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Diesel Exhaust Particles:
On-Road and Laboratory Studies

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**Diesel Exhaust Particles: On-Road and Laboratory Studies**

Thesis for the degree of Doctor of Technology to be presented with due permission for public examination and criticism in Sähkötalo Building, Auditorium S4, at Tampere University of Technology, on the 21st of November 2008, at 12 noon.
Abstract

Traffic is one of the most important sources of particulate pollution and its role is emphasized especially in roadside and urban environments. Because the fine particles of the ambient air have an impact on human health and environment, the interest in the formation and the characteristics of traffic related particles has been increased. Also, the limitations for particle emissions have become stricter causing a continuing need to improve vehicle technology. Both to estimate the effects of traffic related particles, on human health and on atmospheric environment, and to minimize the emissions, the studies concerning the particle characteristics and the formation mechanisms are needed. Within the vehicle fleet, diesel vehicles make a relatively high contribution to particle emissions. For diesel vehicles, the submicron exhaust particles can typically be divided into a nucleation mode and an accumulation mode. In addition to particle size, particles in the nucleation mode and the accumulation differ from each other by structure, composition and formation mechanisms.

This thesis is based on experimental studies of traffic related particles in roadside environment and on the exhaust particle measurements conducted with individual diesel vehicles and with a diesel engine. With the individual vehicles, both on-road and laboratory experiments were made. While the on-road chasing measurements provide information on particle formation and characteristics in real-world conditions, the measurements on chassis dynamometers and at an engine test bench were conducted in order to clarify the correlation between the laboratory measurements and the real-world emission and to study the particle formation and the particle characteristics in well-defined conditions. The focus of this thesis is in the nucleation mode particles.

In roadside environment, the particle number concentration depends on traffic rate and it is dominated by the nucleation mode particles. In winter conditions, the particle concentration is higher because the conditions seem to favour the formation of the nucleation mode particles.

The formation of the diesel exhaust nucleation mode particles can be divided into different paths. If the nucleation mode particles are observed without an exhaust after-treatment, the particle formation is based on the existence of non-volatile core particles in raw exhaust and on the particle growth by hydrocarbon compounds during the exhaust dilution and cooling process. When a diesel oxidation catalyst is used, the formation of the nucleation mode particles can be based on the formation of the non-volatile core particles and, further, the particle growth by hydrocarbon or sulphur compounds depending on the engine load. However, in the case of the oxidation catalyst, also the sulphur driven nucleation during the dilution and cooling process is possible. In this case, the nucleation mode particles seem to be volatile and the particle formation is affected by exhaust dilution conditions and driving history. When a diesel particle filter is used, the formation of the nucleation mode particles occurs during the dilution and cooling process and the formation seems to be sulphur driven.

The particle characteristics and trends in the particle formation seem to be similar in the real-world conditions and in the laboratory measurements. This indicate that, using appropriate exhaust sampling and dilution methods and parameters, the laboratory measurements can be used in the studies concerning both the nucleation mode particles and the accumulation mode particles of diesel exhaust.
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List of publications


Other publications related to the research field but not included into the thesis:


### Abbreviations

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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AIS</td>
<td>Air Ion Spectrometer</td>
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<tr>
<td>CPC</td>
<td>Condensation Particle Counter</td>
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<td>CRDPF</td>
<td>Continuously Regenerating Diesel Particle Filter</td>
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<td>DMA</td>
<td>Differential Mobility Analyzer</td>
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<td>DOC</td>
<td>Diesel Oxidation Catalyst</td>
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<td>Dp</td>
<td>Particle mobility diameter</td>
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<td>DPF</td>
<td>Diesel Particle Filter</td>
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<tr>
<td>DR</td>
<td>Dilution Ratio</td>
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<td>ELPI</td>
<td>Electrical Low Pressure Impactor</td>
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<tr>
<td>ESC</td>
<td>European Stationary Cycle</td>
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<tr>
<td>FSC</td>
<td>Fuel Sulphur Content</td>
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<tr>
<td>GMD</td>
<td>Geometric Mean Diameter</td>
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<td>MFC</td>
<td>Mass Flow Controller</td>
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<td>RH</td>
<td>Relative Humidity</td>
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<tr>
<td>SMPS</td>
<td>Scanning Mobility Particle Sizer</td>
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<tr>
<td>THC</td>
<td>Total Hydrocarbon Concentration</td>
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<tr>
<td>PAH</td>
<td>Polycyclic Aromatic Hydrocarbon</td>
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<tr>
<td>CAN</td>
<td>Controller Area Network</td>
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<td>OBD</td>
<td>On Board Diagnostic</td>
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1. Introduction

Within the past decades, the concentration and the size distribution of fine particles in urban environment has been studied widely. Based on these studies, the particle concentration is significantly higher in the urban environment compared to the concentrations in rural environment (e.g. Ketzel et al. 2003, Laakso et al. 2003). In urban areas, the diurnal variation of particle number concentration correlates with the amount of traffic (Laakso et al. 2003, Hussein et al. 2004) and, consequently, the highest particle concentrations have usually been observed near traffic routes (e.g. Shi et al. 1999a) and, especially, in street canyons (Wehner et al. 2002, Ketzel et al. 2003, Longley et al. 2003). Typical submicron particle number size distributions measured in urban areas consist of two or three different modes which are usually called nucleation mode, Aitken mode and accumulation mode (Laakso et al. 2003, Hussein et al. 2004). The modes are distinguished mainly by particle size; the nucleation mode is in particle sizes below 30nm, the Aitken mode is between 20-100 nm and the accumulation mode is in particle sizes larger than 90 nm (Hussein et al. 2004). The highest particle number is typically found within the size range of the nucleation mode, both in urban background measurements (Laakso et al. 2003, Hussein et al. 2004) and in the measurements near traffic routes (Shi et al. 1999a, Wehner et al. 2002).

Different individual vehicles (heavy-duty trucks and buses, diesel passenger cars, gasoline passenger cars) have a variety of emission profiles. Thus the traffic emission is a mixture of particles emitted directly from different vehicles. The relationship between the particulate emissions from individual vehicles and the whole traffic emission is not fully understood. For diesel vehicles, the submicron exhaust particles can typically be divided into two separate groups depending on particle size and particle properties. In number based size distributions, these two groups are most frequently named as nucleation mode and as accumulation mode (Kittelson et al. 1998). Particles in the accumulation mode and the nucleation mode differ from each other in structure, composition and formation mechanisms. Nucleation mode particles have been reported to consist mainly of water, sulphuric compounds and hydrocarbons and they are frequently reported to be volatile. Accumulation mode consists of solid agglomerated soot particles and semivolatile compounds adsorbed or condensed on these particles. The mean particle diameters of the nucleation mode and the accumulation mode are typically between 3-30 nm and 40-100 nm, respectively.
Traffic particle emissions are generated in our immediate environment. The highest particle concentrations have been measured on highways, on roads, and in street canyons. All these are places where millions of people get daily exposed to the traffic related particles. In addition, the traffic emissions affect the aerosol particles of ambient air e.g. in pedestrian areas, on bus stops and in residential areas near traffic routes and they have a contribution to the urban background aerosol affecting the aerosol particle number, the particle size distribution and the particle properties everywhere in urban areas. Thus, people are widely exposed to the particle emissions of traffic in their daily life.

In epidemiological studies, the high concentration of the fine particulate matter in ambient air is associated with higher human mortality (Dockery et al. 1993) because of the increased risk of cardiovascular and pulmonary diseases, e.g. lung cancer (Samet et al. 2000, Pope et al. 2002). In the study of Peters et al. (2001), the elevated fine particle concentrations were associated with the risk of an acute myocardial infarct. Pulmonary inflammation has been observed in healthy human volunteers (Ghio et al. 2000) and in rats (Saldiva et al. 2002) when they were exposed to the particles concentrated from ambient air. In rats, the greater inflammation occurred in the segment of the respiratory tract where particle deposition is most efficient (Saldiva et al. 2002). Several studies have shown that diesel exhaust particles have inflammatory effects on human lung epithelial cells (e.g. Dybdahl et al. 2004, Mazzarella et al. 2007). Dybdahl et al. (2004) made also in vivo studies for mice and observed that the exposure on diesel exhaust particles causes the breaking of the DNA strands both in human lung epithelial cells and in the lungs of mice. However, they did not observe an increase in the mutation frequency. It is proposed that diesel exhaust particles can penetrate into cells and cause DNA damage and cancer because they can cause intracellular formation process of reactive oxygen species (ROS) (Ichinose et al. 1997, Suzuki et al. 2008). In addition to effects on cardiovascular diseases, diesel exhaust particles seem to affect the function of the human brain (Crüts et al. 2008).

Although the health effects of particles have been linked to cardiovascular and pulmonary diseases and particles seem to affect the central nervous system, the exact affecting mechanisms and harmful characteristics of the particulate matter are still unclear. It has been proposed that the inflammatory effect of particles is related to particle number, particle size or particle surface area (Stoeger et al. 2006, Wittmaack 2007, Su et al. 2008) or to the metals (Carter et al. 1997) and the hydrocarbon compounds in the particles.
In order to minimize the harmful effects of the ambient aerosol, traffic emissions should be taken into account in the plans of traffic routes and land use near the routes. Public transport should be favoured and, in the most polluted regions, traffic rates and vehicle emissions could be limited. Probably the most efficient way to limit the vehicle emissions is the international emission standards. In Europe, the particle emissions have been limited effectively by the legislation of the European Union. EURO I limits for heavy duty diesel engines and EURO I limits for diesel passenger cars entered into force in 1992 giving the limits for certain gaseous and for particulate emissions. After that the emission limits have become stricter. For example, EURO I limits for the particulate emissions of heavy duty diesel engines were 0.612 and 0.36 g/kWh, depending on the engine power, while EURO V will limit particulate emissions below 0.02 g/kWh since 2008. In the future, also the particle emissions of the gasoline vehicles will be restricted. In addition, the limitations of the emitted particle number will be coupled with mass based particle emission limits.

The particle emissions can be controlled by several means. One of the most important factors in the particle formation is the type and the composition of fuel. The decrease in the fuel sulphur content affects the particle emissions so much that the effect has been observed in roadside environment (Wåhlin et al., 2001). The use of oxygenated fuels and the reduction of the fuel aromatics have a clear reducing effect on the particle emissions. Furthermore, the lubricant oil contributes on particle emissions and by modifications on lubricant oil formulation, the reduction in particle emission can be reached. The soot particle emissions can be reduced also e.g. by modifying the fuel and air mixture, the fuel injection timing and the adjustment of the combustion temperature. An effective way to reduce the particle emissions is use of an exhaust after-treatment. From the viewpoint of the exhaust soot particles, the most effective after-treatment device is a diesel particle filter (DPF) which can collect even 90% of the solid particle mass. However, the collected particles can cause the choking of the DPF; thus, the DPF have to be regenerated. To avoid the problems related to to the regeneration, the open channel filters with lower collecting efficiency have been developed. In addition, although the diesel oxidation catalyst (DOC) has been developed to remove the gaseous pollutants, it has a contribution also to the particulate emissions.

1.1. Objectives of the study

The study presented in this thesis is closely related to the LIPIKA project funded by the FINE programme of Tekes (Finnish Funding Agency for Technology and Innovation). The target of the project has been to clarify the correlation between real particle emissions of traffic and laboratory
emission measurements of vehicles. The focus has been on the characteristics and the formation of the nucleation mode particles in exhaust of diesel vehicles. The project aimed to clarify the role of the nucleation mode in a real exhaust plume and in roadside environment and, based on that, to commit on the importance to measure the nucleation mode particles in the laboratory emission measurements of vehicles and engines. The correlation between the particle measurements in laboratory and the real-world emissions of individual vehicles was studied, in addition to the effects of technology parameters (vehicle type, exhaust after-treatment, fuel), the driving conditions and the dilution on exhaust particles. Also the processes affecting the exhaust particles after the emission were studied. The project started in 2002 and continued to the end of April, 2006 and it was performed in co-ordination between Tampere University of Technology, Finnish Meteorological Institute, Helsinki Polytechnic, VTT Technical Research Centre of Finland and Finnish Institute of Occupational Health.

Figure 1.1. Factors affecting the formation of the nucleation mode particles in diesel exhaust and the measuring methods used in the LIPIKA project.

In the LIPIKA project, several measurement methods were used (see Fig. 1.1). Roadside measurements and measurements in a traffic tunnel provided information on the real traffic emission and on the processes affecting the particles after the emission. The roadside measurements were conducted simultaneously by stationary measurement stations and a laboratory vehicle developed in the project. In the on-road chasing measurements, the particle emissions of individual diesel vehicles were studied using the laboratory vehicle. The on-road measurements focused on
particle emissions in real life dilution and cooling conditions. Laboratory measurements were conducted on heavy duty and light duty chassis dynamometers and on an engine dynamometer. In these measurements, the exhaust sampling and dilution were performed in a controlled way and the effects of the dilution parameters (dilution ratio, temperature and relative humidity of dilution air) were tested. The use of similar vehicles, fuels and lubricant oils both in the on-road and in the laboratory conditions made it possible to study the correlation between the measurement methods. On the other hand, the use of different vehicles, exhaust after-treatment devices and fuels gave information about particle formation and about effects of vehicle technology parameters on it. In addition to Papers I-VI, the results of LIPIKA project have been reported e.g. by Pirjola et al. (2004), Arnold et al. (2006), Pakkanen et al. (2006) and Kerminen et al. (2007).

The targets of this thesis can be divided into three parts. First, the contribution of traffic to the particle concentration and to the particle size distribution in urban roadside environment is clarified. Second, the role of the nucleation mode in real-life driving and dilution conditions is clarified and compared to the results achieved in laboratory measurements. Third, the properties and the formation mechanisms of the nucleation mode particles are studied, both in the engine and vehicle laboratories and in real driving conditions on road. Papers I and II present the results of the roadside measurements whereas the focus of Papers III-VI is on the properties and the formation of diesel exhaust particles. The correlation between laboratory and on-road measurements of the nucleation mode particles is presented mainly in Paper III.

All Papers I-VI are based on the measurements of the LIPIKA project. Author has participated in the project and the measurement coordination and planning. Author was responsible for the part of the measurements reported in Paper I and participated in the measurements reported in Paper II. Author made the main fraction of the particle measurements and the data analysis related to Papers III-V and was responsible for the particle measurements presented in Paper VI. Author participated in the data analysis and the writing process of all Papers I-VI being responsible in writing process of Papers III-V. The density analysis of the atmospheric aerosol particles (Paper I) and the exhaust ion measurements (Paper VI) are subjects of other theses. Consequently, they are not widely discussed in this thesis.
2. Aerosol particles in roadside environment

In an urban environment, traffic is one of the most important sources of submicron particles. In addition to the several studies based on particle mass measurements (e.g. Kirchstetter et al. 1999, Ntziachristos et al. 2007), the significant role of traffic has been observed also in the measurements of particle number concentrations. The highest particle concentrations have typically been measured in street canyons (Wehner et al. 2002, Ketzel et al. 2003, Longley et al. 2003), on road and in roadside environment (e.g. Shi et al. 1999). Traffic contributes significantly to the ambient aerosol in the vicinity of traffic routes. For example, Hitchins et al. (2000) measured that at a distance of 100-150 m downwind from the road the concentration of fine and ultrafine particles decreased to approximately half of the concentration at 15 m from the road. Zhu et al. (2002) found that the ultrafine particle concentrations decrease exponentially as a function of distance from highway and reach the background concentrations at 300 m downwind from the freeway. In addition, the particulate traffic emissions contribute to the urban background aerosol causing the strong traffic related diurnal variation of the particle concentration to large urban areas (Hussein et al. 2004).

As discussed in the previous chapter, the particle size distributions measured in urban atmosphere consist of two or three modes. The modes are distinguished mainly by particle size so that the nucleation mode is in the particle sizes below 30nm, the Aitken mode is between 20-100 nm and the accumulation mode is in the particle sizes larger than 90 nm (Hussein et al. 2004). Because in the roadside environment the most significant particle sources are individual vehicles, particle formation and growth differs from typical processes elsewhere in the atmosphere. For example vehicles’ type, fuel composition and technology level affect the particle emissions and the particle concentration and the size distribution in roadside environment. Thus, the use of similar names for modes is not straightforward. However, in roadside environment the size distribution is typically dominated by the nucleation mode with a peak size of around 20 nm (Shi et al. 1999, Wählin et al. 2001b, Wehner et al. 2002, Janhäll et al. 2004, Ketzel et al. 2004).

In an aerosol mass spectrometer study conducted near a motorway (Schneider et al. 2005), the contribution of the traffic was seen as a pronounced amount of organic species in the accumulation mode particles. On the other hand, the results of Schneider et al. (2005) indicated similar aerosol mass fractions for sulphate, nitrate and ammonium near the motorway and in the background aerosol.
The exhaust aerosol undergoes several dynamical processes after the emission. The evolution of the particle size distribution and the processes affecting the exhaust particles can roughly be divided into two stages depending on the process timescale. The first step is the immediate dilution and cooling of the exhaust. During that stage, within the few seconds, the evolution of the exhaust particle size distribution is governed by the decrease in solid particle number concentration due to the rapid dilution and, in suitable conditions, the formation of the nucleation mode particles. In addition, gas-to-particle conversion can affect the properties of solid exhaust particles due to adsorption and condensation of semivolatile exhaust and ambient air compounds. In the second stage, the exhaust dilution and mixing with the ambient air continues dominating the evolution of the particle size distribution. At the same time, the exhaust particles can undergo physical and chemical changes due to dynamical aerosol processes like coagulation (Zhu et al., 2002, Barone and Zhu, 2008) and condensation (Wehner et al, 2002). The processes depend on dilution and meteorological conditions (e.g. Bucowiecki et al. 2002, Charron and Harrison 2003, Zhang and Wexler 2004, Wehner et al. 2002). The effects of these processes can be seen e.g. as a change in the size of the nucleation mode particles or as a chance of the particle composition and morphology (Barone and Zhu, 2008).

Kuhn et al. (2005a) studied the volatility of the aerosol particles near the highway using the Tandem Differential Mobility Analyzer (TDMA) with heater between the two DMAs. They observed relatively high volatility for the aerosol particles; for the 120nm particles the volume loss was about 65% and for the 20nm particles 95%, when the aerosol sample was heated to 110 °C. In addition, Kuhn et al. (2005b) observed both the volatile and the non-volatile particles in the particle sizes 45nm and 90nm whereas in the particle sizes 18nm and 27 nm most of the particles were volatile. Barone and Zhu (2008) reported that the aerosol on and near a freeway consist of several morphologies, e.g spheres, aggregates and irregularly shaped. A fraction of the particles was internally mixed including multiple different particles. The fraction of the particles having multiple inclusions increased as a function of the distance from freeway indicating the important role of the coagulation during the aerosol dispersion in the roadside environment.
3. Diesel exhaust particles

Diesel exhaust is a complex mixture of gaseous components and particles. The most significant gaseous compounds are NO and NO\(_2\), CO, CO\(_2\), SO\(_2\) and hydrocarbons. Submicron exhaust particles can be divided into two groups based on particle formation and characteristics. In the size distribution of exhaust particles, these groups are usually seen as two different modes (Kittelson 1998) called nucleation mode and accumulation mode. The use of the mode names similar to atmospheric aerosol modes can lead to misunderstanding, especially in the case of the diesel exhaust accumulation mode. In atmospheric science, the accumulation mode particles have been widely understood as a long-time result of dynamic aerosol processes; thus the initial particle sources can be various. Instead, in diesel exhaust, the accumulation mode consists of soot particles originated from diesel combustion process and volatile compounds. In some publications, the accumulation mode is called soot mode. The accumulation mode has a significant contribution both to the total particle mass and to the total particle number. If the nucleation mode exists, it can have significant contribution to the total particle number of the exhaust aerosol.

3.1. Nucleation mode particles

In diesel exhaust, the nucleation mode consists of particles in the size range of 3-30 nm in diameter (Figure 3.1). The lower size limit comes from the limitations of instruments used in particle studies; thus, it is possible that also smaller particles exist. In several studies the lower size limit of the instruments has been approximately 10\,nm causing difficulties in data interpretation. Nucleation mode particles have been reported to consist mainly of water, sulphuric compounds and hydrocarbons (e.g. Kittelson 1998, Tobias et al. 2001, Schneider et al. 2005) and they are frequently reported to be volatile (Schneider et al. 2005). In several studies, the formation of nucleation mode particles has been reported to take place during the dilution and cooling processes of exhaust gas. In addition to the volatility properties of the nucleation mode particles, the observations that the measured distribution and particle concentration depend on dilution parameters, such as dilution ratio and the temperature and the relative humidity of the dilution air (e.g. Mathis et al. 2004) support this assumption. The tendency of nucleation has been connected with a high sulphur or a high hydrocarbon content in exhaust gas (e.g. Vaaraslahti et al. 2005). Therefore, the formation of nucleation mode particles indirectly depends on engine parameters, fuel and lubricant oil properties, and exhaust after-treatment systems.
Figure 3.1. Typical particle size distributions of diesel engine exhaust. Three examples for nucleation mode is shown: particle size near the detection limit, nucleation mode and accumulation mode are clearly separable (left pattern); the whole nucleation mode in measurement range, nucleation mode and accumulation mode are clearly separable; nucleation mode and accumulation in nearly equal particle sizes (right pattern). Also typical detection limit (3 nm) is shown.

The sulphur-driven formation of the nucleation mode particles is widely accepted in the research field. The conception is based on three groups of observations. First, the nucleation mode exists when an oxidising exhaust after-treatment is used. Second, nucleation is enhanced at high engine loads. Third, the sulphur level in fuel and lubricant oil affects nucleation. These observations have been discussed more in detail below.

Maricq et al. (2002) studied the effect of exhaust after-treatment on exhaust particles using both blank and catalyzed substrates in the catalyst. Both after-treatment systems were tested with low sulphur and high sulphur fuel. As a result, nucleation existed only when the high sulphur fuel and an active catalyst were used. Vogt et al. (2003) reported similar results for a passenger car; the nucleation mode existed at high load when an oxidation catalyst was installed.

When an oxidation catalyst or another catalyzing exhaust after-treatment device is used, the nucleation mode is most frequently seen at high load. In addition to dynamometer studies (e.g. Vaaraslahti et al. 2005), Maricq et al. (2002) have seen this behaviour also in wind tunnel studies.
and Vogt et al. (2003) in on-road studies. Vaaraslahti et al. (2005) conducted measurements with a CRDPF (Continuously Regenerating Diesel Particle Filter) at four different engine loads and observed the nucleation mode only at highest, 100% load. The reason to the effect of engine load can be an increase in the exhaust temperature resulting in a more efficient conversion of $\text{SO}_2$ to $\text{SO}_3$ (Maricq et al. 2002, Giechaskiel et al. 2007). $\text{SO}_3$ can then react with water vapour molecules producing sulphuric acid. Based on nucleation modelling, the exhaust particle concentration can increase due to homogeneous nucleation of water and sulphuric acid vapours, if the exhaust concentration of the sulphuric acid is high enough and the exhaust dilution conditions are suitable (Shi and Harrison 1999, Du and Yu 2005, Lemmetty et al. 2006, Lemmetty et al. 2008, Du and Yu 2008).

The effect of fuel sulphur content on nucleation mode particles has been studied e.g. by Maricq et al. 2002, Vogt et al. 2003, Khalek et al. 2003 and Vaaraslahti et al. 2005. If an oxidising exhaust after-treatment is used, the results are clear: higher fuel sulphur content enhances the formation of the nucleation mode. Vaaraslahti et al. (2005) reported that with a heavy duty diesel engine also the sulphur of the lubricant oil affects particle formation. The correlation is very clear between the total volume of nucleation mode particles and sulphur available from fuel and lubricant oil (Vaaraslahti et al. 2005).

The formation of nucleation mode particles has been observed to be unstable even when dilution conditions, driving parameters and technology parameters have been kept constant. This behaviour has been linked to the storage and release of sulphuric compounds in after-treatment devices (Vaaraslahti et al. 2005, Kittelson et al. 2006b). It is possible that, at low engine load, the sulphuric compounds are stored into after-treatment devices. At high loads, the sulphur can detach and cause an additional increase in the concentration of the sulphuric compounds in the exhaust. Therefore, the time depended or the exhaust gas temperature depended behaviour can be linked to sulphur and the formation of nucleation mode particles may be a sulphur driven process (Vaaraslahti et al. 2005, Kittelson et al. 2006b).

Modelling of nucleation and particle growth requires detailed knowledge about the exhaust flow and the concentrations and chemical properties of exhaust compounds. Because our information on these issues is limited, exact modelling is difficult or even impossible. However, certain simplified but important conclusions can be made based on the models of binary homogeneous nucleation of sulphuric acid and water, which is best-known candidate for nucleation mechanism in diesel.
exhaust. First, it is possible that, in diesel exhaust, sulphuric acid and water nucleate via homogeneous nucleation (Shi and Harrison 1999, Vehkamäki et al. 2003, Lemmetty et al. 2006, Arnold et al. 2006, Vouitsis et al. 2008, Lemmetty et al. 2008). Second, in addition to the sulphuric acid concentration, the particle formation depends on the exhaust dilution and cooling processes (Du and Yu 2005, Lemmetty et al. 2006) and on the concentration and properties of organic species (Vouitsis et al. 2008). Third, some published experimental results cannot be explained by nucleation of sulphuric acid and water.

Saito et al. (2002) and Lehmann et al. (2003) have reported experimental results which differ from the results connected to sulphur driven nucleation. They observed increased tendency of nucleation at low loads. Vaaraslahti et al. (2004) found the nucleation mode with an oxidation catalyst and a particle filter at high load, but without after-treatment at low load. They proposed that these two cases represent two different processes of nucleation mode formation. At high load, the process is sulphur dominated, while, at low load, hydrocarbon species are important. The high air-fuel ratio at low loads keeps temperature low and combustion inefficient, thus favouring hydrocarbon formation. In addition, Mathis et al. (2004) have conducted laboratory experiments which show that hydrocarbons have a clear effect on the nucleation mode concentration. Tobias et al. (2001) found that the hydrocarbon compounds from unburned fuel or oil formed most of the nanoparticle mass whereas sulphuric acid was present at concentrations of a few percent. However, the formation of initial particles from gas phase hydrocarbon compounds seems to be impossible (Schneider et al. 2005, Tobias et al. 2001); Tobias et al. (2001) proposed that the nucleation of sulphuric acid and water is the formation mechanism of small nuclei and nucleation is followed by condensation growth by hydrocarbons. Also an ion-mediated nucleation process has been proposed as a formation mechanism of the diesel exhaust nucleation mode particles (Yu 2001, Yu 2002). Sakurai et al. (2003a, 2003b) studied the volatility and composition of diesel nanoparticles and found that the nanoparticles comprise of at least 95 % unburned lubricating oil. They observed that the particles are internally mixed, consisting volatile and non-volatile compounds. Non-volatile compounds were found in the nucleation mode particles at idle conditions by Kittelson et al. (2006a).

Because of the sensitivity to sampling and dilution conditions, the laboratory measurements of nucleation mode particles performed with different sampling and dilution techniques cannot be directly compared. In addition, results of laboratory measurements may differ considerably from real emissions on road because of differences in exhaust dilution processes (e.g. different time-scale of the dilution process and dilution ratios). In addition, the dilution on road is naturally affected by
ambient air temperature and humidity. Because alternative measurement methods are difficult to standardize, laboratory measurements made on a chassis dynamometer or at an engine test bench remain the most important method in emission studies. However, the on-road measurements are needed to clarify the role of nucleation mode particles in real world driving conditions and the correlation between the laboratory measurements and the real emission.

On-road studies of diesel vehicles have been reported by Vogt et al. (2003), Kittelson et al. (2000, 2006a, 2006b), Giechaskiel et al. (2005) and Casati et al. (2007). According these studies, there is a good agreement between laboratory and on-road measurements concerning the accumulation mode. In the study of particle emissions of a diesel passenger car (Giechaskiel et al. 2005), the appearance of the nucleation mode in a laboratory was similar to the on-road measurements but the particle size was larger in the laboratory. They proposed that the reason to the larger particle size was lower dilution ratio. It should be noted that, in general, the nucleation mode is sensitive to sampling conditions; thus the laboratory measurements may differ considerably from on road emissions depending on chosen sampling and dilution technique and the dilution parameters (e.g. Mathis et al. 2004).

Schneider et al. (2005) performed a combined particle size distribution and mass spectrometer measurement with a diesel passenger car. In the case of the nucleation mode (vacuum aerodynamic diameter 55 nm), they reported a 90% sulphuric acid mass fraction for sulphuric compounds. On the other hand, Tobias et al. (2001) reported sulphuric acid mass fraction 5%. Regardless of the differences in the results, both Schneider et al. (2005) and Tobias et al. (2001) proposed the nucleation of sulphuric acid and water as the nucleation mechanism. Also ammonia has been found in diesel particles when a nucleation mode has been observed, and it has been stated that ammonia can play a role in nucleation (Kleeman et al. 2000, Lemmetty et al. 2007). However, the chemical composition of the smallest particles ($D_p < 20$nm) is not known because of the low mass concentration of the particles.

As a summary, the exact composition and formation mechanisms of nucleation mode particles are unknown. This combined with the sensitivity of nucleation to the measurement methods (sampling and dilution) has caused a need for the measurements of nucleation mode particle properties, composition and formation trends and, on the other hand, for the measurements on road and in roadside environment.
3.2. Accumulation mode particles

Accumulation mode particles consist of solid carbonaceous agglomerates, frequently called soot particles, with adsorbed and condensed semi-volatile species. The formation of soot particles occurs during the combustion process in the fuel rich and high temperature regions of the combustion chamber. These areas are formed due to the limited diffusion of oxygen into the fuel droplets. The whole formation process includes several phases: the formation of initial compounds, nucleation, the surface growth of primary particles and agglomeration (e.g. Tree and Svensson, 2007). The initial precursors of soot are formed via the fuel pyrolysis process. In the pyrolysis process, the molecular structure of fuel organics is changed and compounds like polycyclic aromatic hydrocarbons (PAH) are formed. In the nucleation phase, these compounds form solid nuclei, which have diameters between 1.5-2 nm. In the surface growth process gas-phase compounds like acetylenes are attached on these nuclei and particle size and mass are increased. However, particle number remains constant. The surface growth can continue in cooler regions where there is no nucleation. In the agglomeration phase, the particles collide and can be attached with each other causing the formation of fractal-like solid soot particles. A competitive reaction for the soot formation process is soot oxidation which can occur at any time during the soot formation process. As a result of soot formation and oxidation, exhaust diesel soot particles are fractal like particles (Geometric Mean Diameter (GMD) typically 40-100 nm) consisting of spherical primary particles. The primary particles are typically larger than 20 nm in diameter (Wentzel et al. 2003, Tree and Svensson, 2007) but in modern diesel engine the diameter can be smaller. Su et al. (2004) conducted measurements with a modern medium duty diesel engine and reported primary particles approximately 12 nm in diameter. At the same time, Su et al. (2004) noticed that soot was more reactive and was oxidised at lower temperatures, when the results were compared to the measurements with an older engine.

During the dilution and cooling processes of diesel exhaust, semi-volatile hydrocarbons and sulphuric compounds can adsorb or condense on the surfaces of the soot particles. For example, Burtscher et al. (1998) reported decreases in particle mobility size when the temperature of the diluted and cooled exhaust sample was elevated. The decrease depended on engine load so that the most significant decrease (from ~55nm to ~36 nm) was observed at idle and at 50 % load the particle size was nearly constant at all temperatures below 400 °C. However, because of the fractal structure, soot particles may have much void volume between primary particles, and gas-to-liquid processes can change particle mass without changes in mobility diameter. Ristimäki et al. (2007)
reported volatile mass fractions of 25% and 45% for accumulation mode particles. For the density of volatile matter, they reported 0.8 g/cm$^3$. This indicates that the volatile matter can be hydrocarbons originating from lubricant oil and fuel, which is in good agreement with Sakurai et al. (2003a). However, the volatile fraction of accumulation mode particles seems to depend on exhaust after-treatment; the results of Schneider et al. (2005) indicate that when diesel oxidation catalyst is used, sulphur compounds may have important role in condensation process.
4. Experimental

4.1. Methods

Due to the strong effect of exhaust dilution on the formation of nucleation mode particles, the measurements presented in this study were performed using different measurement methods. First, traffic emissions were studied in roadside environment. Second, the particle size distribution, particle number and particle characteristics in the exhaust plume of individual diesel vehicles were studied in real-world driving and dilution conditions. These measurements were made by chasing individual vehicles with the laboratory vehicle equipped with aerosol instruments and instruments to measure gaseous pollutants. Third, laboratory measurements with diesel vehicles and engine were performed. The laboratory measurements made it possible to study the effects of dilution parameters, fuels and exhaust after-treatment in well-defined sampling and dilution conditions. In addition, the use of similar vehicles, fuels and lubricant oils both in the laboratory and on-road chasing measurements enabled the comparison between results.

4.2. Instrumentation for particle measurements

The particle measurements were conducted mainly using a SMPS (Scanning Mobility Particle Sizer), a Nano-SMPS, an ELPI (Electrical Low Pressure Impactor), and a CPC (Condensation Particle Counter). All the devices are widely used in aerosol studies. In Paper IV, the electrical charge of particles was measured using an AIS (Air Ion Spectrometer).

The SMPS consists of a DMA (Differential Mobility Analyzer) and a particle counter. In DMA, an aerosol sample is first led through a neutralizer so that the particles achieve the Boltzmann equilibrium charge distribution (Hinds 1999). After that the sample enters the classifier section which allows only the particles within a narrow electrical mobility range to proceed to the exit. The electrical mobility range is fixed by aerosol and sheath air flows and by an electric field inside the classifier section. Exiting particles are counted by a particle counter. In this study, two DMAs with different designs were used (DMA 3085, TSI Inc. and DMA 3071, TSI Inc). CPC 3025 (TSI Inc ) was used as a particle counter. Both pairs of the devices were used in the scanning mode (Nano-SMPS and SMPS) (Wang and Flagan 1990) to get a particle size distribution with high resolution.
The operating principle of the CPC is based on the saturation of the aerosol flow by water or alcohol and on the immediate cooling of the aerosol to achieve the supersaturated condition where particles grow to droplets (Hinds 1999). The number concentration of the droplets is measured with optical counters. In this study a butanol-based Ultrafine Condensation Particle Counter is used (CPC 3025, TSI Inc.) (Stolzenburg and McMurry, 1991). The CPC 3025 has been designed to measure particle concentration down to 3 nm (with 50 % counting efficiency) and it is suitable for the urban aerosol and vehicle emission studies.

The ELPI (Electrical Low Pressure Impactor) (Keskinen et al. 1992) consist of a corona charger, a cascade impactor and a filter stage (Marjamäki et al. 2002), a multichannel electrometer and a computer unit. Particles are charged by the corona charger and after that they are collected; particles larger than 30 nm on collection plates of the cascade impactor and particles smaller than 30 nm on filter stage. The electric current caused by the collected particles with electric charge is measured by electrometers. The electric current data can be used to calculate the particle size distribution. In Paper V, the ELPI has been used also in particle density analysis (Ristimäki et al. 2002), together with the SMPS, and to evaluate the active surface concentration of the exhaust aerosol (Ntziachristos et al. 2004a). In addition, due to the high time resolution, an ELPI is useful device when there are rapid changed in the source strength.

Diesel exhaust ion distribution measurements reported in Paper VI were made with an AIS (Air Ion Spectrometer) (Mirme et al. 2007). To allow simultaneous distribution measurement for positive and negative aerosol ions, the AIS consists of two DMAs for particle classification, electrometers to measure the electric charge of ions and a filtering system for the sheath air.

The particle volatility was studied using a thermodenuder (Dekati Inc.) (see e.g. Ntziachristos et al 2004b). In the thermodenuder, the diluted sample is led through a heater where volatile compounds are evaporated. After the heater, the evaporated compounds are gradually cooled and absorbed in active charcoal. During the measurements, the temperature of the heater of the thermodenuder was adjusted to 265-270°C. Particular measurements were performed to study the particle volatility into more detail. In these measurements, the temperature of the thermodenuder was altered from room temperature up to 192 °C (Paper IV) or up to 250 °C (Paper VI).

The “Sniffer” laboratory vehicle (Pirjola et al. 2004) was used both during roadside measurement campaigns and during on-road chasing measurements. In addition to the instruments for aerosol
particle measurements (ELPI, SMPS, Nano-SMPS, CPC), the laboratory vehicle was equipped to measure also gaseous compounds and weather conditions.

4.3. Roadside measurements

Paper I and Paper II present results of four roadside measurement campaigns conducted in the Herttoniemi district of Helsinki. The investigated highway (Itäväylä) is the main road consisting of three lanes in both directions. (Figure 4.1). At highway, the day time (06:00-20:00) average traffic rate was 3290 vehicles/hour during the summer campaigns and 2910 vehicles/hour during the winter campaigns. The traffic rate was peaked during the morning and evening rush hours i.e. 6:00-10:00 and 15:00-18:00, respectively, when the traffic rate reached ~4000 vehicles/hour.

Figure 4.1. The measurement site of roadside measurements. Wind sector S1 (255°-345°), studied in Papers I and II has been marked with dashed lines.

The measurements were performed during two winter campaigns (10-26 February 2003 and 28 January – 12 February 2004) and two summer campaigns (12-27 August 2003 and 6-20 August 2004). Simultaneous stationary measurements were made at distances of 9 m and 65 m from the nearest edge of the highway (Figure 4.1). The instruments of the stationary measurements were in two similar cabins. In both cabins, the aerosol sample was taken at 5.7 m above the ground level.
and the sampling lines were identical. A sample flow was fed through the cabin roof with a 3 m long sampling tube, 25 mm in diameter. At the same time with the stationary measurements, measurements were conducted on the highway by the laboratory vehicle “Sniffer”. In addition to the driving on the highway, measurements were made by “Sniffer” also at the edge of the road, at bus stops, in summer times also at the grass area between the lanes, and in the urban background site approximately 600 m Northwest of the road. Dispersion studies with the “Sniffer” were conducted mainly near the stationary measurement cabins.

The cabins of were equipped with condensation particle counters (CPC 3025, TSI Inc.). With a CPC, a passive diluter with a dilution ratio of approximately 1:4 - 1:6 was used. During the campaigns in 2004, a Nano-SMPS was used in the 9m cabin (measurement range 3 - 57 nm). The SMPS was used in the 65 m cabin during all the campaigns. The SMPS measurement range covered the particles from 5 to 160 nm. An ELPI with filter stage was used in both cabins. Both measurement stations were equipped also with aethalometers (Hansen et al., 1982) in order to measure black carbon concentrations. The results of the aethalometer measurements have been presented by Pakkanen et al. (2006) and they are not included in this thesis.

The laboratory vehicle “Sniffer” measured particle size distributions using an ELPI with filter stage and an Hauke type Scanning Mobility Particle Sizer (SMPS) with an ultrafine condensation particle counter CPC 3025 (TSI, Inc.) or with UF-02Proto (Mordas et al., 2005). The total number concentration of particles larger than 3 nm was measured with a CPC 3025 (TSI, Inc.) after the passive dilution system with a dilution ratio of 1:3. In the “Sniffer”, the sampling tube length was 2.20 m and the sample residence time was approximately 7 – 8 s. In addition, “Sniffer” was equipped with CO and NOx analyzers.

Meteorological data (wind speed, wind direction, temperature and relative humidity) was measured at the 9 m cabin with a Vaisala weather station (Milos500, Vaisala) and with a weather station (Vaisala) on the roof of “Sniffer”. The meteorological conditions during the summer and winter campaigns are presented in Paper I and they were typical for summer and winter seasons in Helsinki.

Paper I concentrates on the stationary particle measurements conducted when wind was blowing from the road to the measurement cabins (in the sector S1, wind directions 255°-345°). The wind sector is marked into Figure 4.1 with dashed lines. Paper II concentrates on the data measured with
the laboratory vehicle and classified according to the wind sectors S1, S2 (5-55° and 185-235°, wind blowing along the highway) and S3 (75-165°, wind blowing perpendicular to the highway but to the opposite direction than in the sector S1).

4.4. Laboratory and on-road chasing measurements of diesel emissions

4.4.1. Vehicles and engines.

Papers III-VI report the results of the emission measurements conducted with four diesel vehicles and with a diesel engine. The measurements with the vehicles were made at chassis dynamometers and on-road. Two of the vehicles were heavy duty diesels (a bus and a truck) and two were diesel passenger cars. The tested vehicles represent different vehicle types and emission levels and they were equipped with different exhaust after-treatment devices. The measurements with the diesel engine were conducted at an engine test bench without after-treatment devices, with a diesel oxidation catalyst (DOC) and with coated diesel particle filter (DPF). The descriptions of the vehicles and the engine are given in Table 4.1.

In the measurements with the heavy duty diesel bus, the sulphur contents of the diesel fuel (Fuel Sulphur Content, FSC) and lubricant oil were 50 ppm and 8100 ppm, respectively. The diesel truck was tested using fuel with FSC less than 10 ppm, and some measurements were conducted also with fuel doped to FSC 47 ppm. The sulphur content of the lubricant oil was 3370 ppm. In the case of the passenger cars, the sulphur contents of the fuel and lubricant oil were 5 ppm and 2500 ppm, respectively. Same fuel and oil were used in both the passenger cars. In the measurements conducted with the diesel engine the FSC was 36 ppm.

Several steady-state driving conditions were used with all vehicles. The parameters of each driving condition are presented in Papers III-VI. In the cases of heavy duty diesel vehicles, the driving parameters were recorded by tapping into the Controller Area Network (CAN) of the tested vehicles. In the tests of the passenger cars, the driving parameters were recorded with a KTS vehicle diagnostic system manufactured by Bosch. The KTS was tapped into the on-board diagnosis system (OBD) (Euro 3 vehicle) or into the control unit of the engine (Euro 2 vehicle). The parameters were used to achieve similar driving conditions in the laboratory and on road. In the case of the Euro IV engine, the specific test cycle was used with all after-treatment and fuel combinations. The test cycle consisted of four steady-state driving conditions corresponding to the European Stationary
Cycle (ESC) modes 3, 10, 11, and 12. Before each cycle, the ESC mode 12 was used to warm the engine. The order and the durations of each mode periods were kept similar in all tests in order to ensure the repeatability of test set and comparability of runs with different after-treatment systems. The test cycle was similar to that used by Vaaraslahti et al. (2004, 2005).

<table>
<thead>
<tr>
<th>Vehicle type / Paper</th>
<th>Model year</th>
<th>Emission level</th>
<th>Exhaust after-treatment</th>
<th>Displacement (dm$^3$)</th>
<th>Mileage (km)</th>
<th>Max. torque (Nm@rpm)</th>
<th>Max. power (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel bus / Paper III</td>
<td>2002</td>
<td>Euro III</td>
<td>DOC</td>
<td>9.0</td>
<td>270 000</td>
<td>1100 @ 1100 – 1200</td>
<td>169 kW</td>
</tr>
<tr>
<td>Diesel truck / Paper IV</td>
<td>2005</td>
<td>Euro IV</td>
<td>Without after-treatment</td>
<td>11.7</td>
<td>5500</td>
<td>2100 @ 1100 - 1350</td>
<td>309 @ 1900</td>
</tr>
<tr>
<td>Diesel passenger car / Paper V</td>
<td>1999</td>
<td>Euro 2</td>
<td>DOC</td>
<td>2.46</td>
<td>190000</td>
<td>290 @ 1900-3100</td>
<td>103 @ 4000</td>
</tr>
<tr>
<td>Diesel passenger car / Paper V</td>
<td>2003</td>
<td>Euro 3</td>
<td>DOC+ DPF</td>
<td>2.72</td>
<td>10000</td>
<td>440 @ 1900</td>
<td>150</td>
</tr>
<tr>
<td>Heavy duty diesel engine/ Paper VI</td>
<td>2006</td>
<td>Euro IV</td>
<td>DOC/DPF/ without after-treatment</td>
<td>10.6</td>
<td></td>
<td>2220@ 1000-1400</td>
<td>324@ 1900</td>
</tr>
</tbody>
</table>

*Table 4.1. Tested vehicles and engine.*
**4.4.2. Laboratory measurements.**

Laboratory measurements were performed on a heavy-duty chassis dynamometer, on a light duty chassis dynamometer and at an engine test bench. In order to study the exhaust particle number, particle size distribution and particle characteristics, partial flow sampling and dilution was used. The exhaust sample was taken from the exhaust pipe downstream the exhaust after-treatment device. The primary dilution was performed with a porous tube type diluter (Mikkanen et al. 2001). In normal case, the relative humidity (RH) of dilution air was closed to zero and dilution air temperature (T) was set to 30 °C and measured before the dilution air entered the primary diluter. When the effect of the dilution parameters were studied (Papers III and IV), also RH was measured. The flow rate of the dilution air was kept constant (50 lpm) and adjusted with a mass flow controller (MFC). The flow rate of the exhaust sample was adjusted with a mass flow controller in the by-pass flow line and, except the particular studies reported in Papers III and IV, it was adjusted so that the dilution ratio (DR) of the primary dilution was 12. The primary diluter was followed by an ageing chamber (volume 2.4 dm³, residence time 2.6 s). After that the chamber, ejector type diluters (DR 8) were used to dilute the sample into the measurement range of the instruments. Dilution ratio values were calculated using CO₂ concentrations in raw exhaust and after either the ageing chamber (Papers III and IV) or after the first ejector diluter (Papers V and VI). The CO₂ concentration in the dilution air was measured and it was taken into account when the dilution ratio was calculated. The measurement setup used in the laboratory is presented in Figure 4.2.

The sampling system was a modified version of the partial flow sampling system developed for the “Particulates” research program of the EU (Ntziachristos et al. 2004b) and it has been used in several studies (e.g. Vaaraslahti et al. 2004, Vaaraslahti et al. 2005, Mathis et al. 2004, Gieshaskiel et al. 2005).

Particle size distributions were measured with an ELPI, a SMPS and a Nano-SMPS and the particle volatility measurements were conducted with a thermodenuder. In the measurements conducted with the heavy duty diesel engine, the exhaust ion size distributions were measured with an AIS. The exhaust concentrations of the gaseous compounds (HC, NOₓ, CO and CO₂) were measured with a Pierburg Ama 4000 I exhaust gas measuring system (heavy duty vehicle measurements) or AVL exhaust gas measuring system (passenger car measurements).
4.4.3. On-road measurements

The on-road measurements were performed on a closed test track in the test centre of Nokian Tyres and on a straight low traffic road in Alastaro, Finland (Figure 4.3). The emissions were measured by chasing the vehicles with the “Sniffer” mobile laboratory vehicle (Pirjola et al. 2004). Particle size distributions were measured with an ELPI, a SMPS and a Nano-SMPS. In addition, analyzers for NO\textsubscript{x}, CO, and CO\textsubscript{2} were used. Relative wind speed and direction, ambient air temperature and relative humidity were measured and a GPS unit was used to measure the velocity and the position of the vehicle.
The background concentrations of particles and gases were determined between the chase runs. The exhaust dilution ratio was calculated using the raw exhaust concentrations and the measured concentrations of CO\textsubscript{2} or, in the case of the Euro III diesel bus, using the raw exhaust concentrations and the measured concentrations of exhaust particles in size range 57-160 nm. The particle number concentration within this size range was measured with second and third stages of the ELPI. The range corresponds to the soot mode of diesel exhaust particles which is reported to be stable during dilution (Maricq et al. 2002, Vogt et al. 2003). The raw exhaust concentrations of the gaseous compounds and particles were measured during the laboratory measurement campaigns (see above).

In order to study the evolution of the exhaust particle size distribution and the time scale of the nucleation particle formation, the on-road chasing measurements were conducted at different distances behind the test vehicles. A laser-based meter was used to measure the distance between the test vehicle and the laboratory vehicle.

![Figure 4.3. On-road chasing measurement of vehicle particle emission.](image-url)
5. Traffic related particles in roadside environment

Papers I and II present the results of the roadside measurement campaigns. Paper I is based on the data measured in the stationary measurement sites while Paper II is based on the measurements made with the laboratory vehicle, focusing on the dispersion of particle emissions in roadside environment.

A clear correlation was found between traffic rate and particle concentration. This can be seen in Figure 5.1, where the particle concentrations are presented with respect to the traffic rate. Figure 5.1a presents data for the particles smaller than 63 nm and Figure 5.1b for the particles larger than 63 nm. The traffic seems to affect both particle classes so that higher traffic rate causes higher particle concentrations at roadside. The correlation between NO\textsubscript{x} and the total particle number refers also to the role of traffic as a particle source (the result is presented in Paper II). However, the effect of traffic is more significant in smaller particle sizes. In addition, in the smaller particle size range the effect of season was clear. Compared to the particle concentration in summer, the wintertime concentrations of the smaller particles were 2-3 times higher while, for particles larger than 63 nm, the effect of season was negligible.

During the roadside measurements, a typical roadside aerosol size distribution was bimodal. In Paper I, these modes are called Mode I and Mode II and in Paper II the nucleation mode and the accumulation mode. In this thesis the latter terms are used. In Figure 5.2, the distributions measured

![Figure 5.1. Concentrations of two different size fractions as a function of traffic rate: (a) particles smaller than 63 nm, (b) particles larger than 63 nm. Concentrations were measured at a 9 m distance from highway. Adapted from Paper I.](image)
during rush hours in winter and summer are presented. Distribution measurements were conducted at a distance of 65 m from the highway when the wind direction was in the sector S1 (see Figure 4.1). Both in winter and in summer the particle size distribution was dominated by the nucleation mode. In addition, the nucleation mode was clearly affected by season; in winter the concentration of the nucleation mode particles was higher while the concentrations of the accumulation mode particles were nearly unchanged. Similar results were obtained from the measurements conducted with the laboratory vehicle (Paper II).

![Graph of particle size distributions](image)

**Figure 5.2.** Typical particle size distributions measured during rush hours in winter and in summer. In the upper corner the distributions are presented on a log-log scale. Adapted from Paper I.

Based on the dispersion studies (Paper II), the decrease in particle number is significant when the distance from the highway increases. In the wind sector S1, the total particle concentration decreased to 35% in summer and 39% in winter when the concentrations measured at 65 m were compared to the concentrations measured at the distance of 9 m from the highway edge. In the wind sector S2, the decrease was steeper, at 65 m distance the maximum concentration was 19% of the concentration measured at 9 m from the highway edge. The results confirm the role of traffic as a fine particle source and, on the other hand, show that the highest particle concentrations and thus the highest human exposure on particles occur near traffic routes.

Exhaust aerosol undergoes several dynamical processes during dilution. These processes can modify particle size and particle number and thus their effect can be seen in particle size
distribution measurements. In the roadside measurements reported in Paper II two clear changes of size distribution was observed. The dominating effect is the decrease of particle number when the distance from highway increases. This effect is mostly caused by continuous mixing of air to the less polluted ambient air. Another, especially in winter observed change was the shift of nucleation mode to the larger particle sizes. The shift is probably caused by condensation of volatile compounds on nucleation mode particles.
6. Diesel particle characteristics and formation

The results of Papers III-VI are presented in this chapter. The main focus points are the characteristics and the formation of the nucleation mode particles, and the comparison of laboratory and on-road measurements. Unless mentioned otherwise, the presented particle concentrations have been calculated to raw exhaust. Thus the results measured with varied measurement and technology parameters can be compared. It should be noted that the calculated raw exhaust concentration values for the nucleation mode are purely theoretical if the mode is formed during the dilution process.

The nucleation mode particles were observed with all tested vehicles. In several measurements, the diameter of the nucleation particles was smaller than 10 nm. However, the existence and the properties of the nucleation mode particles and the particle size distributions were strongly affected by driving conditions and driving history, exhaust dilution conditions and vehicle technology parameters. The most significant factor was exhaust after-treatment which affected both the formation of the nucleation mode particles and the characteristics of the particles. Thus, the results concerning the nucleation mode are discussed here in the order presented in Table 6.1. The results for each exhaust after-treatment system are presented in separate sections and, within each section, the results concerning the heavy duty vehicles and the heavy duty engine are presented first. Passenger cars without exhaust after-treatment were not tested.

<table>
<thead>
<tr>
<th>Exhaust after-treatment</th>
<th>Paper</th>
<th>Vehicle type</th>
<th>Measurement method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel particle filter (DPF)</td>
<td>VI</td>
<td>Heavy duty engine</td>
<td>Engine dynamometer</td>
</tr>
<tr>
<td></td>
<td>V</td>
<td>Passenger car</td>
<td>On-road / dynamometer</td>
</tr>
<tr>
<td>Without after-treatment</td>
<td>IV</td>
<td>Heavy duty truck</td>
<td>On-road / dynamometer</td>
</tr>
<tr>
<td></td>
<td>VI</td>
<td>Heavy duty engine</td>
<td>Engine dynamometer</td>
</tr>
<tr>
<td>Diesel oxidation catalyst (DOC)</td>
<td>III</td>
<td>Heavy duty bus</td>
<td>On-road / dynamometer</td>
</tr>
<tr>
<td></td>
<td>VI</td>
<td>Heavy duty engine</td>
<td>Engine dynamometer</td>
</tr>
<tr>
<td></td>
<td>V</td>
<td>Passenger car</td>
<td>On-road / dynamometer</td>
</tr>
</tbody>
</table>

Table 6.1. The order of the discussion.
6.1. Nucleation mode particles

6.1.1. Diesel particle filter (DPF)

Paper VI presents the results of the laboratory measurements conducted with a modern heavy duty diesel engine. When the engine was equipped with a coated DPF, the nucleation mode was observed at high loads (75% and 100%). At 75% load (ESC mode 12), the particle size distributions were measured with and without a thermodenuder treatment for the exhaust sample. According to these measurements, the nucleation mode particles were volatile (see Figure 6.1); practically all the nucleation mode particles evaporated when the exhaust sample was treated by the thermodenuder.

![Figure 6.1. Exhaust particle size distributions of a heavy duty diesel engine equipped with a coated DPF with and without the thermodenuder. The arrow shows the change in size distribution when the thermodenuder was switched on (with the thermodenuder, particle concentration was zero, not shown on the log scale). Modified from Paper VI.](image)

The measurements conducted with a Euro 3 passenger equipped with the combination of a DOC and a DPF have been reported in Paper V. The measurements were conducted on road both in the winter and in the summer using ultra-low sulphur fuel. The on-road measurements were complemented with laboratory measurements at similar driving conditions.
With the DPF equipped passenger car, the concentration of the accumulation mode particles was always under the detection limit of the measuring instruments. The concentration of the nucleation mode particles varied between the background level and $10^6$ #/cm$^3$ (8 m behind the vehicle) due to the effects of the engine load, differences in the driving history and the changes in the exhaust temperature. To take the driving history into account, the measurement were made using the driving cycle consisting of low load and high load driving conditions driven repeatedly one after the other (Figure 6.2). At low load (driving condition 2 of Paper V), the exhaust particle size distribution and also the particle concentrations were in the background level. At high load (driving conditions 3-5 of Paper V) the particle concentration was higher due to the formation of the nucleation particles. However, the exhaust particle concentration varied strongly, from the background level at the beginning of the high load run to values reaching $10^4 - 10^6$ #/cm$^3$ at the end of the run, depending on the engine load (Figure 6.2). Another trend in particle formation was seen when the high load test runs were compared to each other. The highest concentration was recorded at the end of the first high load run. During the following test runs at the high load, the exhaust particle concentration increased as a function of exhaust temperature but it did not reach as high concentrations as at the end of the first test run (see the trend line in Figure 6.2).

Figure 6.2. Number concentration of the nucleation mode particles in the exhaust plume 8 m behind the DPF equipped passenger car. Measurements were conducted on road at the driving conditions 5 (high load, shaded) and 2 (low load). The test cycle was preceded by long-time driving at low load. Adapted from Paper V.

Within each high speed run, both the particle number concentration and the active surface concentration were clearly correlated to the exhaust temperature upstream of the DPF, as shown in Figure 6.3 for the driving condition 5. The data series labels Test run 1 to Test run 4 refer to the test runs at high load presented in Figure 6.1. In all the tests, the concentrations increased rapidly as the temperature achieved particular values. However, the start-up temperature for the increase of the particle concentration shifted from 320 °C, in the first test run at high load, to 350 °C, in the last test run.
run. The increase of particle number with increasing exhaust temperature has been observed before with heavy duty diesel engines and vehicles (Vaaraslahti et al., 2005; Kittelson et al., 2006b) and it has been linked to the changes in the conversion of SO₂ to SO₃ or to the sulphuric compounds released from after-treatment devices. In the study reported in Paper V, the increase in the start-off temperature and the decrease of maximum concentrations (the trend line in Figure 6.2) indicate that the release of the stored compounds have a dominating effect on the exhaust particle formation when a high load condition is preceded by a long-time driving at low load. The increase in the start-off temperature can be explained by the gradual depletion of the storage during the high load runs so that the depletion cannot be replenished by short 5-minute runs at low load. However, for the last high load runs (3 and 4 in Figure 6.3) the effects of the higher sulphur conversion and the sulphur release cannot be separated.

Figure 6.3. Total number concentration (a) and total active surface concentration (b) of exhaust particles in an exhaust plume of the DPF equipped passenger car at driving condition 5. Measurements were made with ELPI in on-road conditions. The exhaust gas temperature measurement was located upstream of the DPF. Adapted from Paper V.

The dependence of the nucleation mode formation was rather similar for summer and winter (Figure 6.4). At first, this seemed to be inconsistent with previous experimental and modelling studies concerning the diesel nucleation mode formation; e.g. Mathis et al. (2004) and Du and Yu (2006) reported that a decrease in dilution air temperature has been found to enhance the nucleation mode formation. However, in the present case, the lower temperature data in Figure 6.4 was measured at much lower dilution air water concentration. Similar results for winter and summer conditions are consistent with the modelling study of Du and Yu (2006) where they made a sensitivity analysis for ambient air temperature and relative humidity. In our study (Figure 6.4), the median values for the ambient air temperature and relative humidity were -6 °C and 53 % in winter and 19 °C and 79 % in
summer. For these two conditions, the study of Du and Yu (2006) predicts practically equal nucleation mode particle concentrations.

The filter regeneration was achieved by slightly retarding the fuel injection timing, which increases the exhaust temperature, and by portioning an additional catalytic ingredient including cerium into the fuel in order to reduce the oxidation temperature of the soot particles. The regeneration process occurs at 200-400 km intervals. Compared to the non-regenerating conditions, the increase of the exhaust temperature was steeper and the exhaust particle concentration reached higher values during the regeneration process. Differences were significant also in particle size distributions; when the GMD of the exhaust particles was as large as 25 nm during the regeneration, the maximum GMD at the same load but in non-regenerating conditions was below 10 nm. Thus, the particle emission related to the regeneration could easily be separated from other nucleation events. However, it is possible that sulphur compounds contributed to the particle formation process also during the filter regeneration.

Figure 6.4. Particle number concentration in the exhaust plume measured 8 m behind the DPF equipped passenger car. The high load driving condition (driving condition 5) was used and the measurements were conducted in winter (the median values for the ambient air temperature and RH were -6 °C and 53 %) and in summer (19 °C and 79 %). The concentrations were measured with an ELPI in on-road conditions and they are mean values of several tests. The exhaust temperature was measured from the outlet of the exhaust pipe. Adapted from Paper V.
In summary, when a DPF is used, the volatile nucleation mode particles seem to be formed during the dilution and cooling of the exhaust. Although the particle formation can be sensitive to the measuring method, the particle formation is also a real-world phenomenon, not an artefact caused by sampling and dilution methods. The particle formation process seems to be sulphur driven; nucleation is observed at high load and it is affected by storage-release processes. The results are in accordance with several previous studies discussed in Section 4.


Usually, it is assumed that the formation of the diesel nucleation particles is a sulphur driven process. This was the conclusion also in the case of the DPF presented above. However, with the current low FSC values, this is possible only when oxidising after-treatment devices are used. As discussed above, at high exhaust temperatures normally met at high load, these after-treatment devices increase the concentration of sulphuric acid and cause the formation of the nucleation mode particles. However, the formation of the nucleation mode particles has been observed also with low FSC values without after-treatment (e.g. Vaaraslahti et al. 2005). It is proposed that, in such cases, exhaust hydrocarbon compounds may have a significant role in the nucleation process. However, it seems that hydrocarbon compounds do not explain the formation of the small cluster size particles (e.g. Tobias et al. 2001; Schneider et al. 2005); hydrocarbons may have a role in particles’ growth process but the initial origin of such particles has been unclear.

Paper IV presents the results of the measurements conducted with a diesel truck without an exhaust after-treatment. The truck was tested in fifteen different driving conditions. In all conditions, the nucleation mode dominated the particle number size distribution both in the laboratory and in the on-road measurements. Because of the large size of the nucleation mode particles, the removal of the volatile particle fraction (thermodenuder treatment) was required to clarify that the exhaust particle size distributions were bimodal, consisting of the accumulation mode (GMD 37-47 nm) and the nucleation mode.

The existence of the large nucleation mode during the measurements without after-treatment device indicates other nucleation processes than binary homogeneous $\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$ nucleation. However, to clarify the effect of sulphur, the measurements with the diesel truck (Paper IV) were conducted using fuels with different fuel sulphur contents (FSC). In Figure 6.5a, the total particle number
(dominated with nucleation mode particles) is presented for different fuels. No more particles with a higher sulphur level were observed. In addition, the FSC did not have an effect on the exhaust particle size distribution (see Figure 6.5b). Thus, it can be concluded that the fuel sulphur content does not affect nucleation in the studied case. The finding that the nucleation mode was insensitive on the FSC supports the scenario that, with low sulphur fuels, the sulphur driven nucleation needs an oxidising exhaust after-treatment. On the other hand, because the nucleation mode was observed, some other mechanism is required to explain the particle formation.

![Graph](image)

**Figure 6.5.** a) Exhaust particle number concentration measured with undoped fuel A (FSC<10ppm), and with fuel A doped to FSC 48ppm. The measurements were conducted with heavy duty diesel truck in a vehicle laboratory at four driving conditions of Paper IV. b) Particle size distributions with different fuels (the driving condition 8 of Paper IV).

As discussed above, a bi-modal size distribution was observed after the exhaust sample was treated with a thermodenuder (Figure 6.6a). To study the particle volatility in more detail, the temperature of the thermodenuder was altered from room temperature up to 192°C at the driving condition 8 of Paper IV. Figure 6.6b shows the change of the nucleation mode GMD as a function of the thermodenuder temperature. The GMD decreased with increased temperature up to 130 °C, where it plateaus to approximately 6 nm. Further, no significant changes were observed in the nucleation mode at the thermodenuder temperatures above 130 °C. The result indicates that the nucleation mode particles consisted of a non-volatile fraction (later called core particle) and a volatile fraction condensed on it. The GMD of the non-volatile core particles was smaller than 10 nm. Because of the small diameter and, thus, significant losses in the sampling and measurement system, direct and accurate calculations of the number of core particles were impossible. Instead, if a lognormal
particle size distribution was fitted to the measured size distribution of the non-volatile core particles and the number of the core particles was kept equal to the number of nucleation mode particles measured without the thermodenuder treatment, the fitted distribution is in accordance with the measured size distribution (see Figure 6.6a). This indicates that in the studied case, all the nucleation mode particles may have a non-volatile core.

Figure 6.6. a) Particle size distributions in the exhaust plume of the heavy duty diesel truck without exhaust after-treatment. The measurements were conducted on road with and without a thermodenuder at the driving condition 6. b) The nucleation mode GMD as a function of the thermodenuder temperature. Laboratory measurement, driving condition 8. Adapted from Paper IV.

With the heavy duty diesel truck, the measurements on a chassis dynamometer were conducted varying the dilution ratio, dilution air temperature and dilution air relative humidity. As a result, the nucleation mode was observed to be relatively insensitive to the humidity and the temperature of the dilution air. Instead, the dilution ratio of the primary diluter had a clear and systematic effect on the measured size distributions. A higher dilution ratio caused the nucleation mode to be in smaller particle sizes in all tested driving conditions but the total particle number calculated to raw exhaust remained practically unchanged. Because the dilution parameters did not have a clear effect on the particle raw exhaust number concentration, it is concluded in Paper IV that the core particles form before the sampling and dilution process. The effect of the primary dilution ratio on the nucleation
mode particle size indicates that the particle growth is linked to the hydrocarbon concentration in the ageing chamber; the change in the dilution ratio leads to the change of condensable hydrocarbon species in the ageing chamber and, therefore, it affects particle growth and the measured particle sizes. In Figure 6.7a, the effect of the dilution ratio on the total hydrocarbon concentration (THC) in the ageing chamber and, thus, on final particle size is seen. Figure 6.7b shows that the dilution ratio does not have a significant systematic effect on the total raw exhaust particle number.

![Figure 6.7. GMD of the nucleation mode (a) and the total particle number of exhaust particles in respect of the THC in a diluted sample (in an ageing chamber). Laboratory measurement with a heavy duty diesel truck without exhaust after-treatment. Adapted from Paper IV.](image)

Paper VI presents the results of the laboratory measurements made by a modern heavy duty diesel engine. At 75 % load, particle size distributions of the exhaust sample were measured with and without the thermodenuder treatment. When the engine was used without exhaust after-treatment devices, a bi-modal distribution was observed both with and without the thermodenuder. Like in the measurements reported in Paper IV, this indicates that the nucleation mode particles have non-volatile cores.

### 6.1.3. Diesel oxidation catalyst (DOC)

Paper III presents results for the measurements with the Euro III heavy duty diesel bus equipped with a DOC. The measurements were conducted by chasing the bus on road and on a chassis dynamometer in a vehicle laboratory. Two different trends are clearly seen when the GMD and the number of the nucleation mode particles are presented in respect of engine torque (Figure 6.8). At low values of engine torque, the GMD and the number of the nucleation mode particles decreased when the torque increased while, at high values of torque, a clear increasing trend in the GMD and
the particle number was observed when torque increased. The results indicate that there are two different formation processes for the nucleation mode particles.

Figure 6.8. Concentration of the nucleation mode particles and GMD of the nucleation mode measured on road and on a chassis dynamometer. The test vehicle was a heavy duty diesel bus equipped with a DOC. Adapted from Paper III.

Figure 6.9. Exhaust temperature and exhaust hydrocarbon concentration for an Euro III heavy duty diesel bus. Adapted from Paper III.

The exhaust temperature and the exhaust concentration of hydrocarbons are presented in Figure 6.9. As expected, the exhaust temperature increased when the engine torque was increased. At the same time, the increase of the exhaust temperature caused more efficient oxidation of hydrocarbons in the DOC and, thus, decreased exhaust hydrocarbon concentration. From the viewpoint of the particle measurements, the trend in particle size at low torques can be related to this decrease of exhaust hydrocarbon concentration. However, although the exhaust hydrocarbon compounds may have a
role in particle growth process, it seems that the formation of the initial particles cannot be explained by the nucleation of hydrocarbon compounds during the exhaust dilution and cooling process (Tobias et al. 2001; Schneider et al. 2005).

As presented above, the increase of engine torque was followed by an increase of exhaust temperature. In addition to the more efficient oxidation of exhaust hydrocarbons, this causes the more efficient conversion of SO₂ to SO₃ in the DOC (Maricq et al. 2002, Giechaskiel et al. 2007) and, thus, the enhanced formation of sulphuric acid in the exhaust. Although a clear experimental evidence is missing, sulphuric acid is proposed to cause new particle formation in the exhaust. Thus, the trend at high values of engine torque can be caused by sulphur compounds. The conclusion is supported by the use of fuel with relatively high FSC (50 ppm) in these measurements.

![Image](image.png)

**Figure 6.10. Exhaust particle size distributions with and without a thermodenuder for a DOC equipped heavy duty diesel vehicle at the driving condition 7 of Paper III (left side) and for the engine at 75% load (ESC 12) (right side, modified from Paper VI). Laboratory measurements with a Nano-SMPS.**

Although the results were not presented in Paper III, the non-volatile core particles were observed with a DOC equipped heavy duty diesel bus after the exhaust sample was treated with a thermodenuder (Figure 6.10, left side). The result is supported by the measurements with a DOC equipped diesel engine (Paper VI). With the engine, two modes were observed in the particle size distribution both with and without thermodenuder treatment at 75% load (Figure 6.10, right side). With the engine, the particle volatility measurements were made also at different thermodenuder
temperatures. Based on these measurements, the number concentration of the nucleation mode particles decreased about 90% when the temperature was increased from 80 to 150 °C. At the same time, the GMD of the nucleation mode particles decreased from 8 nm to approximately 5 nm. However, no changes were observed in the thermodenuder temperature range 150 – 250 °C.

![Figure 6.11. Effect of ambient air temperature on the concentration of the nucleation mode particles in the exhaust of a heavy duty diesel bus equipped with a DOC.](image)

The result, that the nucleation mode particles had a non-volatile core also when a DOC was used, indicates similar nucleation mode particle formation like when no exhaust after-treatment was used. However, it is possible that with a DOC the nucleation mode consists of both volatile particles and the particles with a non-volatile core. Especially at high load, the existence of volatile nucleation mode particles is possible if the FSC and the conversion of SO$_2$ to SO$_3$ are high enough. This possibility is supported by the effects of dilution parameters on particle the size distribution (Paper III); the decrease of ambient air temperature was followed by an increase in the nucleation mode particle number concentration (Figure 6.11) and in the nucleation mode particle size. The effects of ambient air conditions on the nucleation mode particle formation, especially on the nucleation particle number, indicate that the particle formation occurs during the exhaust dilution and cooling process. In addition, the results presented in Paper V indicate a similar particle formation process for DOC and DPF equipped diesel passenger cars. With a DOC equipped passenger car the nucleation mode was observed only at high load and the nucleation mode particle concentration increased as a function of exhaust temperature indicating the effect of the storage-release process similar to the DPF case. In the measurements with diesel passenger cars, a non-volatile fraction was not observed in the nucleation mode particles.
As a summary, the appearance of the non-volatile core particles indicates that, when a DOC is used, the initial formation of the nucleation mode particles can be similar to the case without an exhaust after-treatment. Based on the results of Paper III, the growth of the nucleation mode particles can be dominated by hydrocarbons or sulphur compounds, depending on driving conditions. Naturally, the roles of sulphuric acid and hydrocarbon species in the particle growth process depend on compositions of fuel and lubricant oil. Results indicate that the nucleation mode can exist also with a DOC when fuel sulphur content is low and when exhaust temperature is low causing inefficient conversion of SO$_2$ to SO$_3$. Thus, the results change the common conception that when an oxidation catalyst is used, the formation of nucleation particles is sulphur driven process. However, in addition to particles with non-volatile core, also volatile nucleation particles can be formed with a DOC. In that case, the effect of driving history has a significant role when fuel with low FSC is used.

6.1.4. What is known about non-volatile core particles?

Both with the tested heavy duty diesel vehicles and with the heavy duty diesel engine, non-volatile cores were observed in the nucleation mode particles. The concentration of the core particles was typically high (even more than $10^8$ particles/cm$^3$, if the concentration is calculated to the raw exhaust) and particle diameter less than 10 nm. The core particles were observed both at low and at high engine load. The effect of dilution parameters reported, in Paper IV, indicates that the core particles exist already in the exhaust pipe before the exhaust sample is diluted. This result is confirmed by the results presented in Paper VI; the core particles are observed without an exhaust after-treatment and with a DOC but are removed from the exhaust using a DPF. Thus the result indicates that the core particles are formed upstream from the exhaust after-treatment. The results that a part of the nucleation mode particles have electric charge (Paper VI) when the particles were observed to carry a non-volatile core indicates that the core particles are formed in highly ionizing, high temperature environment.

In this thesis, the non-volatile core particles were observed only in the studies with the heavy duty diesel vehicles and with the heavy duty diesel engine. With passenger cars (Paper V), nucleation mode particles were volatile. Similar results can be found from other published studies. Mathis et al. (2004) conducted measurements with a diesel passenger car and observed that the formation of the nucleation mode was strongly dependent on the dilution process. Vogt et al. (2003) reported that
with a diesel passenger car the formation of the nucleation mode is caused by sulphur compounds. They observed a nucleation mode when an oxidation catalyst and fuel having a high sulphur content was used. Schneider et al. (2005) performed mass spectrometer measurements and size distribution measurements for exhaust particles and concluded that the formation of nucleation mode particles is caused by sulphuric species. In their study, the nucleation mode particles were volatile. In the studies of Giechaskiel et al. (2005) and Casati et al. (2007), the nucleation mode existed at high load. The dependence on load and the observation that nucleation occurred with fuel having a relatively high sulphur content (280ppm, Giechaskiel et al. 2005; 310 ppm, Casati et al. 2007) indicate that the nucleation mode formation process is sulphur driven. On the other hand, in the exhaust particle studies performed with heavy duty diesel engines the volatile fraction of the nucleation mode particles has been observed by Sakurai et al. (2003) and Kittelson et al. (2006a). In addition, the results of Vaaraslahti et al. (2005) seem to refer to the existence of non-volatile cores in the nucleation mode particles when they showed that the nucleation mode particles were formed without an exhaust after-treatment. Ntziachristos et al. (2006) reported that the formation mechanisms of nucleation mode particles depends on engine type; with light duty vehicles the nucleation takes place at high load conditions, while with heavy duty vehicles the nucleation mode is often observed at low load conditions. They linked the nucleation at low loads to higher exhaust hydrocarbon concentration. Thus, it seems that the formation of the non-volatile core particles is characteristic to heavy duty diesel engines, but not to light duty diesel vehicles like passenger cars. The reason to the formation of the non-volatile core particles with heavy duty diesel engines only can be e.g. more significant lubricant oil consumption in heavy duty diesel engines or the differences in the combustion processes.

The structure and the chemical composition of the non-volatile core particles are unknown. Based on the volatility studies presented here, the core particles do not evaporate in temperatures below 275 °C. The formation of hydrocarbon nanoparticles smaller than 10 nm in diameter has been reported by Dobbins (2007) and Sgro et al. (2008). It is possible that these particles can be linked to the non-volatile core of the nucleation mode particles. However, it seems that also metal oxides may have a role; Lee et al. (2006) reported that the metal doped fuel increases the nucleation mode concentration.

Related to the non-volatile cores of the nucleation mode particles, several questions are open. The material and the formation process of the particles are unknown. To clarify the processes affecting the core particles after the initial particle formation, much more measurements and modelling are
required. The role of exhaust after-treatment seems to be clear, but the effects of other technology factors like fuel, lubricant oil and engine design require further studies. Furthermore, because the formation of the core particles seems to be quite usual with modern heavy duty engines, the role of the particles should be studied also in atmosphere, especially in roadside environment.

### 6.2. Accumulation mode particles

In general, the size distribution and the number concentration of the accumulation mode particles were insensitive to measurement methods (on-road measurement vs. laboratory measurement) and dilution conditions. However, together with the formation of the nucleation mode particles, the gas-to-particle conversion can affect the volatile fraction of the accumulation mode particles. Because of the fractal structure of the solid soot particles, the adsorption and the condensation of gaseous compounds can occur during the dilution and cooling processes of the exhaust without significant change in particle electrical mobility size. However, the adsorbing and condensing compounds can affect the effective density of the particles and thus the aerodynamic particle size. If both the electrical mobility diameter and the aerodynamic diameter are measured simultaneously, the effective density of particles can be estimated.

With the DOC equipped diesel passenger car, the mean effective density of the accumulation mode particles could be estimated as a function of exhaust temperature because both the aerodynamic size distribution (with an ELPI) and the mobility size distribution (with a Nano-SMPS and a SMPS) were measured simultaneously. In Figure 6.12, the change of the nucleation mode particle concentration and the mean effective density of the accumulation mode particles are presented as a function of exhaust temperature during a high load test run. In addition, the effective densities of the accumulation mode particles in the thermodenuder treated exhaust sample and for the accumulation mode particles at low load (condition 2, see Paper V) are presented. At low load, the density of the accumulation mode particles was 1.06 g/cm$^3$ with a standard deviation of 0.06g/cm$^3$ and no significant changes were seen during the test runs. At the beginning of the high load run, both the exhaust temperature and the particle effective density were practically at the same level as at low load. The same effective density was measured also in the vehicle laboratory with the thermodenuder treatment. However, as the exhaust temperature increased during the 5 minute high load run, also the effective density increased, reaching the values in the excess of 1.4 g/cm$^3$. The increase in the particle density was not accompanied by changes in the mobility diameter distribution or in the concentration of the accumulation mode. Similarly, the active surface
concentration based on ELPI measurements was practically constant (Figure 6.12). Thus, the change in the effective density of the accumulation mode particles indicates the condensation of compounds on the particles causing the filling of the void volume within the soot agglomerate particles. Because the increase in the effective density was strongly linked to the exhaust temperature and the effective density reached relatively high values (more than 1.4 g/cm$^3$), the condensing material was likely sulphuric acid or some related compound. This is supported by the existence of the nucleation mode when the effective density of the accumulation mode was high (Figure 6.12, lower figure).

![Figure 6.12](image)

Figure 6.12. The effective density of the accumulation mode particles, the total active surface concentration (upper figure) and the nucleation mode particle concentration (lower figure). A passenger car equipped with a DOC was used at the driving conditions 2 (low load) and 4 (high load) of Paper V. The dashed line shows the effective density of the accumulation mode particles after the treatment with the thermodenuder at the driving condition 4. The measurements were conducted on road.
6.3. Comparison of exhaust particle measurements conducted in laboratories, on road and in roadside environment.

This thesis and several previous studies show that the nucleation mode particles have an important role in urban atmosphere. On the other hand, the nucleation mode has been observed in several vehicle exhaust particle studies conducted in engine and vehicle laboratories. Due to the effects of the particle sampling and dilution methods in laboratory measurements, the correlation between the laboratory measurements of the vehicle emission and real emission has been an open question.

Based on the Papers III-V and for instance on the studies of Kittelson et al. (2000) and Giechaskiel et al. (2005), the nucleation mode particles in diesel exhaust are not an artefact caused by the sampling systems used in laboratory studies. Instead, in Papers III-V, significant number concentration of the nucleation mode particles was observed both in the laboratory and on road with a relatively good correlation (see Figure 6.8). In Paper IV, the nucleation mode was observed to consist of volatile and non-volatile fraction both in the laboratory and on-road. However, the results of the nucleation mode particle measurements depend on measurement methods, on the exhaust sampling and dilution techniques and on the dilution parameters like the dilution ratio, dilution air temperature and dilution air humidity (Figure 6.13). This has to take into account when the results of exhaust particle studies are compared with each other. Although the results like the number and the GMD of the nucleation mode particles seem to be sensitive to measurement methods and dilution schemes, the effects of the technology parameters like exhaust after-treatment and fuel composition seem to be similar and independent on measurement method.

Individual vehicles are major sources of aerosol particles in roadside environment. However, the correlation between the on-road particle emissions of traffic and individual vehicles is difficult to study because of the variety of vehicle types, fuels etc. In addition, several dynamical aerosol processes like condensation, evaporation, coagulation and mixing with ambient air can occur and affect the exhaust particles. However, similar trends can be observed between the roadside particle measurements and the emission measurements of individual vehicles. For instance, cold weather seems to favour the initial formation and growth of the nucleation mode particles in roadside environment (Papers I and II). Similar effects were observed in the measurements of an individual vehicle in Paper III and also in other publications (e.g. Kittelson et al. 2000, Mathis et al 2004, Du and Yu 2006).
In the roadside measurements, the nucleation mode was completely formed when the measurements were conducted on a highway by the laboratory vehicle. Other processes after the nucleation are slow; in addition to the decrease of particle number because of the mixing of air masses, only a minor shift was observed in particle size as a function of the distance from the highway. Similarly, the on-road measurements with individual vehicles (Papers III-V) showed that the formation of the nucleation mode particles is a rapid process and occurs within parts of a second. Apart from the decrease in particle number due to dilution, no significant changes were observed in the exhaust particle size distribution in respect of the residence time in the atmosphere (Papers III and IV). Thus, the time scales of the most effective processes seem to be equivalent.

The accumulation mode observed in the roadside environment is within the same size range of the typical accumulation mode of diesel exhaust. Figure 4.1 showed that the concentration of larger particles (Dp > 63 nm, dominated by the accumulation mode) was depended on traffic rate and, thus, the traffic seems to be a significant source of these particles. The result that the concentration of these particles was not affected by weather is qualitatively similar to the studies with individual diesel vehicles (e.g. Ristimäki et al. 2005).

![Graph](image-url)

**Figure 6.13.** Effect of dilution air temperature and RH on the concentration of the exhaust nucleation mode particles. Laboratory measurements on a chassis dynamometer were performed using 12 as the dilution ratio of the primary diluter. The test vehicle was a heavy duty diesel bus equipped with a DOC. Adapted from Paper III.
7. Summary and conclusions

Human exposure to fine particulate matter in ambient air has been observed to affect human mortality and health. Traffic is one of the most important particle sources in urban atmosphere contributing wide areas around traffic routes. From the viewpoint of human health, the effects of traffic related particles can be adverse especially because of the vicinity emission sources to people. Because the contribution of diesel vehicles on the traffic particulate emission is relatively high, this thesis has focused on the formation and the characteristics of the diesel exhaust particles.

Several measurement methods were used in this thesis. While the roadside measurement campaigns produced information about traffic emissions and factors affecting it, the on-road and the laboratory measurements with individual diesel vehicles and with a diesel engine clarified the particle formation and characteristics in more detail. In addition to the effects of sampling and dilution, the effects of vehicle technology (exhaust after-treatment, fuels) on the exhaust particles were studied.

The results of this thesis show that the nucleation mode particles dominate the number based particle size distribution in a roadside environment. The on-road studies of the exhaust particles have shown that the nucleation mode particles are real and, in some cases, a dominating part of the particle emissions of diesel vehicles. Thus, the role of the nucleation particles should be taken into account when the effects of particle emissions on environment and human health are studied and estimated. Based on the comparison of the laboratory and the on-road measurements of the diesel exhaust particles, the laboratory measurements conducted with individual vehicles can be performed so that the results concerning the nucleation mode particles correlate to real-world emission.

Figure 7.1 demonstrates the results concerning the formation of the nucleation mode in diesel exhaust. If the nucleation mode is observed when a diesel particles filter (DPF) is used, the particles of the mode are totally volatile. The formation of nucleation mode particles has been reported to be dependent on the sulphur available from fuel and lubricant oil (Vaaraslahti et al. 2005) and on the existence of sulphuric acid in the exhaust gas (Arnold et al. 2006). By modelling, the formation of these particles can be explained with the homogeneous nucleation of sulphuric acid and water during the exhaust dilution and cooling process (e.g. Lemmetty et al. 2008). In this study, the nucleation mode particles were volatile, the nucleation mode existed at high loads only and the
formation of the particles was affected by the driving history (the storage and the release effects of sulphur compounds). Thus, in the case of a DPF, the results of the present study confirm a sulphur driven particle formation process.

In the case of heavy duty diesels, non-volatile nanosized particles may exist in non-diluted exhaust. If a vehicle or an engine is not equipped with an exhaust after-treatment, the particles can act as the core particles of partly volatile nucleation mode particles. The particle growth occurs during the dilution and the cooling of the exhaust sample due to the gas-to-liquids processes of exhaust compounds. As a result, the nucleation mode particles with a non-volatile and a volatile fraction are formed. Based on the results presented in Paper IV, the volatile compounds are hydrocarbons if no after-treatment is used.

The use of an oxidation catalyst (DOC) does not remove (all) the core particles from the exhaust gas. Thus the core particles can act as seeds for the nucleation mode particles like in the case without an exhaust after-treatment. However, the results indicate that a DOC may change the composition of the volatile fraction of the nucleation mode particles. This can be seen from the results of Paper III where the GMD of the nucleation mode particles is presented in respect of engine torque. At low values of the torque, the particle growth seems to be dominated by hydrocarbons and the formation process of the nucleation mode particles seems to be similar to the case without an after-treatment. At high values of engine torque, the particle growth seems to be driven by sulphur compounds due to the more efficient conversion of SO₂ to SO₃ and, thus, the higher exhaust concentration of sulphuric acid. In addition, it is possible that new particle formation occurs during dilution via the homogeneous nucleation of sulphuric acid and water. However, this process requires relatively high sulphur content in fuel and in lubricant oil and/or significant storing and release of sulphur compounds in an exhaust after-treatment.

Several results of this thesis indicate that the non-volatile core particles of the nucleation mode are formed before the exhaust sampling and dilution. First, when the non-volatile cores were observed in the nucleation mode particles, the particle number concentration was insensitive on the exhaust dilution parameters. Second, it seems that a DPF removes the core particles from the exhaust gas indicating that the initial formation of the core particles occurs before an exhaust after-treatment. Third, when the nucleation mode particles were observed to contain non-volatile core, the nucleation mode was partly charged indicating that the formation of the core particles occurs at in highly ionizing, high temperature environment.
Figure 7.1. Processes affecting the formation of the nucleation mode when the non-volatile core particles exist (upper) and when the non-volatile core particles do not exist (lower) in raw exhaust.

In the measurements conducted with diesel passenger cars, the non-volatile core particles were not observed. Instead, the volatile nucleation mode particles existed at high load and the formation was strongly depended on exhaust temperature. The result indicates that there is a storage-release process of sulphur compounds in the exhaust line, most probably in the oxidation catalyst. The storage-release process allows new particle formation during the dilution process also when the sulphur concentrations of fuel and lubricant oil are low.
In order to prevent the effects of particle emissions on environment and human health, the vehicle technology is under continuous development. This development requires knowledge about particle properties and formation mechanisms. From this point of view, the results of this thesis can be used to decrease the number based particle emission or to change the exhaust particle characteristics. In summary, by using appropriate exhaust after-treatment (e.g. a DPF or an open channel filter, see Heikkilä et al. 2008), the core particles can be removed from the exhaust gas. In that way the formation of the nucleation mode particles can be prevented or, in the case of high exhaust sulphuric acid concentration, the particle properties and composition can be changed. Also, it may be possible that the initial formation of the core particles and, thus, the nucleation mode particle emission can be reduced by the development of fuels, lubricant oils and combustion process in general. However, much more measurements are required to clarify the role of vehicle technology factors in the formation process of the core particles. To reduce the number of the volatile nucleation mode particles and the volatile fraction of the accumulation mode, the most effective way may be to decrease the sulphur content of fuel and lubricant oil and, thus, to minimize the formation of sulphuric acid in the exhaust.
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