution would be less important for the obtained results.

Summary of the obtained results from the different cars.

<table>
<thead>
<tr>
<th></th>
<th>Number conc. (#/cm³)</th>
<th>Surface conc. (µm²/cm²)</th>
<th>Mass conc. SMPS (µg/m³)</th>
<th>Mass conc. TEOM (µg/m³)</th>
<th>GMD (nm)</th>
<th>σg</th>
</tr>
</thead>
<tbody>
<tr>
<td>VW1 (chamber)</td>
<td>260 000</td>
<td>15 000</td>
<td>252 (532)</td>
<td>287</td>
<td>96</td>
<td>1.75</td>
</tr>
<tr>
<td>VW2 (chamber)</td>
<td>88 000</td>
<td>5 000</td>
<td>79 (170)</td>
<td>103</td>
<td>93</td>
<td>1.79</td>
</tr>
<tr>
<td>Peugeot 307 SW (chamber)</td>
<td>5 000</td>
<td>190</td>
<td>3 (5)</td>
<td>13</td>
<td>71</td>
<td>2.00</td>
</tr>
<tr>
<td>VW1 (norm.)</td>
<td>8.1*10⁶</td>
<td>460 000</td>
<td>7 750</td>
<td>8 900</td>
<td>96</td>
<td>1.75</td>
</tr>
<tr>
<td>VW2 (norm.)</td>
<td>7.1*10⁵</td>
<td>405 000</td>
<td>6 400</td>
<td>8 400</td>
<td>93</td>
<td>1.79</td>
</tr>
<tr>
<td>Peugeot 307 SW (norm.)</td>
<td>1.6*10⁵</td>
<td>6 000</td>
<td>96</td>
<td>416</td>
<td>71</td>
<td>2.00</td>
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</tbody>
</table>

Table 9.1. Summary of total particle concentrations during measurements with purpose to study the reproducibility of the system. “Chamber” is the mean value measured inside the chamber when the car had been turned on for 15 minutes. “Norm.” is the chamber concentration multiplied with the respective total dilution factor. The SMPS mass conc. values in brackets are the total volume conc. VW1 and VW2 refers to first and second experiment with the Volkswagen Passat.

<table>
<thead>
<tr>
<th></th>
<th>CO</th>
<th>NO</th>
<th>NO2</th>
<th>NOx</th>
<th>CO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>VW1 (chamber)</td>
<td>4-6</td>
<td>5-9</td>
<td>0</td>
<td>5-9</td>
<td>1 300</td>
</tr>
<tr>
<td>VW2 (chamber)</td>
<td>0-1</td>
<td>2-3</td>
<td>0-0.4</td>
<td>2-3</td>
<td>-</td>
</tr>
<tr>
<td>Peugeot 307 SW (chamber)</td>
<td>2-3</td>
<td>3-4</td>
<td>0</td>
<td>3-4</td>
<td>1 300</td>
</tr>
</tbody>
</table>

Table 9.2 Summary of the highest obtained gaseous levels inside the chamber during experiments mentioned in table 9.1.
**Peugeot 405**

This car was the first car used. The car had not been driven for a few years and was likely in bad shape. It was therefore only used to control the overall functionality of the dilution system. Due to its bad conditions this car was immediately discarded as an option for the future measurements and no results obtained from this car is presented. The generated exhaust was extremely smelly and could not be used for a longer time period. Also the size distributions changed from one day from another indicating that the car engine and exhaust system was not stable. Also the maximum total mass concentration inside the chamber, ~40 µg/cm³, was low compared to the levels of CO and NOₓ (16 ppm and 5 ppm).

**Volkswagen Passat**

The second car used was A VW Passat, model year 98. This car was intended to be a more appropriate choice for the future measurements. The car model is very common on Swedish roads and has during the latest years been the second most selling diesel car in Sweden (BilSweden 2008). The VW was primarily used at two different occasions, VW1 and VW2, separated with 7 days to be able to evaluate the reproducibility of the dilution system. The average size distributions inside the chamber from these two different cases are seen in figure 9.1. The car was at both occasions running for 15 minutes, which gave a stable mass concentration inside the chamber. The outdoor temperature was 4-5 °C and at idle the engine was running at about 900 rpm.

![Figure 9.1. Measured average number size distribution of VW1 (*), VW2 (o) in the chamber. The VW1 and VW2 curves are averages of five SMPS scans (~15 min) obtained when the mass concentration was stable (290±10 µg/m³ for VW1 and 103±12 µg/m³ for VW2). Primary dilution ratio for VW1 was 7 and for VW2 it was set to about 27.](image-url)
The difference in peak height between the two curves can be explained by the primary dilution ratios that were used in the calculations. In case VW1, the primary dilution factor was set to 6-7 while in case VW2 it was set to 27-30. A higher flow rate of the primary dilution air created a higher pressure inside the dilution stage, hence less raw exhaust was able to penetrate to the mixing point. In order to better compare the results, and get a better clue of the reproducibility of the dilution system, the obtained concentrations were multiplied with the respective total dilution ratios. These ratios were 31 for the VW1 and 81 for the VW2. This gave an estimate of the particle concentration and size distributions in the raw exhaust, figure 9.2.

![Figure 9.2. Normalized particle size distributions from VW1 (*) and VW2 (o). Normalized according to the measured total dilution ratios.](image)

The two curves, VW1 and VW2, are in well agreement to each other, with a geometric mean diameter between 93-96 nm. The difference in the peak height can be explained by two facts. The first one is the inaccuracy of the combustion gas analyzer at the low NOx concentrations that were present inside the chamber. The calculated total dilution ratios will therefore not be exactly correct. The second reason, and the most important, is simply that the emissions from the car were slightly different. The main conclusion is that the shape of the distributions agrees well and that the geometric mean diameter has about the same value.
Figure 9.3. Normalized mass concentrations from the SMPS data from VW1 (*) and VW2 (o). The method with effective density, presented in section 8.4, has been used. The total mass concentrations are the integral of the curves and these numbers are presented in table 9.1.

Figure 9.3 shows the normalized mass distribution obtained from the SMPS data. Again both curves correlate well to each other.

The two experiments indicate that the reproducibility of the extraction and dilution system is good. It is also confirmed that the primary dilution ratio does not seem to affect the accumulation mode. This gives an opportunity to control the concentration inside the chamber simply by adjusting the primary dilution flow rate.

The total particle number emissions from the engine (~7.5*10^6 cm^3) are in agreement with values found in the literature that are obtained during measurements with a similar engine and fuel (Wong C 2003). The geometric mean diameter of 93-96 nm is slightly higher compared to values found in the literature, which varies between 50-90 nm. The larger mean diameters from a low loaded engine may be explained by the residence time of the raw exhaust between the engine and the first dilution stage. Due to the idling mode, the volumetric exhaust flow rate is low and the residence time in the car exhaust system is therefore long. This will lead to more coagulation, compared to if the engine was loaded. Also, the exhaust extraction pipe, that lead the exhaust to the first dilution stage, further increased the residence time.
**Peugeot 307 SW**

The third car used was equipped with a DPF. As described in section 3.1.3., this gave reasons to believe that a nucleation mode could appear. The primary dilution factor was set to about 8.

![Normalized Size distribution Peugeot 307 SW](image)

**Figure 9.4. Particle size distribution from the Peugeot 307 with a logarithmic y-scale. Primary dilution factor 8.**

A tendency of a nucleation mode could possibly be seen in figure 9.4 when a logarithmic y-scale is used. However, as can be seen in table 9.1 both the number and mass concentrations were very low. No conclusions regarding a possible nucleation mode can be drawn from the results.

Despite the low mass concentrations it is interesting to compare them with the values obtained from the VW Passat. This comparison gives an estimate of the efficiency of the DPF. The car with a DPF emits about 98% percent less particle mass (measured with the SMPS), indicating that statements saying that DPF reduces the mass emissions by about 99 % can be confirmed. The DPF is very efficient. However these low emissions make this type of car not suitable to use in the intended studies, especially in human exposure studies. If higher concentrations were to be obtained more exhaust had to be led into the chamber. This however, results in too high gas concentrations that may exceed the recommended health limits.
9.1 Suggestions on how to use the dilution system for human exposure studies

In the future human exposure studies it is requested that the mean particle concentration inside the chamber should be around 300 µg/m³ and the concentration should vary with time. This is most easily achieved by starting the car in pulses. When the engine is turned on the concentration inside the chamber increases and when it is turned off the concentration decreases, due to the continued ventilation. The total mass variation and mean particle size distribution during such experiment (VW3b) are shown below.

Figure 9.5 Total mass concentrations (TEOM) inside the chamber during the VW3b experiment. The y-axis is the total mass concentration (µg/m³) and the x axis show the timescale of the experiment. The concentration was varied by turning the car engine on and off during certain times, shown to the right. Mean value 260 µg/m³.

Figure 9.6 Total number concentrations inside the chamber during the VW3b experiment. The y-axis is the total number concentration (cm⁻³) and the x axis show the timescale of the experiment. The concentration was varied by turning the car engine on and off during certain times. Mean value 116 000 cm⁻³.
Figure 9.7 Mean particle size distribution during the VW3b experiment.

The average geometric mean diameter during this experiment was 102 nm. This is slightly higher compared to VW1 and VW2, where the car engine was running continuously. When the car is turned off no “fresh” exhaust enters the chamber and coagulation will turn the peak of the distribution to slightly larger diameters. The smallest GMD during the experiment was 93 nm and was obtained in the beginning of the experiment. The largest GMD diameters were obtained the moment the car was turned back on. This value was typically about 110 nm.

<table>
<thead>
<tr>
<th></th>
<th>Min. number conc. (#/cm³)</th>
<th>Max. number conc. (#/cm³)</th>
<th>Mean number conc. (#/cm³)</th>
<th>Min. mass conc. (µg/m³)</th>
<th>Max. mass conc. (µg/m³)</th>
<th>Mean mass conc. (µg/m³)</th>
<th>GMD (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VW3b (chamber)</td>
<td>58 000</td>
<td>207 000</td>
<td>116 000</td>
<td>148</td>
<td>394</td>
<td>260</td>
<td>102</td>
</tr>
</tbody>
</table>

Table 9.3. Summary of mean values and extremes during experiments with purpose to achieve a mean concentration of about 250-300 µg/m³ inside the chamber. VW3b refers to the third experiment with the Volkswagen Passat. Mass concentrations were measured with the TEOM.

<table>
<thead>
<tr>
<th></th>
<th>Highest value in chamber (ppm)</th>
<th>Exposure limit¹ (ppm)</th>
<th>Peak limit² (ppm)</th>
<th>Exhaust source³ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>4.0</td>
<td>35</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>NO</td>
<td>1.3</td>
<td>25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NO₂</td>
<td>1.0</td>
<td>2</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>CO₂</td>
<td>725</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 9.4 Highest gas concentrations reached inside the chamber during the VW3b experiment and health limits (Arbetsmiljöverket 2005). ¹ Highest permitted average level during one working day. ² Hygienic level during 15 min exposure. ³ Highest average concentration during one working day if exhaust is the source of the gas.
The levels of CO and NOx are within the health limits and the particle mass concentration compared to the gaseous levels is in agreement with other health effects studies. Crütz et al. (2008) exposed ten volunteers to diesel exhaust produced from a heavy duty engine. When they had a particle mass concentration of 300 µg/m³, the hazardous gaseous levels was 7.5 ppm CO, 4.5 ppm NO and 1.6 ppm NO₂.

It should be noted that the car had been on service two weeks before the VW3b experiment. During this service diesel filters were changed and a fuel additive was added to the diesel tank. A week after the service the experiment denoted VW3a was performed. This experiment is presented in appendix D. Due to the additive in the diesel fuel the particle emissions changed drastically. It was decided to wait one week to let the remaining diesel in the tank be used and let the tank be filled up with new diesel. This experiment, one week later, is the VW3b experiment. The particle size distribution was again the same as during the VW1 and VW2 cases but the total mass and number emissions from the engine had changed compared to these two. This meant that during VW3b more exhausts were needed to be discarded in order to make sure that the concentrations in the chamber were not too high.
10.1 Conclusions
The designed exhaust extraction and dilution system has proven to give results that make it possible to use it in the intended studies. However some improvements must be performed before it can be used in more than pilot studies.

The reproducibility of the dilution system has shown to be good. Due to the idling condition the dilution is less important for the final particle size distribution and the main parameter that affects the result is the car. During exposure studies it is crucial not to exceed the health limits of hazardous gas components. This makes cars equipped with particle filters not suitable. If such car is used, the required particle concentrations would lead to very high concentrations of CO and NOx. Finding a car with reasonable particle/gas ratios are important and the VW Passat has shown to do so. Desired mean concentrations can be achieved by turning the car engine on and off in pulses of different length.

The location of the car, standing outside, and idling mode is not optimal. The number geometric mean diameters are larger than those that would have been obtained if the car was running in a transient cycle. A nucleation mode is not formed from a low loaded car engine.

All the experiments share the fact that there was a very distinct smell of diesel exhaust inside the chamber. This makes it impossible to do “blind tests” during human exposure studies. The smell was also noticeable in the room that surrounded the chamber and at the parking lots where the car was standing. Between two measurements it is important to know if something has happened to the car. Examples are for instance if something has been changed on the car, like different fuel, fuel additives or parts that have been changed.

10.2 Suggestions for improvement
The main issue that has to be solved, before exposure studies can be performed, is the smell of diesel. A reasonable level of the smell has to be established. It is possible that the smell, that are present in the chamber, is impossible to endure during longer time periods. The smell in the surrounding local should be avoided if an underpressure, instead of overpressure, is used in the chamber. This will prevent the air inside the chamber to penetrate through the small holes on the chamber walls.

It is possible that the condensation that takes place in the car tail pipe further increase the magnitude of the smell. This condensation is more significant when the car is turned on and off with small intervals. Every time the car is turned off the exhaust system cools down. A continuously running engine might result in less smell. The variation of the mass concentration inside the chamber could instead be achieved by disconnecting the exhaust extraction system from the tail pipe. However, a car engine is not designed to run at idle during longer time periods and this could lead to other problems.

The urban atmosphere contains not only an accumulation mode but also a nucleation mode. These smaller particles are believed to have different health effects than the larger particles. The optimal system would contain an engine- or vehicle-dynamometer. This would make it possible to run transient cycles that should be more relevant regarding the ambient air. At the time being, this is not possible.

The time between that the car has to be turned on and off is about 10 minutes. This time period is very short and makes it necessary to frequently run back and forth between the chamber and the car. If lesser amounts of raw exhausts are allowed to enter the dilution system, the time that the car needs to be turned
on could be increased. This would mean that the engine needs to be turned off less frequently. Lower amounts of raw exhausts can be achieved by increasing the primary dilution flow rate.
References


Acknowledgments

During the last 6 months I have had the privilege to spend my time at the department of Ergonomics and Aerosol Technology (EAT). These months belong to the more interesting and instructive ones that I have experienced during my almost five year long education. I would like to say “Thank You” to all the people working at the department, people that always were, and are, good company. My special thanks go to Joakim Pagels, my examinator, and Aneta Wierzbicka, my supervisor. Despite the overwhelming work load you sometimes seem to endure, you are always happy to help and always with a good spirit. Fredrik Rassner and Jenny Rissler – For letting me borrow your cars. Without cars this would not have been a good work. Lennart Strömberg – For helping me in the construction of the dilution system and in the manufacturing of the necessary parts. Anders Gudmundsson – For always seeing opportunities and solutions and for helping me with practical issues. Thanks to Andreas Dahl for helping me finding and ordering things. Also thanks to the thesis workers Axel Eriksson, Erik Nordin and Magnus Lindskog for many happy moments. We always worked fine together.
Appendix A
Start up schedule for the dilution system.

1. Connect the two heating wires.
   - This is by far the most time consuming part. The time needed to reach a desired temperature is very dependent on the outdoor temperature. At least one hour is needed.
   - The heating is much faster if the airflow through the pipe is zero. This is achieved by plugging the exhaust pipe connection and close the valve to make sure that no air flow is present inside the tube.
   - The exhaust temperature is dependent on the outdoor air temperature. A value of at about 70°C is expected for a preheated car, running at idle, and this temperature is therefore desired in the wires.
2. Start the car engine and let it run for 10-15 min to warm up
3. While the car is getting warm adjust the primary dilution flow with the valve positioned above the air conditioning unit.
4. Check the pressure inside the chamber. The overpressure should not be above 5 Pa in order to avoid air coming into the chamber through all the sampling holes on the chamber walls. If the overpressure is too high or too low, adjust the exhaust fan speed.
5. Make sure that all the needed instruments are turned on.
6. Turn of the car and connect the flexible hose to the car exhaust pipe. Adjust the nut if necessary to make it fit better.
7. Turn on the car once more. The chamber is now getting filled.
8. Control the gas levels in the undiluted and diluted gas concentrations.
   - The stabilization time for the gas analyzer is about 20 seconds so every measurement should last at least this time period, recommended ~30 sec. Measure both flows (diluted and undiluted) with an interval of 1 min. These measurements can be repeated several times to make sure that the engine is running in a stable way. Measure/control the levels inside the chamber.
9. Turn of the car when the concentrations have reached the desired levels inside the chamber.
10. Wait a time period to let the concentrations inside the chamber decrease. This time is dependent on the desired concentrations.
11. Start the car again.
    - It is not necessary, but it can be good to check the gas concentrations in the raw exhaust and diluted exhaust once more to check that everything is as it should be.
12. Repeat step 9-11.
13. When the measurements are finished, stop the car, close the valve for the dilution flow and disconnect the heating wires.
    - It is important that the car is turned off before the dilution valve is closed.
Appendix B
Mass balance over the exposure chamber

\[ In + Produced = Out + Accumulation \]

If the terms *Produced* and *Accumulation* are assumed to be zero the mass balance is simplified to

\[ In = Out \]

Let \( y(t) \) be the concentration inside the chamber at time \( t \).

This gives the following mass balance

\[ F_1 \cdot C_{in} = F_2 \cdot \frac{y(t)}{V} \]

Assumption: \( F_1 = F_2 = F = 1.8 \text{ m}^3/\text{min} = 5 \text{ air exchanges per hour}. \)

The concentration change inside the chamber is given by the derivate of \( y(t) \).

\[ y'(t) = In - Out = F \cdot C_1 - F \cdot \frac{y(t)}{V} \]

\[ y'(t) + \frac{F}{V} y(t) = F \cdot C_1 \]

By multiplying all terms with the integrative factor \( e^{\frac{t \cdot F}{V}} \), the differential equation can be solved. The solution is presented below.

\[ y(t) = C_1 \cdot V + (C_{start} - C_1 \cdot V) \cdot e^{-\frac{t \cdot F}{V}} = C_W \cdot V \]

\( C_W \) is the outlet concentration from the chamber, that is the concentration inside the chamber at time \( t \). The equation presented in section 8.1 is derived by taking out \( t \) in the above equation.
Appendix C
Calculations of deposition losses due to diffusion.

The penetration, \( P \), of particles is given by the following two equations.

\[
P = 1 - 5.50 \mu^{2/3} + 3.77 \mu \quad \text{if } \mu < 0.009
\]

\[
P = 0.819 \exp(-11.5 \mu) + 0.0975 \exp(-70.1 \mu) \quad \text{if } \mu > 0.009
\]

\( \mu \) is the deposition parameter given by the equation

\[
\mu = \frac{LQ}{D}
\]

where \( L \) is the tube length, \( D \) is the diffusion coefficient and \( Q \) is the volume flow rate. The diffusion coefficient is given by

\[
D = \frac{kT C_c}{3 \pi \eta d}
\]

where \( k \) is the Boltzmann constant, \( T \) is the temperature in Kelvin \( \eta \) is the viscosity of the air, \( C_c \) is the Cunningham factor given in section 2.2 and \( d \) is the particle diameter. A penetration value of 1 means that no deposition occurs and all the particles are exiting the pipes. A value equal to 0 means that all the particles are deposited on the pipe walls. The deposition curve between \( \mu=10^{-4} \) and 1 is shown in figure C1. Q is set to 400 l/min, which is the lowest flow rate used.

![Penetration of particles (Diffusion losses)](image)

Figure C1. Penetration of particles within \( \mu=10^{-4} \) and 1.

The most likely deposition mechanism in the transport system is diffusion because of the small particle sizes and the long transport distances. The residence time is longest in the transport pipe between the
primary and secondary dilution and deposition due to diffusion is therefore most likely to take place there. Calculations are also performed for the copper pipe where the flow is lower and the temperature is high. The relevant particle size range for the diesel aerosol is within 10-600 nm.

**Figure C2. Penetration of particles in a size range of 10-600 nm through the transport section between the primary and secondary dilution stage. The calculations are based on a volume flow rate of 400 l/min, which is the lowest flow rate used during the experiments. The tube length is set to 6 m.**
Figure C3. Penetration of particles between the size range of 10-600 nm through the copper pipe. The calculations are based on a volume flow rate of 30 l/min, which was the lowest achievable exhaust flow during the experiment. The tube length is set to 1 m.

Both figures C2 and C3 show penetration values above 98%. This indicates that deposition of diesel particles due to diffusion is very low. This should mean that the overall losses in the dilution system are very small and negligible. However, losses due to thermoporesis are not characterized within this work.
Appendix D
Experiment VW3a

Case VW3a (Volkswagen Passat case 3) was intended as an evaluation on how the dilution system can be used in human exposure studies. During the time between the VW2 and the VW3a experiments (a timescale of about a month) the car had been on service. During this service diesel filters had been changed and an additive, called Pro Tech diesel fuel, had been added to the diesel. This is used to clean and lubricate the diesel and exhaust system. It is a complex mixture of many different chemicals and it completely changed the obtained results. A typical size distribution from the VW3a measurements is shown in figure D1.

![Figure D1 Typical size distribution from VW3. A nucleation mode is present and is explained by the additive in the diesel fuel.](image)

The additive in the diesel fuel resulted in a nucleation mode which was not present during VW1 and VW2. It was also confirmed that the emissions of both CO and particulate matter was higher than before. The CO concentration was about twice as high compared two VW1 and VW2 while the NOx concentrations were reduced. Despite the changed emissions this “failure” in reproducibility may lead to an assumption that the dilution system should be able to reproduce a nucleation mode once such mode should be present. It was decided to skip the measurements regarding human exposures during this day and let the car be driven during a week in order to burn of the additive from the diesel. This next experiment is denoted VW3b.

During the VW3b experiments the particle size distribution was back to the same as those obtained in VW1 and VW2. However the emissions of CO and particulate matter were still high and the extraction of the diesel exhaust had to be slightly changed. The changes meant that the extra tail pipe was not fully blocked but some exhausts were allowed to exit through it. This assured that less exhausts entered the dilution system.