Nanoparticles from Shipping and Road Traffic

Olof Jonathan Westerlund

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UNIVERSITY OF GOTHENBURG

Department of Chemistry and Molecular Biology

University of Gothenburg

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Department of Chemistry and Molecular Biology

Atmospheric Science

University of Gothenburg

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Abstract

In the urban environment road traffic is the dominant source of aerosol particles while in coastal and harbour areas shipping is also a significant source. For shipping there are no direct regulations regarding particle emissions. For road traffic the emissions of particle mass has been regulated for over two decades but only during the last few years particle number has been included in emission regulations. Generally, nanoparticles are better described by their number rather than mass since they contribute insignificantly to the total particle mass of urban particles. Furthermore, particle number is believed to be a better metric for describing health effects than particle mass. Particle number and mass of the nanoparticles is however more difficult to measure both because of their small size but also because they are part of a highly dynamic system with constant exchange with the gas phase.

The studies described in this thesis were conducted with the aim of increasing the knowledge on the emissions of nanoparticles from shipping and city transit buses. The focus has been on size resolved particle number emissions. The evolution of nanoparticles was studied by conducting measurements by extractions from the inside of the exhaust system and from the exhaust plume.

Emissions of nanoparticles depend on combustion conditions, exhaust aftertreatments, the fuel and ship/vehicle variations. In this study engine load and engine speed was found to be the most important factors studying individual vehicles or ships. For example, manoeuvring of a ship in the port areas was found to contribute to up to a factor of 64 times higher particle number emissions than during stable engine load at open sea. It was found the variation between vehicles or ships was the most important factor when studying a fleet of vehicles or ships operating on different fuels and/or exhaust aftertreatments. For example, from a selection of 35 buses a few diesel fuelled buses were responsible for most of the particle mass emissions while a few buses fuelled with compressed natural gas were responsible for most of the particle number emissions. Controlling these extreme emitting individuals or specific operating conditions could be an effective way of reducing the total emission of nanoparticles.

Nanoparticles extracted from the exhaust system are different compared to the nanoparticles found in the exhaust plume. In the ship exhaust system a soot mode was often found together with a volatile nucleation mode. In the ship exhaust plume the volatile nucleation mode coagulated quickly leaving soot covered with volatile material. Soot emissions were lower for the studied buses which supress condensation and the lower total number concentrations in the bus emissions reduce the rate of coagulation. Nucleation mode particles for the studied buses were found both in the exhaust system and in the exhaust plume. Nucleation versus condensation of volatile material has implications for the measured particle number and in addition, soot covered with volatile material has a denser structure than soot without condensable material.

Non-volatile particles with a diameter of ~10 nm were found in the ship plume measurements which were not present in the on-board measurements. A hypothesis of organo-sulphates being formed in the exhaust plume was presented which could explain the formation of these particles. This emphasis that processes in the atmosphere can be of importance but they will not be covered in on-board or laboratory measurements.

List of Publications

Paper I

Size resolved particle emission factors for individual ships

Jonsson, Å. M., Westerlund, J. and Hallquist, M.

Geophysical research letters, 2011, (38), L13809

Paper II

Particle and Gaseous Emissions from Individual Diesel and CNG Buses

Hallquist, Å. M., Jerksjö, M., Fallgren, H., Westerlund, J. and Sjödin, Å.

Atmospheric Chemistry and Physics, 2013, (13), 5337-5350

Paper III

On-board Nanoparticle Measurements from a SCR-equipped Marine Diesel Engine

Hallquist, Å. M., Fridell. E., Westerlund. J. and Hallquist, M.

Environmental Science and Technology, 2013, (47), 773-780

Paper IV

Characterization of fleet emission from ships through multi-individual determination of size-resolved particle emissions in a coastal area

Westerlund, J., Hallquist, M. and Hallquist, Å. M.

Atmospheric Environment, 2015, (112), 159-166

Paper V

On-board measurements of particulate and gaseous emissions from an in-use Euro V SCR equipped bus

Westerlund, J., Jerksjö, M., Sjödin, Å., Hallquist, M. and Hallquist, Å. M.

Manuscript in preparation for Atmospheric Chemistry and Physics

List of Abbreviations

AIS	Automatic Identification System
CMD	Count Median Diameter
CNG	Compressed Natural Gas
CO	Carbon Monoxide
CO_2	Carbon Dioxide
CPC	Condensation Particle Counter
DOC	Diesel Oxidation Catalyst
Dp	Particle Diameter
DPF	Diesel Particulate Filter
EEPS	Engine Exhaust Particle Spectrometer
EGR	Exhaust Gas Recirculation
EF	Emission Factor
FSC	Fuel Sulfur Content
GSD	Geometric Standard Deviation
HBEFA	Handbook Emission Factors for Road Transport
HC	Hydrocarbon
HDV	Heavy Duty Vehicle
HFO	Heavy Fuel Oil
HSD	High Speed Diesel Engine
K	Kelvin
kWh	Kilowatt hour
LDV	Light Duty Vehicle
MDO	Marine Diesel Oil
MGO	Marine Gas Oil
MSD	Medium Speed Diesel engine
nm	nanometer, 10^{-9} meter
NO	Nitrogen Monoxide
NO_2	Nitrogen Dioxide
NO_X	Nitrogen Oxides ($NO + NO_2$)
NP	Nanoparticles
PAH	Polycyclic Aromatic Hydrocarbons
PASS	PhotoAcoustic Soot Sensor
PN	Particle Number
PM	Particle Mass

$PM_{2.5}$	Mass of particles with a diameter < 2.5μm
PM_{10}	Mass of particles with a diameter < 10μm
POA	Primary Organic Aerosol
ppm	Parts Per Million
RPM	Revolutions Per Minute
SCR	Selective Catalytic Reduction
SECA	Sulfur Emission Control Area
SMPS	Scanning Mobility Particle Sizer
SOA	Secondary Organic Aerosol
SOF	Soluble Organic Fraction
SO_X	Sulfur oxides (SO_2 + SO_3)
SSD	Slow Speed Diesel Engine
SVOC	Semi-Volatile Organic Carbon
UFP	UltraFine Particles
VOC	Volatile Organic Carbon
μm	Micrometer, 10^{-6} meter

Table of Contents

1 Introduction

New pollutants are frequently emitted to the environment before solid knowledge of the risk they possess is available. Historically, many negative impacts by these pollutants long time after they were introduced have been discovered. Even longer time pass by before appropriate regulations controlling these pollutants are in place.

Today, there are in many countries regulations for a number of key atmospheric pollutants. However, there are still many air pollutants that are unregulated. Nanoparticles are one such class of pollutants that only recently is being addressed. Nanoparticles have many sources of which some are natural and have always been present and others are anthropogenic. The increase in traffic has dramatically increased the human contribution of nanoparticles and the emissions are concentrated in urban environments. The aim of this thesis is to contribute with knowledge on emissions from road traffic and shipping which can lead to improved regulations and better urban air quality. Four sets of measurements, outlined below, have been performed to describe nanoparticle emissions and their evolution in the atmosphere.

Plume measurements:

Paper I and IV: Measurements of the ship fleet entering and leaving the port of Gothenburg. Measurements were conducted next to the main shipping route in the entrance to the port. 734 ship passages by 154 individual ships were registered. Paper I reported the successful characterisation for this ship fleet and paper IV focused on the different type of ships passing the site.

Paper II: Measurements from a selection of city diesel and compressed natural gas (CNG) fuelled buses with different emission standards and with different exhaust aftertreatments. The measurements were performed under controlled conditions at bus depots with limited influence of other traffic sources. 28 diesel fuelled and 7 CNG fuelled busses were analysed.

On-board measurements:

Paper III: Measurements on a Selective Catalytic Reduction (SCR) equipped passenger ship. Unlike the plume measurements in Paper I, II and IV this paper focused on details of the ship´s engine parameters to study particle emissions during different conditions driving a routine route.

Paper V: Measurements on an SCR equipped diesel bus during a predetermined driving route that included typical driving modes of city, urban and rural driving. Similar to Paper III the particle emissions were studied together with thorough details of engine parameters.

Strengths and weaknesses of both on-board and plume measurements are described and discussed. But more importantly the complementary information provided from the two types of measurement methods can be used to draw new conclusions not possible from only one type of measurement.

By measuring inside the engine with different dilution ratios, measuring directly outside the tailpipe and after several minutes of atmospheric dilution in the exhaust plume knowledge is gained on the different components of nanoparticles from traffic and their evolution from the combustion process to the air that we breathe.

2 Background

Aerosol particles are defined as a solid and/or liquid suspended in air. They can be classified by source, composition or size. Commonly they are classified by size into coarse particles with a diameter of 2.5–10 μm, fine particles of <2.5 μm, ultrafine particles (UFP) of <0.1 μm and nanoparticles which are defined by different sizes in the literature. This thesis focuses on nanoparticles which is defined as particles with a diameter <560 nm based on the key instrument´s measurement range.

Nanoparticles are a heterogeneous class of pollutants ranging from manufactured nanoparticles used for various industrial applications to nanoparticles from combustion sources or biogenic sources. This thesis focuses on anthropogenic particles produced from two combustion sources; road traffic and shipping. Nanoparticles are preferably presented by its number size distribution and in the urban environment the dominant source is road traffic contributing to 40-50% of all particle number.[1, 2] In harbour regions shipping can be the most dominant source.[3] Globally secondary organic aerosol (SOA) from traffic and particles from biomass burning also has a significant impact.[4]

2.1 Composition of aerosol particles

The nanoparticles in this thesis are either generated inside the engine or in the exhaust plume unlike larger particles that stems from wear and tear of road surface, wheels or brakes and from re-suspension of dust. A Typical diesel aerosol particle can be illustrated according to Figure 1. Non-volatile soot agglomerates are formed inside the engine. In the exhaust plume by expansion and by decreasing temperature the gases with low saturation vapour pressure condense on pre-existing particles or nucleate to form nucleation mode particles. These are volatile particles[5] that consist of sulphates and/or thousands of different organic compounds. The composition depends on the fuel and the combustion properties. The particles formed in the engine and immediately after being emitted to the atmosphere are often termed primary particles. By aging in the plume emitted compounds, with higher saturation vapour pressure, will be oxidised in the gas phase and can form compounds with a lower saturation vapour pressure that can contribute to the particle phase. These secondary particles consist mainly of oxidised organic matter. SOA are important on a regional and global scale[6] but the magnitude of the traffic contribution to SOA are currently uncertain[7]. Recently, smaller non-volatile core particles with a count median diameter (CMD) of ~10 nm have also been identified. They might consist of soot, metallic ash or organic compounds with very low volatility (black core particles in Figure 1).[8]

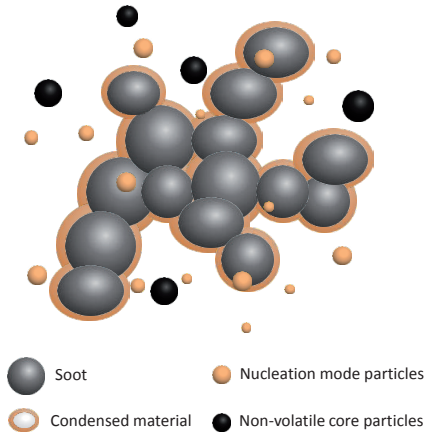

Figure 1. Illustration of a diesel aerosol particle. Adapted from Maricq, M. M. et al.[9]

2.2 The size of aerosol particles

The size of atmospheric particles determines to a large extent their fate after they are emitted. Their sources, sinks and transformation routes in the atmosphere are all depending on the size of the particles (see section 2.3). The common way to express their size is through size distributions with number or mass on the y-axis and size (diameter) on the x-axis (Figure 2). The size distribution of urban nanoparticles is usually described by different modes; soot mode, accumulation mode, nucleation mode and course mode (Figure 3). A size distribution from a combustion source initially contains a soot mode and sometimes a nucleation mode while the accumulation mode is formed during plume evolution.

2.3 Evolution in the atmosphere

Several important processes start simultaneously when particles are emitted to the atmosphere. Figure 2 summarises some of the processes that are important for different particle size modes at different stages during the evolution of the exhaust particles. Since the aerosol evolves in the atmosphere measurements should also be performed in different stages in the exhaust plume. In this thesis measurements were performed from the exhaust system (Paper III and V), during rapid initial dilution (Paper II and V) and during plume evolution (Paper I and IV). These stages are described below.

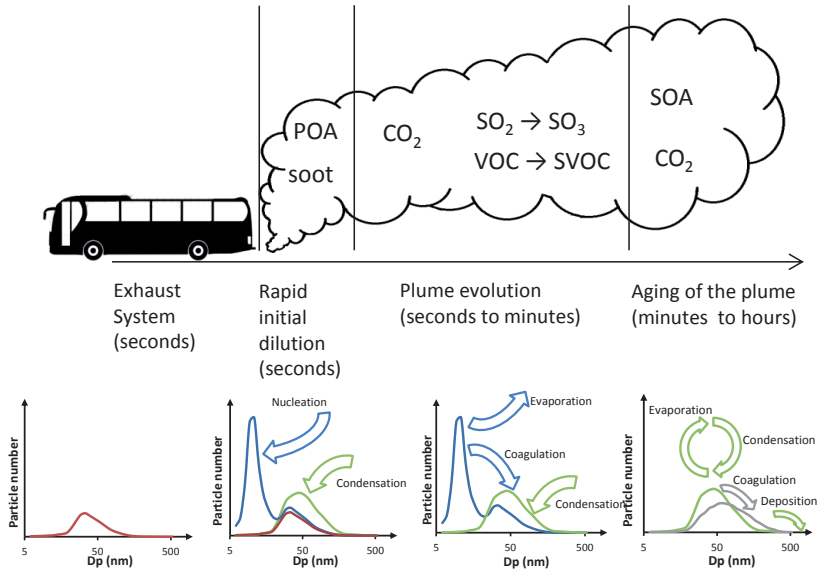

Figure 2. Some main constituents found in an exhaust plume and size distribution of particle number versus particle diameter with corresponding particle dynamics important for different stages of the plume life time.

Exhaust system: Soot agglomerates are formed inside the engine. Soot is the dominant component of the particles before entering the atmosphere. Measurements at this stage without significant dilution would display a unimodal size distribution of a typical soot mode.

Rapid initial dilution: When the exhaust gas exits the engine condensation onto pre-existing particles or nucleation of vapours starts to form primary volatile particles. They form due to the decreased temperature which acts to decrease the saturation vapour pressure of the vapours. High surface area of soot particles tends to favour condensation and supress nucleation while nucleation is favoured by the presence of high concentrations of the vapours in the emissions. The nucleation mode formed from diesel vehicles starts to form already at a dilution ratio of 10 and is fully formed at a dilution ratio of around 100.[10] In the wake of a moving car the dilution ratio can be up to 1000 already after 1-3 seconds[11] indicating significant evolution of the nucleation peak between the tailpipe and the road side. The dilution slows down and the plume processes are less important for the next 10´s of seconds.[12] For shipping the plume is rather undisturbed and will have a slower dilution rate.

As soot particles are initially covered with condensable material their agglomerated soot structure (Figure 1) immediately collapses into more densely packed clusters.[13, 14] When the soot has formed these dense clusters their optical properties depend mainly on the presence of condensed material and their mixing state.

Plume evolution: Volatile constituents of the particles keep evolving also after the initial plume dilution. Generally the nucleation mode particles regardless of combustion source disappear due to coagulation and/or evaporation as the plume evolves and is further diluted. Evaporation leaves an unchanged soot mode but coagulation would change the number size distribution towards larger particles.[15, 16] The time when the plume is considered to become aged is arbitrary. However, after the rapid initial dilution the particles in the ship plume stays relatively unchanged indicating for shipping a

time scale for this stage of at least minutes (Paper IV). Local topography for road emissions complicates the plume evolution that becomes a mix of the fresh plume and the urban aerosol[12] but with time the nucleation mode usually evaporates[17].

Aging of the plume: Particle constituents may evaporate to the gas phase where they can be oxidised to more volatile compounds remaining in the gas phase but they can also be oxidised and re-condense into the particle phase. This makes the lifetime of the volatile fraction shorter than the non-volatile fraction. This cycle of evaporation and condensation continues throughout the life time of the plume and the new particles formed in this stage considered being secondary. Depending on the ratio of evaporation/condensation particles can grow or shrink when aged in the atmosphere. Particles will also coagulate with each other or with pre-existing particles in the atmosphere which increases their size, decreases the number concentration but maintaining the particle mass concentration (PM). Coagulation to form larger particles is responsible for the accumulation mode particles. During aging of the plume also wet and dry deposition becomes important which decreases both particle number (PN) and PM. Soot is chemically inactive and remains more or less unchanged after the initial collapse of the agglomerated structure. Soot can remain in the atmosphere for up to 12 days.[18] Soot has been found to be the main constituents of aged ship plumes.[15, 19]

2.4 Health effects

It is well known that aerosol particles have adverse health effects supported by epidemiological[20] and toxicological studies[21]. The epidemiological studies have mostly focused on particle mass but it has been suggested that the number of particles or their total surface area may be more important metrics for health effects of nanoparticles.[22, 23] The size of the nanoparticles allows them to be inhaled deeper into the lungs where they induce more oxidative damage than the larger particles that are deposited higher up in the lung region.[21] Particle mass and particle number/surface area emissions seldom correlate strongly since the particles contributing to each metric are different. Consequently, additional measurements on number and surface will provide more information than if only aerosol mass is recorded.

The fraction of non-volatile particles are also important to characterize in the emissions from combustion sources[24] since their health effects are different from volatile particles. Volatile particles can deposit in the lung fluid and dissolve and consequently the biological response of them depend on the total mass of the particles.[25] Non-volatile particles do not dissolve so here it is the total accessible surface area that determines the biological response.[25] Volatile particles consist of many hydrocarbons including polycyclic aromatic hydrocarbons (PAH) which are carcinogenic. The volatile organic fraction is believed to be the key constituent that induces inflammatory response in the lung tissue[26]. This effect might increase with a future increase in biofuel usage that produce more volatile organic particle emissions per unit fuel compared to conventional diesel fuel.[27]

2.5 Climate effects

Aerosol particles absorb and scatter solar and terrestrial radiation which leads to direct climate effects.[28] The effect can be either warming or cooling depending on the optical properties of the aerosol particles. For example, soot emitted from combustion sources contribute to warming while sulphate particles contribute to cooling. Aerosol particles can act as condensation nuclei affecting cloud formation which leads to their indirect climate effects.[29] The indirect effect consists of several mechanisms which are more complicated and even if the indirect effect can be both warming or cooling the net indirect effect is cooling.[29] Absorption and scattering of visible light by aerosol particles also limit visibility which is an environmental quality that is more difficult to express or quantify.[30]

2.6 Emissions

Particle emissions and concentrations have independent regulations but they are of course closely coupled. To reduce concentrations of compounds in the ambient air the emissions of the compounds are often controlled. Models are commonly used to estimate total emissions from an area consisting of many sources and used to calculate ambient concentrations resulting from these emissions. One of the most important uncertainties in dispersion models are estimating accurate emissions and the effect of meteorological parameters.[31] For nanoparticles number emission factors (EF) is considered to be the single most important uncertainty[32, 33]. This is because laboratory studies which are most common for emission studies fail to consider the dynamics of the aerosol after it is emitted to the atmosphere[32]. Also, the drive cycles used in laboratory studies cannot fully capture the complete picture of real world driving where for example the quality of a vehicle deteriorate over time and produce higher emissions during their lifetime. In addition, new technologies are constantly being implemented and new input data are constantly needed to update the models.

The emissions are often expressed as EFs which relate the quantity of an air pollutant emitted to an activity associated with that pollutant, for example mass or number of particles emitted per km driven with a vehicle or per kg of fuel burned. The EFs contain more information in emission studies compared to only measuring concentrations in the emissions. Relating a pollutant to the fuel burned takes into account how efficiently the combustion process is generating the pollutant. Relating the pollutant to distance driven by a vehicle takes also the consumption of fuel into account. For heavy duty vehicles (HDV) the pollutant are in regulatory purposes related to the brake work produced by the engine.

EFs are frequently combined within emission inventories where total emissions of a pollutant for a sector or a country can be calculated. Similar to road traffic emission inventories, future ship emission inventories will likely be more detailed in terms of engine load distributions, fleet age, engine age and ship speed[34] where detailed studies on these parameters such as this thesis will serve as the basis for their development.

2.7 Engines, Fuels and Exhaust aftertreatments

The internal combustion engine has seen significant improvements over the years both regarding fuel consumption and emission reduction etc. The emissions are decreased both by improving the combustion process and by the use of exhaust aftertreatments. Details on the combustion process inside the engine is beyond the scope of this thesis but some information on the different engines and exhaust aftertreatments with focus on their effect on the particle emissions are described below.

Diesel fuelled vehicles

Diesel vehicles emit significantly more particles than petrol fuelled vehicles with EFs typically about 2 orders of magnitude higher.[35] A diesel fuelled engine pressurizes air in the cylinders then inject fuel that auto ignites. The short time for the fuel to mix with the air before the combustion process starts is the main key to the higher particle emissions from diesel engines compared to spark ignition engines with port injection. The fuel burns as it is vaporized and high local fuel to air ratios at a certain temperature range determines the soot formation. SOA from diesel engines is lower than from petrol fuelled engines but twice as much SOA as primary organic aerosol (POA) are formed after several hours of simulated atmospheric aging.[36] These particles correspond to an increase in condensation which acts to increase the particle mass concentrations in the aged plume described in Figure 2.

Petrol fuelled vehicles

Petrol fuelled vehicles operate at lower combustion temperatures which is less favouring for soot formation as compared to diesel vehicles that operate at a higher combustion temperature. In addition, they have usually homogeneous spark ignition which allows the fuel to mix with the air before combustion which also reduced soot formation. Their primary particle emissions are therefore often much lower than diesel fuelled vehicles.[37] However, recently smog chamber studies have shown that petrol fuelled light duty vehicles (LDV) contribute with up to 6 times more SOA than POA.[38] In order to reduce fuel consumption development of LDVs running on petrol is towards smaller cylinder size with direct fuel injection and turbo charge. This effectively reduces fuel consumption but the direct injection previously most found in diesel engines will promote soot higher formation in petrol fuelled vehicles.

Compressed natural gas fuelled vehicles

A bus running on CNG have lower particle mass emissions coupled to lower soot particle emissions[39] but instead they are emitting larger amount of volatile nucleation mode particles.[40]

Diesel fuelled ships

Ships mostly run on diesel engines although gas turbine engines or even natural gas burning engines are also used. Ship engines are often much larger than road vehicle engines and commonly operate on slower engine speeds, from <240 rpm for slow speed marine diesel engines (SSD) up to >960 rpm for high speed marine diesel engines (HSD). A common road diesel bus usually operates above 1000 rpm. The large ship engines are usually two stroke engines and because of large size and slow engine speed they have a high thermal efficiency (>50%). The high thermal efficiency together with high loading capacity makes transporting by ships a good choice when considering CO_2 per km or per ton goods shipped. However, the emissions are not extensively regulated and most ships are unlike road vehicles not equipped with exhaust aftertreatment which make their emissions much higher.

The most important difference for the emissions, at least in Europe, is the difference in the fuel used. Diesel for road traffic is a refined product that in the EU is regulated to have below 10 ppm of sulphur content. Ships uses heavy fuel oil (HFO) which is the least refined fuel with high viscosity that consists of long branched organics, more impurities and much higher fuel sulphur content (FSC) and consequently promotes higher emissions of particles, sulphur compounds and hydrocarbons (HC).[41] Recent regulations on ship fuel have forced the shipping industry to switch to marine diesel oil (MDO) or marine gas oil (MGO) which are more refined fuel with lower FSC. The emissions using these fuels will reduce SO_X emissions and sulphur containing particles significantly and may also reduce organic particles but this also depend on the different lubrication requirements of the more refined fuel.[42]

Exhaust aftertreatment

To comply with emission standards, the vehicle industry have developed engines and exhaust aftertreatments that reduces the emissions significantly. For shipping exhaust aftertreatment are scarce and are only found on a voluntary basis. With new FSC regulations both SO_X scrubbers and the use of alternative fuels might become more common. The exhaust aftertreatment systems that have an effect on particle emissions are described briefly below.

SCR is commonly used in heavy duty vehicles (HDV) and can be found also on some ships. The SCR reduces NO_X emissions by adding urea to the exhaust stream that is converted to NH_3 which reacts with NO_X on the catalyst to form N_2 and water. It can reduce NO_X emissions by up to 98% when

operating properly. The drawbacks have been that a high exhaust gas temperature is required which is difficult to reach in city driving conditions and during start-up.[43] There is also a risk that unwanted pollutants are oxidised over the SCR. Sulphur is known to be oxidised to sulphate, organics and particulate organics are also suspected to be oxidised over the SCR.[44] There is also a risk that excess NH_3 from the urea might be emitted.

Another common NO_X emission reduction method is the use of exhaust gas recirculation (EGR). By recycling a small part of the exhaust gases back to the cylinder the temperature and oxygen content are kept low. This makes NO_X formation unfavourable but might decrease engine efficiency and increase particle emissions.

Diesel particulate filters (DPF) are commonly used in both LDVs and HDVs. It effectively removes solid particles by forcing them to deposit on the filter and either continuously or periodically remove them by thermal treatment. Since only solid particles and hence available surface area are removed there have been concerns that condensable material would form a nucleation mode while emitted to the atmosphere.[9]

In diesel vehicles a diesel oxidation catalyst (DOC) can be present to oxidise HC and carbon monoxide (CO). In addition the DOC reduces the soluble organic fraction (SOF) of aerosols.[45]

2.8 Regulating nanoparticles

The constant exchange of nanoparticle constituents with the gas phase together with the small size of nanoparticles makes them a challenging pollutant to regulate. Legislation for particles has mostly focused on particle mass. PM_{10} and $PM_{2.5}$ are used to regulate ambient particle concentrations which are the mass of particles with a diameter below 10 and 2.5 μm respectively. These metrics are for example regulated within EU as environmental quality standards and further on the Swedish national level. In Europe emission legislation for newly produced vehicles started in 1992 with the emission standard Euro1. The compounds regulated within the emission standards have evolved over time and contain both gases and particles. Since Euro V particle number emission limits were introduced in addition to the previously controlled particle mass emissions but so far only for the solid particles above 23 nm. In conformity on-board testing using portable emissions measurement systems (PEMS), also used in Paper V, was introduced in both the Euro VI standard and in United States emission legislation. For shipping no extensive air pollutant regulations exists. SO_X and NO_X emissions are regulated by regulation 14 in MARPOL Annex VI. Regulation on FSC limits has been strengthened on both a global level and with tougher regulations in selected sulphur environmental control areas (SECA). This will directly reduce the sulphate fraction of the aerosol[19] but might indirectly decrease soot and/or condensed hydrocarbons. The impact on hydrocarbon emissions also depends on the new lubrication demand using a cleaner fuel[42]. Locally there also exist regulations for both FSC and ship speed limits to improve air quality in shipping intensive areas.[46]

The problem with only regulating particle mass is illustrated in Figure 3. A particle mass size distribution and a particle number size distribution looks completely different for a typical urban aerosol. Urban particles associated with high mass are usually; dust, wear from breaks or road surfaces, bioaerosols etc. while particles associated with high number are the combustion related nanoparticles of soot, sulphates, POA, SOA etc. Nucleation mode particles contribute extremely little to the particle mass and hence regulations of mass needs to be complemented with regulations for particle number.

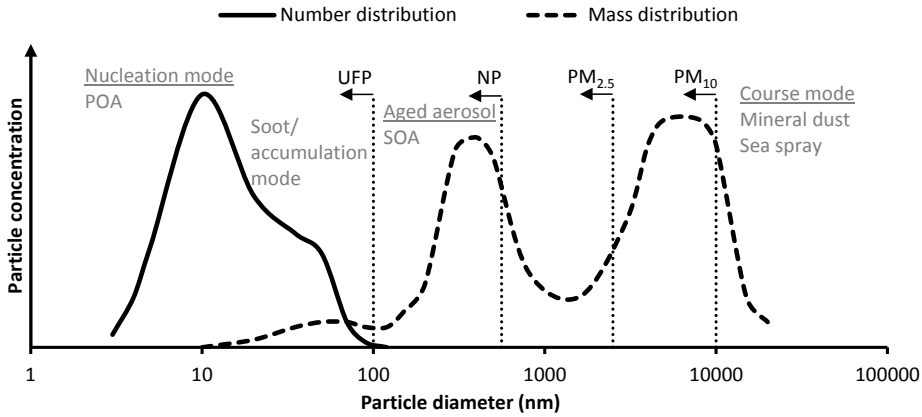

Figure 3. Conceptual illustration of a particle number and mass size distribution for a typical urban aerosol. Included are examples of constituents in each mode and the size range for ultrafine particles (UFP), nanoparticles (NP), $PM_{2.5}$ and PM_{10}.

3 Method

Measuring nanoparticles is a challenge. Aerosol particles are a dynamic system with particles and gases in constant exchange with each other and with the environment. Distinguishing nanoparticles by size from larger particles is relatively new and there exist few regulations for them. Partly this is linked to the fact that there has not existed a standardised method or standardised instruments to measure emissions of nanoparticles. The Euro standard is the first standardised method for nanoparticle emissions but it so far only regulates solid particles above 23 nm. Instruments are available to measure different properties of the nanoparticles and several different measurement methods are available. The methods can be divided into controlled laboratory measurements with chassis or engine dynamometers which are also the preferred methods for regulatory purposes. The other possibility is to perform measurements in real-world conditions which could be flux measurements in a confined road tunnel, chasing studies flying, sailing or driving through the exhaust plume or on-road and on-board studies.

3.1 Physical properties of aerosol particles

Particle size distributions

Complementing particle number measurements with size distribution measurements is one possibility to gain more information of nanoparticles. The size distribution of nanoparticles can provide information about the content of the particles and how they will evolve in the atmosphere. In this thesis measurements have been performed at different plume ages ranging from inside the exhaust system, next to the tail pipe and finally after up to 5 minutes of atmospheric aging. Instruments with a very high time resolution is required ($\geq$1 Hertz) in these measurements. In this thesis the engine exhaust particle spectrometer (EEPS) was used in all studies. Since this instrument is a major component of this thesis it is below described in detail.

The TSI EEPS model 3090 (Figure 4) measure particle number size distribution of particles between 5.6 and 560 nm with a time resolution of up to 10 hertz. The particles are separated by size using two bipolar diffusion chargers and then passing the particles through an electrical field, separating them by their electrical mobility. The particles will pass a flow of clean sheath air where small particles will deposit early and large particles will deposit late. The size segregated particles are then deposit on 22 electrodes and the current they induce are measured and converted to a size distribution.

The accuracy of the EEPS is commonly compared to the more established particle instruments for particle number measurements (Condensation Particle Counters, CPC) and for size distributions (Scanning Mobility Particle Sizer, SMPS). There have been indications that particle morphology and the use of bipolar charging used in the EEPS is responsible for discrepancies compared to the CPC and SMPS.[47, 48] In Paper III an SMPS and in Paper I and IV a CPC was run together with the EEPS to ensure reliable results measured by the EEPS. A discrepancy of around 25% between the instruments has been found in comprehensive studies comparing the EEPS to other established particle instruments[49]. The measurements within this thesis was well within this range

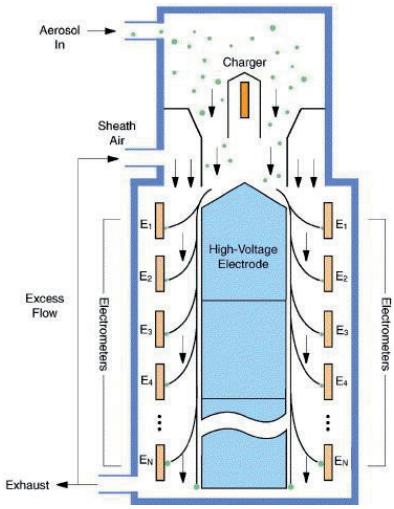

Figure 4. Schematic figure of the TSI 3090 Engine Exhaust Particle Sizer (EEPS) spectrometer (TSI).

Particle mass

Particle mass was calculated from the number size distribution measurements. These calculations required two assumptions. The first was to assume a unit particle density of 1 g cm^{-3} since the constituents of the combustion aerosol is unknown. For comparative purposes the density of SOA is 1.06-1.45[6] g cm^{-3} and the density of fresh soot is 1.8-2[50] g cm^{-3}. The second assumption is that all particles are spherical. Salt particles and fresh soot can have highly non-spherical shapes.[14] SOA and aged soot with condensed material tend to have a spherical shape with a density closer to 1 compared to fresh emissions.

Particle volatility and soot

Particle volatility was examined in Paper I, III and IV by using a thermodenuder (Dekati Inc.) which consist of a heating part running at 523 K and an absorbing part where vaporised material is deposited on active coal. This allowed the non-volatile fraction of the particles to be studied. The main constituent of the non-volatile fraction is soot which was explicitly measured in Paper V with a photoacoustic soot sensor (PASS).

3.2 Complementary gas measurements

In Paper II, III and V complementary gas measurements were performed. They were used to provide information on combustion conditions and exhaust aftertreatment functionality. The gases measured were nitrogen monoxide (NO), nitrogen dioxide (NO_2), CO, HC and O_2.

3.3 Emission factors

The plume EFs in Paper I, II, IV and V was derived with an established method of ratios [37, 51, 52] and with a similar method for gases[53] using a remote sensing device. The ratio of pollutant/CO_2 was used since CO_2 is a direct result of fuel combustion, assuming complete combustion. The dilution of both particles and gaseous pollutants are assumed to be the same as the dilution of CO_2. Applying CO_2 as a tracer compound implies that the plume dispersion does not need to be calculated. In Paper I, II, IV

and V fuel specific EFs were calculated with equation (i). Δ[particles] and Δ[CO_2] are the time integrated concentrations during plume episodes with background concentration subtracted as defined, according to Figure 5, to 30 seconds before the plume was observed. EF_{CO_2} according to previous studies was assumed to be 3.2 kg (kg fuel)$^{-1}$ for diesel engines.[54] For CNG fuelled busses a carbon content of 74.9% was used assuming complete combustion.

$$\text{Fuel specific } EF_{part} = \frac{\Delta[\text{particles}]}{\Delta[CO_2]} \text{ x } EF_{CO_2} \qquad \text{(i)}$$

$$\text{Distance, brake or time specific } EF_{part} = \frac{[\text{particles}] \text{ x measured exhaust flow}}{\text{distance, brake work or time}} \qquad \text{(ii)}$$

In Paper II, III and V the EFs were also reported as distance, brake, and time specific EF. Particle number and mass per km, kWh or s was calculated according to equation (ii). In Paper III and V the engine parameters necessary for these calculations were measured and in Paper II fuel consumption was estimated according to average values from the Swedish environmental protection agency[55].

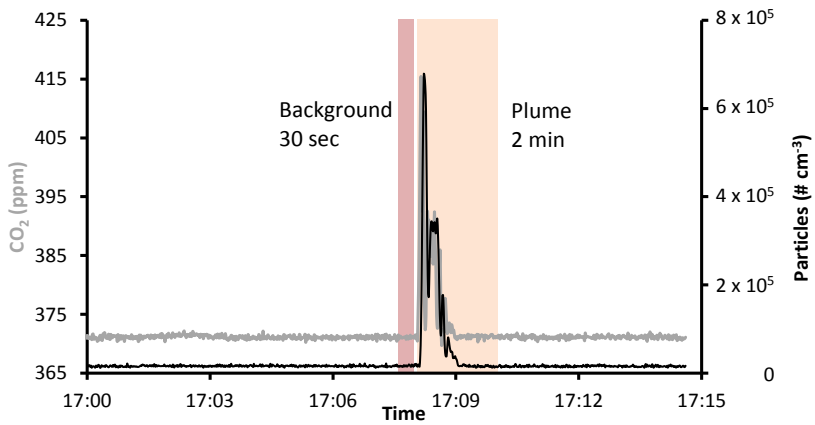

Figure 5. Time series of CO_2 (grey line) and particle number (black line) concentrations and definition of plume episodes (orange field) and background (red field).

4 Results and Discussion

Two main methods were applied to characterize the particle emissions from shipping and road traffic.

- **On-board measurements** to thoroughly examine engine parameters effect on the particles formed inside the exhaust system before atmospheric dilution affects the particles, but also next to the tailpipe including short atmospheric dilution (Paper III and V).
- **Plume measurements** to study emissions from numerous vehicles/ships after atmospheric dilution of up to ~5 minutes (Paper I, II and IV).

On-board and plume measurements are complimentary and can together be used to study the evolution of nanoparticles from the exhaust system throughout the lifetime of the plume. The emissions depend on many factors where some answers are given in this thesis. Variations of the emissions within ship/vehicle fleets depend on fleet composition and how they are operated within the specific area studied. Variations within an individual ship/vehicle depend mainly on operating conditions and if exhaust aftertreatment systems are working properly. Effects of vehicle/ship operating conditions in plume measurements are difficult to study since usually no information of engine parameters is available and the results are only instantaneous snapshots of the emissions. It is however important, the fuel specific EF_{PN} during harbour operation can be up to 64 times higher than those generated under stable engine loads used in the open sea (Paper III). The fuel specific EF_{PN} for acceleration was 7-10 times higher than for the stable engine load (Paper V).

4.1 Emissions from ship and vehicle fleets

Emissions were studied from a selection of 35 city buses (Paper II) and from the whole ship fleet entering and leaving the port of Gothenburg (Paper I and IV). The bus plume measurements in Paper II were performed by controlling where and when the buses accelerated achieving more homogenous measurements with better reproducibility. This is illustrated in Figure 6 with three consecutive bus passages passing the measurement site with corresponding peaks in PN and CO_2 concentrations. Engine parameters during acceleration from stand still are similar between vehicles and passages but still the variation within the buses studied was significant with a relative standard deviation of 80% and 99% for diesel vehicles without DPF and for CNG buses respectively.

Fleet measurements under normal operating conditions were performed for a large number of ships in Paper I and IV. A large variation within the fleet was evident. Figure 7 shows the 734 EFs from unidentified ships together with the fleet average and one standard deviation for particle number and mass (Paper I). The fleet had a relative standard deviation of 60% for number and 73% for mass. This method was for the first time used to study a large ship fleet. In Paper IV, further analysis of the data is presented where 135 different ships were identified and analysed.

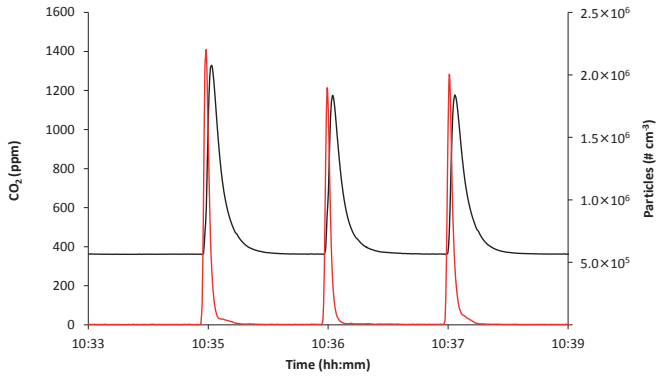

Figure 6. Emission signals for three successive passages of the same bus during controlled acceleration in bus depots. Particle number (red line) and CO_2 (black line).

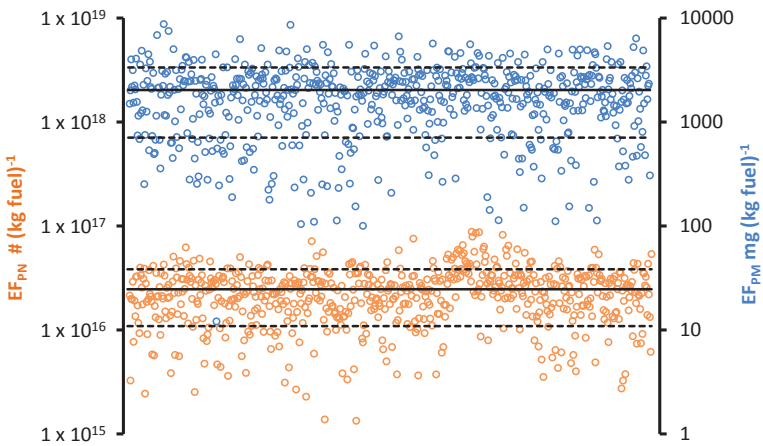

Figure 7. EF_{PN} (orange symbols) EF_{PM} (blue symbols) from Paper I. Average emission factors (solid lines) and 1 standard deviation (dashed lines) are included.

4.2 Classes within the fleets

Bus classes

Emission regulations for road traffic has been strengthened continuously and within the European union new Euro classes has led to a constant demand on new and more effective engines and exhaust aftertreatments. Figure 8 shows fuel specific EFs for four different Euro classes with different exhaust aftertreatment technologies fuelled with CNG or diesel. Buses belonging to newer Euro classes did not necessary have lower nanoparticle emissions. The highest fuel specific EF_{PN} was found for the enhanced environmentally friendly vehicle (EEV) class and higher EF_{PM} than the fleet average was found in all Euro classes for the diesel vehicles. Exhaust aftertreatment and fuel were found to be more important than Euro class. The use of DPFs resulted in 5 times lower EF_{PN} and 3 times lower EF_{PM} than the Euro class average. One risk with DPF is re-condensation of vapours after the filter of small particles (<30 nm)[56] but this was not observed in this study. The reason is probably because of the low FSC in Swedish diesel together with low organic emissions of condensable gases that, for the measurements described in Paper II, were below the detection limit for most buses. The use of EGR increased EF_{PM} most likely because of increased soot emissions that in EGR equipped buses depend on decreased oxygen content.[9] CNG fuelled buses generally had high EF_{PN} attributed to volatile nucleation mode particles while diesel fuelled vehicles generally had high EF_{PM} attributed to soot particles.

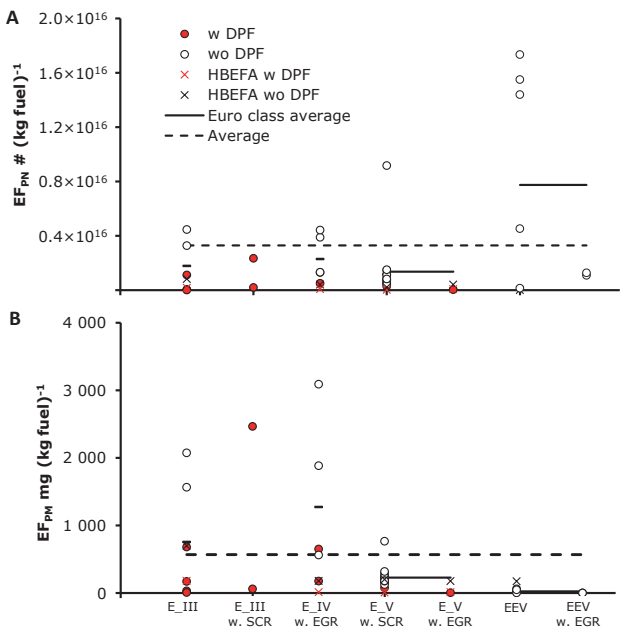

Figure 8. EF_{PN} (A) and EF_{PM} (B) for all the buses studied divided into Euro class for the driving mode *acceleration.* Without DPF (white circles), with DPF (red circles), average of all represented Euro classes (dashed line), average of an individual represented Euro class (solid line). Crosses are EFs obtained by the HBEFA 3.1 model with DPF (red) and without (black).

Ship classes

Euro classes similar to those of road traffic do not exist for ships and the use of engine exhaust aftertreatment is yet scarce. To categorize the ships, automatic identification system (AIS)-data was used to distinguish between physical differences of the ships. The categories were cargo ships (consisting of the ship classes: oil tankers, tankers, container ships and roro ships), passenger ships, pilots, tug boats and high speed ships. EF_{PM} versus EF_{PN} for the categories together with individual passages are presented in Figure 9. The EF_{PM} of cargo and passenger ships were similar while EF_{PN} was different for the classes within the cargo category. Cargo ships usually have slow speed engines with fixed pitch propellers while passenger ships usually have controlled pitch propellers which have implications for the engine load used at a certain ship speed and hence also their emissions. Pilot and tug boats have lower EFs for both number and mass compared to cargo and passenger ships. Pilots and tug boats had medium speed diesel engines (MSD) or HSD and operated on low FSC fuels (0.1% compared to 0.5% or 1% for the other ships) and since they are supporting vessels their general operation pattern contained more variable engine load.

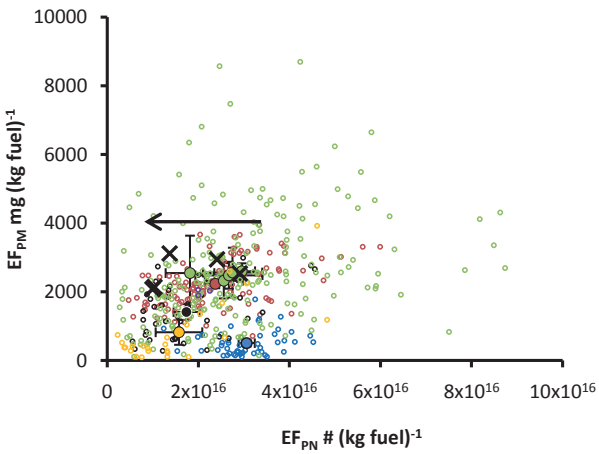

Figure 9. EF_{PM} values plotted against the corresponding EF_{PN} values for all passages and ship categories. Data for *Pilot ships* are shown in yellow, *Tug boats* in black, *Passenger ships* in red, *Cargo ships* in green, and the *High speed passenger ship* in blue. Large symbols represent mean values for ship categories/classes while small symbols represent individual ship passages. Error bars represent 95% statistical confidence intervals for the means of EF_{PN} and EF_{PM}. Crosses are data from airborne measurements (Beecken et al.)[57] where the arrow indicate increasing distance away from the ships.

4.3 Emissions for individual ships and vehicles

Buses

On-board measurements were performed on a selected bus on a route consisting of rural, urban and city driving (Paper V). This route was driven four times. Height profile, vehicle speed profile, engine load and cumulative emissions of particles and NO_X can be found in Figure 10. NO_X did not follow the same emission pattern compared to particles and soot. NO_X are strongly associated with engine exhaust temperature which is in indicator of SCR functionality since it requires a high enough temperature to work properly. This was clearly found when comparing the first two kilometres after which a satisfactory engine exhaust temperature was reached and the emissions were similar between the cycles. The exhaust temperature was ~100 K lower at the beginning of the first drive cycle compared to the second and this caused higher emissions of NO_X. The exhaust temperature reached this critical value, around 475 K, also during city driving where the NO_X emissions increased rapidly.

The situation was different for particles and soot. The particle emissions depend mainly on the combustion conditions. This is illustrated in Figure 10C for time specific EF_{PN}. Increase in engine load and acceleration clearly corresponded to peaks in EF_{PN} and episodes of stable engine load had distinctly lower emission. In the on-board measurements the dilution ratio and time before measurements was not sufficient to induce significant condensation or nucleation and most of the particles were therefor of non-volatile character. The SCR can also oxidize HC and SO_2 which can have an effect on the volatile fraction of the aerosol.

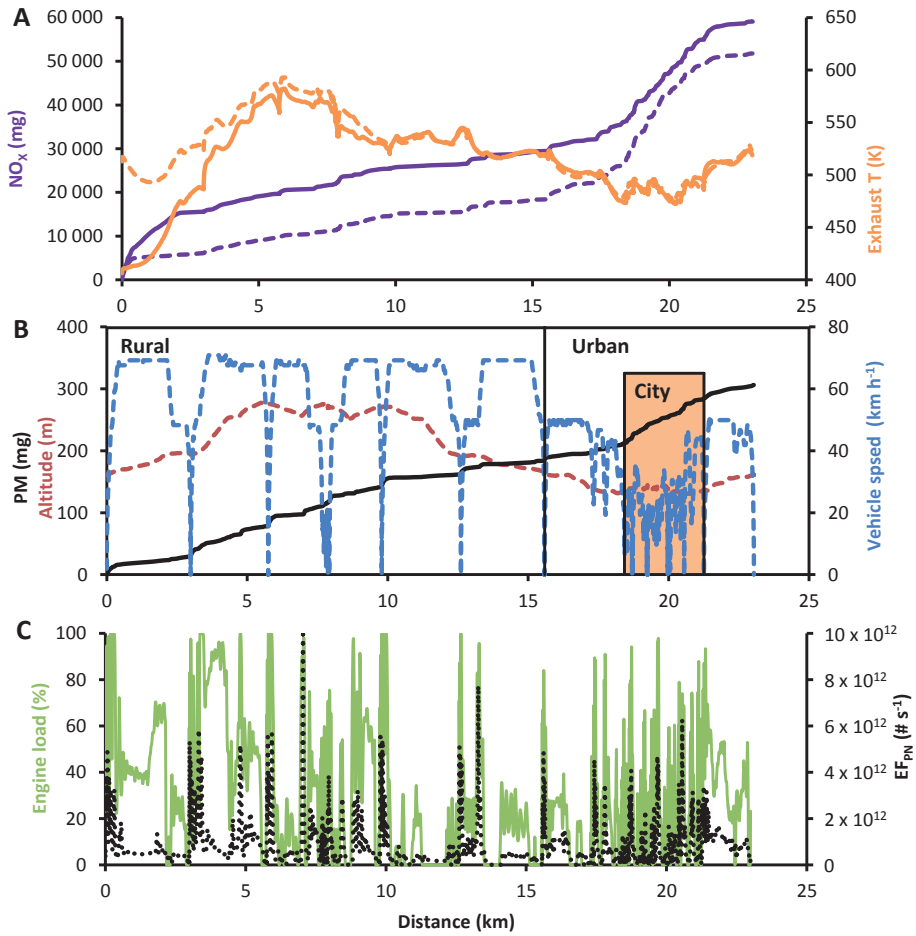

Figure 10. A: Cumulative NO_X emissions and exhaust gas temperature for two repetitive drive cycles with different starting exhaust temperature (dashed vs. solid lines). **B:** Vehicle speed, GPS altitude and cumulative particle mass emissions. **C:** Instantaneous engine load and time specific EF_{PN}.

Ships

Similarly to the bus studied in Paper V the ship studied in Paper III had NO_X emissions that were high in the beginning of the route during manoeuvring and then decreased significantly (by a factor of >10) when SCR function was established. The fuel specific EF_{PM} were highest during high engine load in analogy to the bus emissions. Fuel specific EF_{PN} had the opposite trend which depends on dominant nucleation mode found at stable engine load. The presence of this mode is highly depending on dilution ratio and the comparison to other on-board measurements is difficult. Higher emissions during manoeuvring than during stable engine load at sea have implication for local air quality. The harbour regions where most manoeuvring takes place are often located close to where people live. Global and regional effects for air quality and climate are more dependent on the total emissions where the emissions during the stable engine load episodes become more important.

Two individual ships that passed the measurement site several times (57 passages) were found to have distinctly different particle emissions compared to the average ship fleet. Engine parameters were not available during these plume measurements but their emission features were found for all passages. One high speed ship with a gas turbine engine had low EF_{PM}, high EF_{PN} (Figure 9) and emitted smaller particles (Figure 11A) than the average fleet. This feature are typically observed for these types of engines.[54] The high speed ship had a size distribution that was similar to that of the CNG-fuelled buses in Paper II with a CMD of 13 nm and 21 nm respectively. This can be compared to the diesel vehicles without DPF in Paper II which had a CMD of 73nm. This is a typical characteristic of low soot emitters that instead emit more volatile particles.

The second selected ship was an SCR equipped passenger ship (Figure 11B) that had extremely high non-volatile particle number emissions when accelerating (~3 times higher than during deceleration). This is not believed to be soot particles because of their small size (CMD 15 nm) but rather a product of atmospheric aging discussed more thoroughly for the whole fleet in section 4.5 The SCR is suspected of having an additional effect on the formation of this non-volatile particle mode.

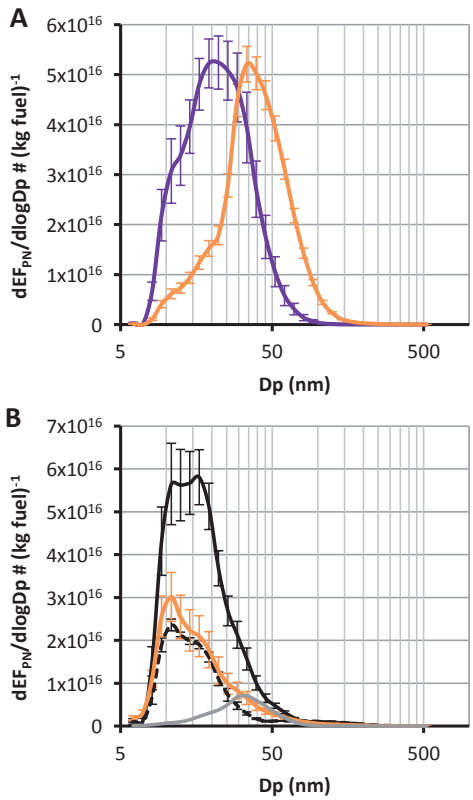

Figure 11. A: Size resolved fuel specific EF_{PN} for for the high speed ship (purple) and the total fleet (orange) from Paper I and IV. **B:** Size resolved fuel specific EF_{PN} for the non-volatile particles of the SCR ship accelerating (black solid) and decelerating (black dashed) and for the whole fleet (orange) studied in Paper I and IV but also 75% engine load for the ship studied in Paper III (grey).

4.4 Non-volatile particles

In Paper I and IV two periods of measurements were performed. In one part the total particle emissions were measured and in the second part non-volatile particle emissions were measured. For the ship studied in Paper III non-volatile particles were also characterised. The aerosol was in these studies heated in a thermodenuder to vaporize all volatile particles that subsequently was adsorbed in a coal trap to prevent re-condensation. For the plume measurements (Paper I and IV) 46% by number and 24% by mass of the particles were found to be non-volatile. For the on-board measurements (Paper III) around 50% by number and 30% by mass of the particles were non-volatile. These ratios are similar to other plume measurements for number[15] while for mass the literature is scarce.

In the ship on-board measurements the volatile fraction was mainly found in the nucleation mode (Figure 12B) while in the ship plume measurements they were condensed onto the non-volatile soot particles (Figure 12A). This has implications for the soot structure. Fresh soot measured on-board is most likely found as agglomerates while after atmospheric processing it will be collapsed into a denser structure due to the condensed material upon the soot particles.[13, 14] For measurements of particle size distributions determined by mobility diameter the less dense soot agglomerates observed on-board will appear as larger particles than the more dense soot structure typically found in the plume.

The instrument used in the on-board measurements had a higher cut-off size compared to the instrument used in the plume measurements, 12.6 nm compared to 5.6 nm. Since a large part of the size distribution measured on-board was below the cut off size all volatile particles were not captured and hence the ratio of non-volatile to total particle number is most likely much lower in the on-board measurements than during the plume measurements. Large differences in the size distributions for non-volatile particles during the on-board and plume measurements were also observed (Figure 12). CMD during on-board measurements were 28 nm but only 13 nm in the plume measurements. In the plume measurements a soot mode was visible as a shoulder in the size-distribution with similar number of particles as in the on-board measurements. However, in the plume measurements a new non-volatile particle mode appeared which has not been observed earlier. A possible explanation is presented in section 4.5 and in Paper IV.

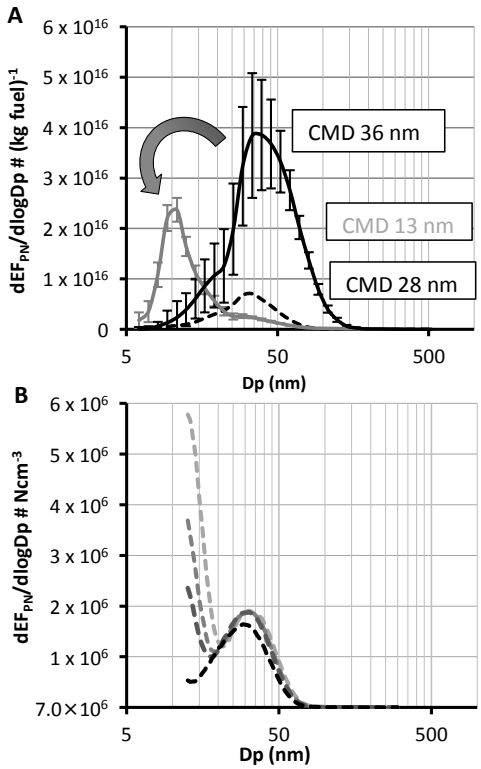

Figure 12. A: Average EF_{PN} from the plume measurements (Paper I and IV) for all ship passages for total EF_{PN} (black line) and EF_{PN} for non-volatile particles (grey solid line). Included is also the non-volatile particles found at stable engine load during the on-board measurements (black dashed line) (Paper III). **B: S**ize distribution for the on-board measurements (Paper III) during stable load from low (light grey) to high (black) evaporative temperatures used in the thermodenuder.

4.5 Real world dilution and plume processing

One major advantage of plume measurements is that the aerosol particles measured are the same as the aerosol particles people are exposed to.[10] On-board measurements lack the crucial component of real world dilution. Instead this dilution is mimicked and varied to represent atmospheric dilution which has proven to be a difficult task.[58] Nucleation is highly dependent on the dilution ratio which is difficult to reproduce in the laboratory.[10] Even though the importance of the dilution ratio on nanoparticles has been known for a long time[59] regulations for vehicle emissions still do not have strict dilution ratio requirements.[10]

Physical effects for aerosol particles

Shipping

For shipping bimodal size-distributions were only found in the on-board measurements. As described in Paper III bimodal size-distribution were observed during open sea operations at a stable engine load of 75% while a unimodal size distribution was occurring during harbour manoeuvring. The bimodal size-distribution consisted of a soot mode at 30-40 nm and a volatile nucleation mode at 12 nm that completely evaporated after heating in the thermodenuder (Figure 12B). In the ship plume measurements (Paper I and IV) exclusively unimodal size distributions were found (Figure 12A). In other similar studies both unimodal and bimodal size distributions have been observed indicating that the local conditions for atmospheric dilution and processing could be of importance.[42, 60]

The lack of nucleation mode particles during the ship plume measurements could be caused by harbour manoeuvring resulting in higher soot emissions that provide a high surface area favouring condensation prior to nucleation. It could also be an effect of the atmospheric dilution and processing. The particles in the nucleation mode could evaporate upon dilution or coagulate with larger particles forming a unimodal size distribution observed as a decrease in PN while PM concentrations are maintained. Condensation of gases like sulphate, organics and water should also be an important process as the hot exhaust cools down, increasing mass. The size distributions in the plume measurements was unaffected by time spent in the atmosphere on the time scales from 30 seconds up to a few minutes. This suggests that initial changes due to nucleation and coagulation of nanoparticles caused by dilution and cooling are done within a very short time frame (<30 s). The EF_{PN} were lower in the plume measurements (Paper I and IV) compared to the on-board measurements (Paper III) but the opposite was found for EF_{PM}. Evaporation of the nucleation mode would decrease both number and mass while coagulation would decrease number but instead maintaining constant mass. Hence, coagulation of the nucleation mode seems to be the most important process. This is confirmed by data from ship plume measurements using airborne platforms where decreasing fuel specific EF_{PN} but not EF_{PM} was observed with increasing distance (<8 km) away from the ships (Figure 9).[57]

Road traffic

For the road traffic measurements the situation was not as distinct as in the ship studies. On-board measurements (Paper V) displayed mostly unimodal number size distributions but bimodal size-distributions were found at steady vehicle speed at high engine load which is known to promote nucleation[61]. The plume measurements (Paper II) showed bimodal size distributions during slow constant vehicle speed but exclusively unimodal size-distributions during acceleration. The bimodal size distribution during slow constant speed driving is believed to occur due to a high ratio of condensed material to soot whereas under acceleration soot emissions increase which decreases this ratio. During the acceleration from stand-still the engine load is close to its maximum which, according to other studies, would result in unimodal size-distributions.[62] The number size distributions for acceleration within the tailpipe, just outside the tailpipe and at roadside are displayed in Figure 13. The fuel specific EF_{PN} increased with increasing atmospheric dilution from the tail pipe to roadside but also the CMD decreased in the order 60, 54 to 52 nm. These are both indicators of increased condensable material with increasing atmospheric dilution. With increased duration of the dilution perhaps a nucleation mode would appear but this was outside the scope of this study.

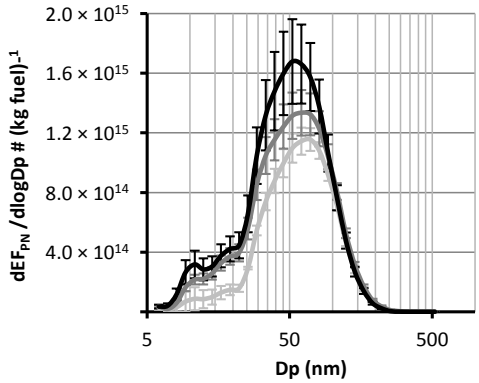

Figure 13. Average particle number size distribution for the first 4 seconds of acceleration from standstill for measurements taken inside the exhaust pipe (light grey line), immediately after the exhaust pipe (grey line) and at road side (black line) together with the 95% confidence interval.

All diesel fuelled buses studied in Paper II displayed unimodal size distributions during acceleration. The bus studied in Paper V spent 17% of the route in acceleration mode but this mode contributed to as much as ~50% of all PN and PM. Since this large fraction of the total particle emissions are unimodal the idea that diesel engines generally have a characteristic bimodal size-distribution seems to not be valid.[9]

The detailed information acquired from on-board measurements enables some speculations on the formation of a nucleation mode. The ratio of condensable material to available soot surface and the concentration of condensable material in the emissions are the most important factors. High engine load promote soot emissions and hence also the available surface area[63]. The condensable material is usually organics or sulphates. High engine load promotes sulphur emissions both from the fuel[64] and from the increased need for lubrication oil[65]. FSC is low in Sweden (<10ppm) and HC was found to be low during nucleation events (Paper V) which means that sulphate from lubrication oil seems to be the main constituent of the nucleation mode. High exhaust gas concentrations at high engine load are believed to promote sulphate driven nucleation even though high soot surface area is also present. In addition SCR catalysts like the one used in the bus studied have been found to increase the volatile particle number emissions.[66]

Chemical effects for aerosol particles

Road traffic

In addition to the physical effects described above also chemical processes due to photooxidation can be important for plume measurements as compared to on-board or laboratory measurements. As the plume ages SOA precursors from combustion can be oxidised and form new particles which are suspected to contribute significantly to globally produced SOA[7]. In this work no direct measurements of chemical transformation that can prove SOA formation were performed. However, an interesting phenomenon was observed when comparing non-volatile particles from ship plume measurements and on-board measurements.

Shipping

The non-volatile particle mode with a diameter of about 10 nm were clearly observed in the plume measurements (Figure 12A) while no such mode were present in the corresponding on-board measurements (Figure 12B). This suggests that these particles are formed in the atmosphere after exiting the exhaust system. Our explanation is that low volatile material such as oligomers or organosulphates are somehow produced in the ship plume. Organosulphates are known to be formed in acidic conditions[67], during rapid cloud droplet evaporation[68] and have been associated with combustion[69]. All of these conditions are fulfilled in a ship plume. Only a minor fraction (< 1%) of the total aerosol need to converted, i.e. a small part of the size distribution indicated by an arrow in Figure 12A, to explain our observations. Further support for this hypothesis was found when studying the effect of acceleration on the non-volatile particles (Figure 14). With increasing acceleration the non-volatile particles with diameter 250-300 nm decreased which is closely related to soot that is known to decrease with increasing engine load[70]. The opposite was observed for smaller particles (~10 nm) which instead increased with increasing acceleration. High engine load increase NO_X emissions[71], increase FSC to sulphate conversion[72], increase lubrication oil demand[65] and might alter organic content. This will then increase the acidity of the particles and thus promotes the conditions required for formation of organosulphates.

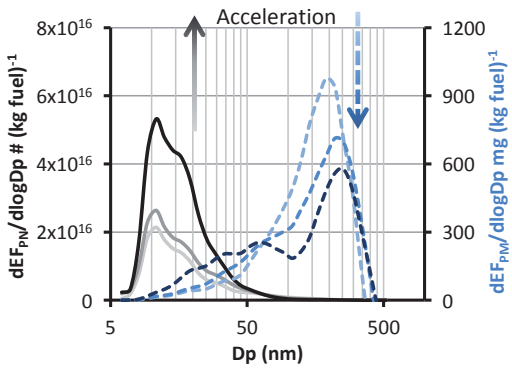

Figure 14. Size-resolved EF_{PN} (black lines) and EF_{PM} (blue dashed lines) of non-volatile particles for cargo and passenger ships. The data are divided from deceleration (-0.02±0.01 knots s^{-1}), neutral (0.00±0.01 knots s^{-1}) to acceleration (0.02±0.01 knots s^{-1}).

4.6 On-board measurements versus plume measurements

Until recently neither plume measurements nor on-board measurements have been enforced for legislation purposes. Instead, the most common measurement method applied for legislation purposes is laboratory measurements where driving conditions are controlled trough driving cycles of predetermined accelerations, decelerations and constant speed modes. These are not necessary directly translatable to on-board and plume measurements. On one hand real world measurements are probably closer to the actual emissions including authentic driving conditions where the emissions are exposed to atmospheric dilution but on the other hand more variables are involved which enhance the uncertainties compared to controlled laboratory measurements which are more easily reproduced and replicated.

Fleet measurements

Fleet measurements are excellent in studying a large number of vehicles or ships. Since the emissions are measured after emitted to the atmosphere they cover real atmospheric conditions and traffic conditions that are hard to replicate in the laboratory. This also implies that the pollutants measured are close to what people are actually exposed to which is especially important for nanoparticles that are highly affected by dilution and photochemistry.[24] The fleet measurements done in this work were also relatively cheap to perform which often is an important limitation to ship/vehicle studies.

On the downside the measurements are not standardised and the variations in atmospheric conditions affects their repeatability. Only a snapshot of the plume is captured and analysed. The emissions of the snapshot are not representative for all operating conditions of that specific individual ship or vehicle. This can be overcome with experimental design, such as in the bus study, where the buses were characterised in an accelerating mode (see section 4.1).

Underlying causes to the emissions might not always be examined in plume measurements. For example, ship/vehicle speed, acceleration, or classes are often studied even though they are not the determining factor for the emissions. They still serve as good indicators of the controlling factors that could be for example engine load, engine type or the use of exhaust aftertreatments. Different classes often have similar emissions. Vehicle/ship speed can be deceptive but if treated properly it is generally a good approximation for the underlying controlling factors and it is widely used (see section 4.8).

On-board measurements

To account for detailed operating conditions of an individual ship/vehicle but still perform measurements on actual driving conditions on-board measurements are very suitable.

For on-board measurements there often exists parallel detailed information on engine parameters that can be utilised in the analysis. However, on-board measurements are usually more time consuming and costly per ship/vehicle studied compared to plume measurements and typically only one or a few vehicles/ships are tested. The fact that only one or a few vehicles are tested makes the representativeness of the findings to the whole fleet somewhat uncertain.

Soot for example is formed during combustion in the cylinder under local conditions of high fuel/air ratios and within a certain temperature interval. A change in engine load might favour combustion within the soot formation temperature interval in one case while the same change in engine load might move the combustion outside of this temperature range for another case.

In analogue to the laboratory measurement a drawback of on-board measurements is that often dilution of the exhaust to reach a temperature and concentration range matching the instruments is required. This dilution might be straight forward for gaseous pollutants but might have significant effects for aerosol particles.

4.7 PN, PM and soot

Both PM and PN are reported in all 5 Papers. The actual measurement of the EEPS is particle number for 32 particle size bins ranging from 5.6 to 560 nm. The particles are assumed to be spherical with a density of 1 g cm^{-3} in order to convert PN to PM. In exhaust plumes the condensed material promotes spherical particles with a density approaching 1 g cm^{-3}. For the bus studied in Paper V also soot was measured.

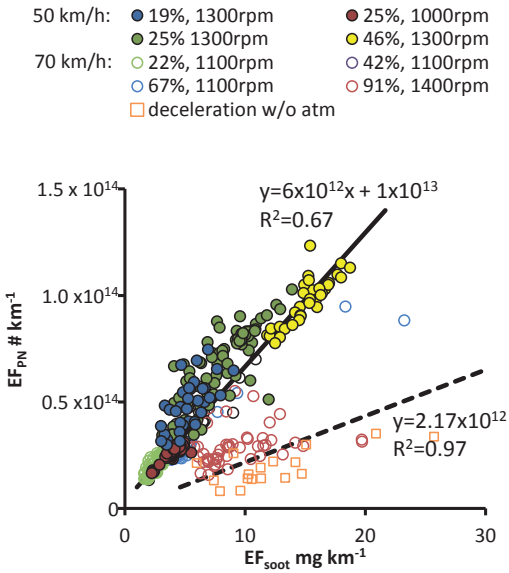

Figure 15. Distance specific EF_{PN} versus EF_{soot} for the stable engine conditions at 50 and 70 km/h and deceleration. The 91%,1400rpm case and deceleration was excluded from the linear regression since it clearly deviated from the other operating conditions. Dashed line for a Euro IV LDV (Kirchner et al.)[73]

Unimodal number size distributions were observed under most conditions. For the unimodal size distributions, regardless of engine load, engine speed and vehicle speed a plot of distance specific EF_{PN} vs. EF_{soot} gave a linear relationship (Figure 15) which was also be observed for a Euro IV LDV with lower EF_{PN}/EF_{soot} ratio. This relationship is believed to occur if the size distribution is log-normal with a fixed width and with diameters of 50-70 nm.[74]

The exception from this was when the bus decelerated where much larger particles were found with high distance specific EF_{soot} and low EF_{PN}. Deceleration in a diesel bus often occurs during fuel shutoff which was also the case in the on-board bus measurements. The particles observed during fuel shutoff is then not formed directly from combustion but likely stem from lubrication oil or possible desorption of soot particles previously deposited in the oil film of the cylinder walls[75]. 91% engine load was also an exception with low EF_{PN}/EF_{soot} ratio.

Distance specific EF_{PM} and EF_{soot} for the bus studied in Paper V also displayed a linear relationship. The absolute value of this relationship depends on the density chosen for the PM calculation. However, when comparing the different cycles a higher EF_{PM}/EF_{soot} ratio was found in drive cycles with high HC indicating increased condensed organic material.

A linear relationship between EF_{PN} and EF_{PM} was also found for the ship categories (Figure 9). The only exception was the high speed ship equipped with a gas turbine engine but this is only a single ship out of 135. The relationships between EF_{PN}, EF_{soot} and EF_{PM} for both shipping and road traffic could be used to make assumptions of both PN, PM and soot if only one of these metrics is available.

4.8 Engine operation and emissions

One major difference between shipping and road traffic is that road traffic often travel with a steady vehicle speed related to the speed limit regulations but with a highly variable engine load due to topography and wind. Ships can sail with both stable ship speeds and/or stable engine loads. Usually, and as exemplified in the on-board study (Paper III) stable engine load are the most common driving mode. Studying stable engine load for the ship in Paper III was straight forward but stable engine load for the bus in Paper V was only held for short segments of the route. On the other hand these short but stable engine load segments occurred at different vehicle speed and at different engine rotational speed allowing more driving modes to be studied.

Shipping

In the ship plume measurements ship speed acquired from AIS-data was used as a proxy for engine load. These allowed general conclusions. However, deceleration of a ship can occur if the engine is shut down (zero emissions) but also if it accelerates in the opposite direction with the propellers or simply just by slowing down the ship engines. Generally for the average from many passages acceleration occurs during higher engine loads and for deceleration during lower engine loads. There exists an established method to estimate a value of engine load based on ship speed for fixed pitch propeller engines commonly used in the cargo category.[76] In Paper IV ship speed and acceleration was not converted to an engine load but rather compared relative to each other. In Figure 16 fuel specific EF_{PN} for total and non-volatile particles are plotted against ship speed. Increasing ship speed was associated with higher particle number emissions indicating a positive engine load dependence.

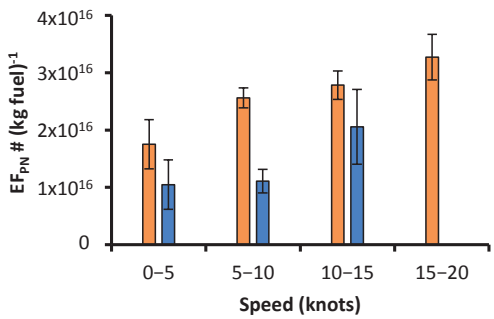

Figure 16. EF_{PN} for the cargo and passenger ships in Paper IV as a function of ship speed for total particles (orange bars) and non-volatile particles (blue bars). Error bars indicate 95% confidence interval.

Acceleration had a significant effect on the non-volatile particles which were thoroughly described in section 4.4. For the on-board measurements, fuel specific EF_{PN} and EF_{PM} also had a positive engine load dependence and also controlled the prevalence of a nucleation mode (Paper III).

The rated engine rotational speed of the ships was also established to be an important factor. For the most abundant cargo and passenger ships in Figure 17 EF_{PM} was found to increase in the order HSD < MSD < SSD. However, since the actual engine speed used will depend on engine load and if using fixed pitch or controlled propellers the conclusions are only indications of a positive engine speed dependence. A similar trend but with higher EFs was found in the Gulf of Mexico where the FSC was limited to 4.5%.

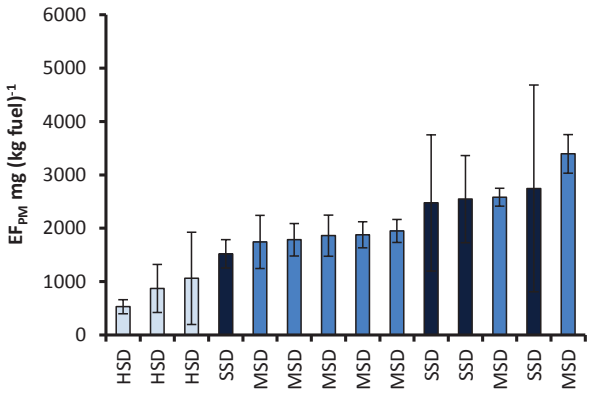

Figure 17. Fuel specific EF_{PM} for different engine speed classes; high speed diesels (HSD), medium speed diesels (MSD) and slow speed diesels (SSD). Error bars represent 95% statistical confidence intervals.

Road traffic

Distance and fuel specific EF_{PN} for different vehicle speed, engine speed and engine load conditions are displayed in Figure 18 A and B for the diesel bus studied in Paper V. Better combustion conditions explain the lower fuel specific EF_{PN} at higher load while increased fuel consumption explains the increase for distance specific EF_{PN} which is a common feature for diesel engines[77, 78]. The same trend was observed both at 50 and 70 km/h but significantly higher emissions were found during 50 km/h for most engine conditions. This is probably because the engine is better tuned to run at 70 km/h.

Engine load of 25% was run with an engine speed of both 1000 rpm and 1300 rpm (Figure 18). The effect on EF_{PN} by engine speed and hence the gear used at this vehicle speed was clearly more important than the engine load. In addition, soot was measured also at 70km/h with 40% engine load at an engine speed of both 1100 rpm and 1400 rpm (Figure 18C). Soot emissions increased with increasing engine speed and were generally higher at 50 km/h compared to 70 km/h.

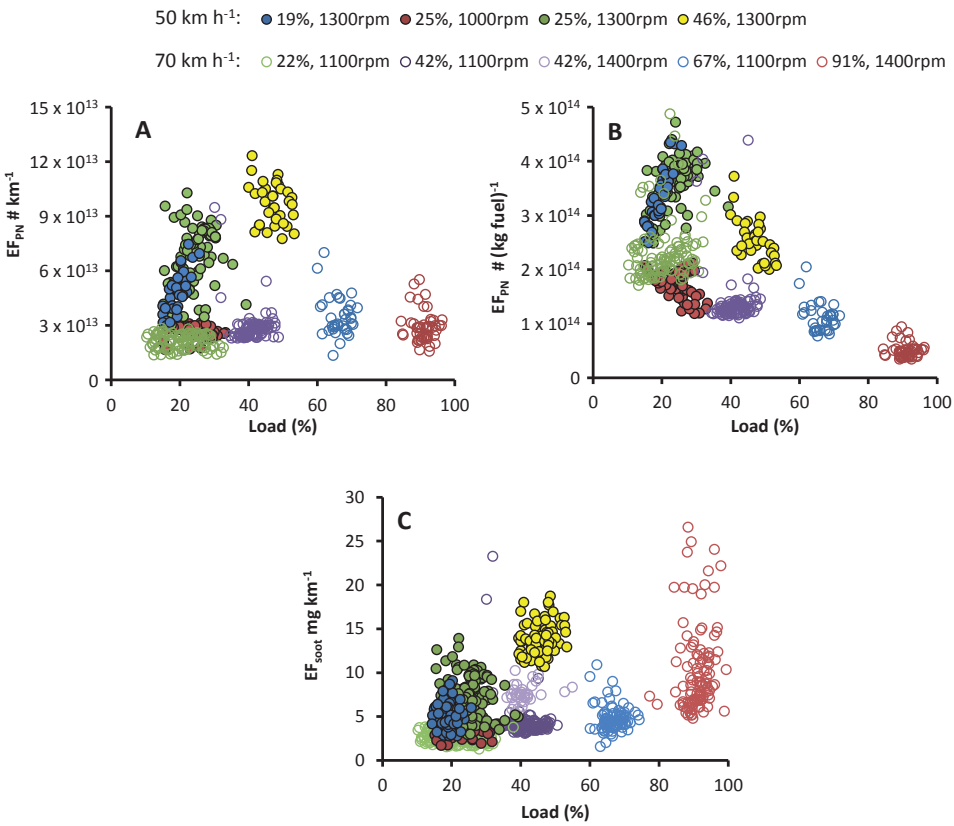

Figure 18. Distance specific EF_{PN} (A), fuel specific (B) EF_{PN} and distance specific EF_{soot} (C) versus engine load for stable vehicle speed episodes divided by different cases of engine speed and engine load.

5 Concluding remarks and outlook

The objective of the work described in this thesis was to increase the knowledge of emission of nanoparticles and their evolution in the atmosphere. There is still a need for further similar work extending the measurements to other types of vehicles, ships, fuels etc. and in different environment. The negative health effects of nanoparticles are well studied and their regulations are likely to be extended in the future. New regulations will promote new emission control technologies. If only particle mass is included in legislation the new technologies will focus on reducing PM but might instead promote an increase in other metrics. Volatile PN was found to increase for newer Euro classes (Paper II) and non-volatile PN emissions from ships was found to increase when non-volatile PM decreased (Paper IV).

One possibility to improve air quality would be to remove or take measures on extreme emitters where plume measurements are the most suitable method for their identification.[79] In previous road studies a small fraction of the vehicle fleet generated most of the pollutants.[52, 80] Among the selection of 35 city buses, 5 out of 7 CNG fuelled buses were among the highest PN emitters and 4 out of 5 Euro IV diesel buses were among the highest PM emitters (Paper II). This shows that efforts could be pinpointed towards a few road vehicles to significantly improve air quality. It also shows that different vehicles will be affected depending on the metric chosen in legislation. For shipping the situation is different. The 10% highest emitters of PN and PM were responsible for 22% resp. 24% of the emissions and similar results have been found for black carbon[60]. This indicates that extreme emitters for shipping are not as important as for road traffic. Likely, this is a result of the lack of extensive regulations on shipping making all individual ships rather high emitters. To reduce the emissions from shipping all ships need to be considered.

Extreme emissions can also be attributed to specific driving patterns or exhaust aftertreatment functionality. On-board or laboratory measurements are best to study the effect of driving pattern and exhaust aftertreatments on the emissions. For the diesel vehicle studied in Paper V exhaust after-treatment functionality controlled by exhaust temperature was the most important factor for NO_X. For PN, PM, soot, HC and CO the combustion condition was most important. High engine load promote lower emissions per unit fuel burned but with higher emissions per distance travelled or per second. Engine speed was also important with increasing emissions at a higher engine speed. Driving at a suitable gear for different vehicle speed limits can be a significant factor. For the ship studied in Paper III it was found that harbour operations resulted in up to 64 times higher fuel specific EF_{PN} compared to stable engine load operation at open sea. These episodes are short compared to a regular shipping route but since they take place close to harbour areas they are very important for local air quality.

The identification of extreme emitting individual ships/vehicles or extreme emissions attributed to driving patterns and exhaust aftertreatment functionality could be a cost effective way to pinpoint efforts for instantaneous improvements of urban air quality.

The reduction in allowed FSC taking place within the SECA-area and local ship speed limits to improve air quality are examples on how to locally improve emissions from the whole ship fleets. In the future these initiatives need to be complemented with regulations on metrics that are more closely related to human health. Initially PM and non-volatile PN similar to road traffic should likely be regulated. However, PM does not cover the nanoparticles very well (see section 2.8) and the PN

regulated for road traffic only cover solid particles above 23 nm. In this thesis the evolution of particles in the atmosphere was found to promote the formation of non-volatile particles smaller than 23 nm (Paper IV). It was also establish that atmospheric processing mainly affects the volatile PN either creating a nucleation mode or condensing on pre-existing particles (Paper I, IV and V). These particles would also be outside the scope of the current particle regulation metrics.

There is a risk that on-board, laboratory measurements and emission models cannot capture the real emissions for the dynamic system of an aerosol. Volatile nucleation mode particles depend strongly on atmospheric dilution conditions which require plume measurements to be studied. The EF_{PN} measured on-board a ship was higher than in the plume which is because of a nucleation mode found in the on-board study (Paper I, IV and V). The nucleation mode particles disappeared by coagulation in the atmosphere on a time scale of <30 s. Besides reducing EF_{PN} significantly it also has implications for the soot structure. When soot is covered with volatile material it collapses from an aggregate structure to a more dense packed spherical structure.[14]

The modelled EFs for the city buses were significantly lower compared to the measured EFs for the same Euro classes and exhaust aftertreatments (Paper II). The reason for this could be that the models often use driving cycles consisting of acceleration, constant speed and deceleration while our plume measurements were performed during acceleration and slow steady vehicle speed. For climate effects the total emissions of a driving cycle could be more representative but for local health effects, for example near bus stops, the different driving modes need to be separated and the transformation occurring during atmospheric dilution needs to be studied. I was found that acceleration completely dominated the emissions compared to deceleration and idle that are driving modes associated with particle exposure at bus stops (Paper V). The model also suggested that diesel fuelled buses had higher EF_{PN} than CNG fuelled busses while the opposite was found in our measurements. The reason for this is most likely that the model according to the Euro V standard only account for non-volatile particles and the particles from CNG fuelled buses are mainly of volatile nature. Soot and CO_2 emissions are effectively reduced by switching from diesel to CNG fuel. However, PN has been associated with an increased health effect and CNG promote higher volatile PN emissions.

The studies presented in this thesis show that non-volatile and volatile particles are affected by different factors where vehicle/ship operating conditions are most important for the non-volatile particles and atmospheric dilution is most important for the volatile particles. Both the non-volatile[26, 27] and volatile[27] exhaust particles have a detrimental health effect. These metrics need to be studied in laboratory studies that currently is the backbone of legislation but also utilising on-board and plume studies to account for real world driving and atmospheric dilution conditions.

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Jannice and Nilas ♥

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