THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Particle Emissions from Ships

Measurements on Exhausts from Different Marine Fuels

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Cover: Remote measurements of the emissions from a ship, photo Niklas Berg.

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Life is like a box of chocolates; you never know what you’re gonna get.
Forrest Gump

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Abstract

Since 1st of January 2015 ships operating in sulphur emission control areas (SECAs) have to use marine fuels with a fuel sulphur content less than 0.1 %m/m. This regulation forces the ship owners to make a fuel shift and use low-sulphur marine fuel oils, use alternative fuels or use scrubbers on-board their ships. One driving force behind the regulation of the fuel sulphur content was to reduce the emissions to air of harmful particles. This thesis focuses on the two first strategies and evaluate how fuel sulphur content and other fuel characteristics affect the particle emissions.

This thesis presents results from particle measurements done in test-bed engine labs and on-board operating ships, with focus on number, mass and sizes of the emitted particles. The on-board measurements considered how a fuel shift from a heavy fuel oil to a low-sulphur residual marine fuel oil and how use of an alternative fuel, in this case liquefied natural gas (LNG) affect the particle emissions. In the test-bed engine measurements the particle emissions from different types of fuels and the effects of fuel sulphur content and other fuel characteristics, primarily the content of aromatics, were investigated.

The results highlight that reduced fuel sulphur contents will not be the only solution for reducing particle emissions, and other fuel characteristics need to be considered. The fuel sulphur content influences the emissions of particles with a diameter of 50 nm or less, whereas other fuel characteristics affect particles in all sizes. An increased content of aromatics did not result in increasing particle emissions, which indicate that the content of aromatics may not play a crucial role with respect to particle emissions from ships. Furthermore, the fuel shift strategy and changing from heavy fuel oil to a low-sulphur residual marine fuel oil, did not affect the number of particles emitted significantly: similar amounts of number of particles were emitted and there was an increase in the emissions of smaller particles. In contrast, the strategy of using an alternative fuel, here LNG, resulted in significant reductions of the particle emissions. Furthermore, the results also highlight the importance of conducting measurements of number of particles emitted when studying particle emissions from ships and in any future regulation of these emissions.

Keywords: particle emission, ship emission, marine fuel, liquefied natural gas, LNG, heavy fuel oil, marine diesel oil, SECA, sulphur emission control area, fuel sulphur content, aromatics

Preface

Some of us see operating ships on daily basis; some of us do not. Most of us see the shipping sector as a necessary part in the chain of transportation of goods around the world. When I started my PhD project in 2008, my view of shipping was that there are ships, they run on some type of fuel and they transport goods and people. Today, 8 years later, this view has changed. There are not just ships; there are different types of ships, and they can run on various fuels and have different types of engines. Furthermore, these ships also have an impact on the human health and climate.

Quite early after I started my PhD study, I decided to focus on particle emissions. It seemed interesting because there is a clear connection between particle emissions and impact on human health. For me, with my interdisciplinary background, this was important. I did not want to just measure something and work with data that could not be related to other factors, such as environment or society. I did not realize my choice would result in busy but fun days on-board ships and in engine labs, but I am very grateful for these experiences and the insights that this PhD project has resulted in.

> *They always take longer than you think, said Rabbit.*
> *How long do you think they'll take? asked Roo.*
> The house at Pooh Corner by A.A. Milne

One important experience and insight from these years as a PhD student is that everything takes time. Everything takes time, and often much longer than you expect. For our experiments in the lab, you quickly learn from your supervisor that when you make a plan, you must multiply the time by three to get a realistic idea of how long your experiments will take. Later, when you finish your experiments, you realize that he was right. This also applies to how the maritime sector works with respect to its environmental influence. It takes years to make a decision regarding a regulation and then several more years for implementation, and so on. For me, this causes a sense of frustration.

> *The more you think, the more you realize that there is no simple answer.*
> Winnie the Pooh

There is also a sense of growing frustration within me related to the fact that some parts of the maritime sector are now overly pleased with their environmental work, thinking 'now the FSC is reduced, this is enough'. Sometimes, you just want to scream, 'Hey guys, you are far behind other sources of air pollution, you cannot stop now!' There are many problems to solve and investigate further. The regulation of fuel sulphur content is a step in the right direction but not the only key to success. On the other hand, there are several ship owners and stakeholders that are working toward new solutions to reduce the environmental impact of ships with a movement towards a more sustainable shipping. I hope, that when you read my thesis you will get an insight in one part of the environmental and health impact from ship operations and realize that the work towards more sustainable shipping must continue.

List of Appended Papers

This thesis is based on the work contained in the following papers:

Paper I	Characterization of particles from a marine engine operating at low loads **Maria Anderson**, Kent Salo, Åsa Hallquist, and Erik Fridell. 2015. Atmospheric Environment (101), pp. 65-71.
Paper II	Particle- and gaseous emissions from an LNG powered ship **Maria Anderson**, Kent Salo, and Erik Fridell. 2015. Environmental Science & Technology (49), pp. 12568-12575.
Paper III	Impact of the 0.1% fuel sulfur content limit in SECA on particle and gaseous emissions – Case of low-sulfur residual marine fuel oil **Maria Zetterdahl**, Jana Moldanová, Xiangyu Pei, Ravi Kant Pathak and Benjamin Demirdjian. Manuscript in preparation.
Paper IV	Impact of aromatic concentrations in marine fuels on particle emissions **Maria Zetterdahl**, Kent Salo, Erik Fridell and Jonas Sjöblom. Manuscript submitted to Fuel.

The author of this thesis changed name from Maria Anderson to Maria Zetterdahl during her time as PhD-student.

List of Other Relevant Publications and Work

Maria Anderson & Karin Andersson. 2012. Syns det inte finns det inte, eller? En studie om hur emissioner från sjöfart hanteras i miljökonsekvensbeskrivningar. Göteborg: Chalmers tekniska universitet. Rapport Nr. R-12:135. ISSN: 1652-9189

Maria Anderson, Kent Salo, Erik Fridell and Åsa Jonsson. 2012. Laboratory measurements of emissions of particulate matter from a marine diesel engine. Poster at 5th GAC Conference on Atmospheric Science, Gothenburg, May 23-24, 2012.

Maria Anderson, Kent Salo and Erik Fridell. 2015. Nanoparticle emissions from LNG and other low sulfur marine fuels. Oral presentation at 19th ETH Conference on Combustion Generated Nanoparticles, Zürich, June 28th to July 1st, 2015.

Maria Anderson, Kent Salo and Erik Fridell. 2015. Particle emissions from LNG and other low sulphur marine fuels. Poster at European Aerosol Conference (EAC) 2015, Milano, September 6th to 11th, 2015.

Hulda Winnes, Jana Moldanová Maria Anderson and Erik Fridell. 2014. On-board measurements of particle emissions from marine engines using fuels with different sulphur content. Proceedings of the Institution of Mechanical Engineers, Part M: Journal of Engineering for the Maritime Environment (230), pp. 45-54.

Maria Zetterdahl, Jana Moldanová, Xiangyu Pei and Ravi Kant Pathak. 2016. Impact of the 0.1% Fuel Sulphur Content Limit in SECA on Particle Emissions – Case of Low-Sulphur Residual Marine Fuel Oil. Oral presentation at 7th GAC Conference on Atmospheric Science, Gothenburg, April 26-27, 2016.

Contribution to Appended Papers

Paper I The author of this thesis participated in the planning of the experiments, conducted the measurements in the test-bed engine lab together with Kent Salo, performed the main part of the data analysis and wrote the manuscript.

Paper II The author of this thesis participated in the planning of the experiments, conducted the on-board measurements together with Kent Salo and Kjell Peterson, performed the main part of the data analysis and wrote the manuscript.

Paper III The author of this thesis participated in the planning of the experiments and conducted the two on-board measurements together with Jana Moldanová and Kjell Peterson from IVL, and was primarily responsible for the real-time particle measurements (except MAAP-measurements) and the analysis of these data. The author also wrote the main part of the manuscript, and participated in the filter sampling during the on-board measurements.

Paper IV The author of this thesis participated in the planning of the experiments, conducted the measurements in the test-bed engine lab together with Kent Salo and Jonas Sjöblom, performed the data analysis of the measurements performed in the test-bed engine lab at Department of Shipping and Marine Technology and was involved in the data analysis and discussion of the results from the measurements at the test-bed engine lab at the Department of Applied Mechanics. The author also wrote the main parts of the manuscript.

Table of Contents

Abbreviations, Acronyms and Terminology

BC	Black carbon
CCAI	Calculated Carbon Aromaticity Index
CCN	Cloud condensation nucleus
CCNR	Central Commission for the Navigation on the Rhine
CH_4	Methane
CN	Cetane number
CNG	Compressed natural gas
CO	Carbon monoxide
CO_2	Carbon dioxide
CPC	Condensation particle counter
cSt	Centistokes
DF engine	Dual-fuel engine
DMA	Differential mobility analyser
DMS	Differential mobility spectrometer
Dp	Diameter of particle
DR	Dilution ratio
EC	Elemental carbon
ECA	Emission control area
EEPS	Engine exhaust particle sizer
EF	Emission factor
EF_{NOX}	Emission factor for nitrogen oxides
EF_{PM}	Emission factor for particle mass
EF_{PN}	Emission factor for particle number
EF_{TSP}	Emission factor for mass of total suspended particles
EU	European Union
FPS	Fine particle sampler
FSC	Fuel sulphur content
g/kg fuel	Gram/kilogram fuel burned
g/kWh	Gram/kilowatt hour
H_2SO_4	Sulphuric acid
HC	Hydrocarbons
HFO	Heavy fuel oil
Hz	Hertz
IMO	International Maritime Organization
ISO	International Standard Organization
IWW	Inland waterways
kV	Kilovolt
kW	Kilowatt
kWh	Kilowatt hour
LNG	Liquefied natural gas
mA	Milliampere
MAAP	Multi angle absorption photometer
MARPOL	International Convention for the Prevention of Pollution from Ships
mbar	Millibar
MCR	Maximum continuous rate
MDO	Marine diesel oil
MEPC	Marine Environment Protection Committee within IMO

MGO	Marine gas oil
MK1	Swedish environmental class 1 diesel
MK3	Swedish environmental class 3 diesel
MW	Megawatt
NECA	Emission control area that consider NO_X, also called NO_X ECA
nm	Nanometres, 10^{-9} m
NO	Nitrogen monoxide
NO_2	Nitrogen dioxide
NO_X	Nitrogen oxides (includes NO and NO_2)
O_2	Oxygen
OC	Organic carbon
OM	Organic matter
PAH	Polycyclic aromatic hydrocarbon
PM	Particle mass
PM_{10}	Mass of particles with diameter <10 µm
$PM_{2.5}$	Mass of particles with diameter <2.5 µm
PN	Particle number
ppm	Parts per million
ppmv	Parts per million by volume
PPR	Sub-Committee on Pollution Prevention and Response
RF	Radiative forcing
RMB30	A low-sulphur residual marine fuel oil
rpm	Revolutions per minute (speed of engine)
SECA	Emission control areas that consider SO_X, also called SO_X ECA
SMPS	Scanning mobility particle sizer spectrometer
SO_2	Sulphur dioxide
SO_3	Sulphur trioxide
SO_X	Sulphur oxides (includes SO_2 and SO_3)
TD	Thermodenuder
THC	Total hydrocarbons
TSP	Total suspended particles
UFP	Ultrafine particles
#/kg fuel	Number/kilogram fuel burned
#/kWh	Number/kilowatt hour
%m/m	Mass-percent
%vol	Volume-percent
µm	Micrometres, 10^{-6} m

Terminology

This thesis includes terminology from different areas. Therefore, a list of the terminology applied in this thesis is included to assist readers. Each term is highlighted by a footnote the first time it appears in the text.

Acidification	Acidification has an impact on land areas, lakes and waterways. Aquatic organisms may suffer from the lowered pH levels and elevated levels of dissolved aluminium in the water. Acidification of lakes may also impact on birdlife. In forests acidification may cause imbalance between nutrients and increased concentrations of metals, which may lead to damage of root systems and slow down decomposition (Elvingson and Ågren, 2004).
Aerosol	A mixture of solid and/or liquid particles in a gas (Finlaysson-Pitts and Pitts, 2000).
Atmospheric deposition	Characterized as either dry or wet deposition and depends on the phase in which a specie reaches the ground. In dry deposition gases or small particles are transported to the ground and absorbed and/or adsorbed to materials without first being dissolved in atmospheric water droplets. In wet deposition the pollutants are dissolved in rain, fog, snow or clouds and transported to the ground as water droplets (Finlaysson-Pitts and Pitts, 2000).
Compression stroke in the 4-stroke cycle	The second stroke in the 4-stroke cycle. During the compression stroke, the piston goes up in the cylinder and ignition occurs when the piston reaches the top dead centre of the cylinder. The inlet valves are closed during this stroke. In diesel engines, the fuel will be injected at the end of this stroke (Heywood, 1988, Stone, 2012).
Compression stroke in the 2-stroke cycle	The first stroke in the 2-stroke cycle. The piston moves up in the cylinder and compresses the charge of air. At the same time, a new charge of air is drawn into the underside of the cylinder through an inlet valve. The fuel is injected at the end of this stroke (Stone, 2012).
Diesel principle	A four-stroke cycle, with heat added during periods of constant pressure in the cycle. The fuel is injected at the moment when the combustion is set to start (Stone, 2012).
Diffusion	The net transport of particles over a concentration gradient, i.e., transport from zones with higher concentrations to zones of lower concentrations (Hinds, 1999). Diffusion can be reduced through shortened transfer tubes and increased gas flow rates (Ushakov, 2012).
Diffusion combustion	Diffusion combustion occurs after the rapid combustion

	(premixed combustion) that occurs after the ignition delay. During the diffusion combustion diffusion between the fuel vapour and air will occur and the rate of diffusion controls the combustion (Stone, 2012). The combustion occurs with a so-called diffusion flame (Heywood, 1988).
Exhaust stroke	The fourth and last stroke in the 4-stroke cycle. The exhaust valves continue to be opened and the exhaust gases leave the cylinder. During this stroke the piston will move up in the cylinder and the remaining gases will be expelled (Heywood, 1988, Stone, 2012).
Expansion, power or working stroke in the 4-stroke cycle	The third stroke in the 4-stroke cycle. During this stroke, the combustion will continue and cause an increase in temperature and pressure within the cylinder that forces the piston down. At the end of this stroke the exhaust valve will open and the pressure in the cylinder is reduced close to the pressure of the exhaust (Heywood, 1988, Stone, 2012).
Ignition delay	The ignition delay is defined by the time interval between start of injection and start of combustion. An increased delay through earlier or retarded injection timing will occur due to a significant change in air temperature and pressure close to top centre. The timing of fuel injection controls at which crank angle the combustion starts (Heywood, 1988). The injected fuel will break up into droplets and be vaporized and mixed with the air and the chemical reactions will slowly start (Stone, 2012).
Induction or intake stroke	The first stroke in the 4-stroke cycle. Here the inlet valve is opened and the piston goes down in the cylinder and new air is drawn into the cylinder (Heywood, 1988, Stone, 2012).
Isokinetic sampling	Isokinetic sampling is when the sampling probe is aligned parallel to the streamlines of the gas in the tube and the velocity of the gas that enters the sampling is equal to the velocity of the free gas in the tube. There is no distortion of the streamlines in the flowing gas. It ensures that the concentration and size distribution of particles in the sampling probe are the same as that found in the flowing stream. The opposite of isokinetic sampling is anisokinetic sampling, which results in misleading size distributions and wrong estimations of the concentrations. Anisokinetic sampling appears when the sampling probe cause curved streamlines of the flowing gas (Hinds, 1999).
Non-volatile particles	Compounds, e.g., elemental carbon, heavy hydrocarbons and metals that remain solid/stable even at ignition temperatures of soot (approx. 500°C) (Kwon et al., 2003).
Otto principle	The Otto principle is a four-stroke cycle in which the heat addition occurs during the periods of constant volume.

	The air and fuel are premixed and the injection is initiated by an external source, such as injection of the pilot fuel in a dual-fuel engine running on gas (Heywood, 1988).
Power stroke in the 2-stroke cycle	The second and last stroke in the 2-stroke cycle. The combustion in the cylinder increases the temperature and pressure and forces the piston to move down. The exhaust valve will be uncovered at the end of this stroke and the exhaust gases leave the cylinder (Stone, 2012).
Primary particles	Particles emitted directly to the atmosphere from a source (Finlaysson-Pitts and Pitts, 2000, Hinds, 1999).
Radiative forcing (RF)	The impact of a factor that may cause climate change, e.g., greenhouse gases. RF is a measure of how the energy balance in the Earth-atmosphere system will be influenced when a factor or factors that have an impact on the climate is/are changed. The word radiative comes from the fact that these factors influence the balance between incoming and outgoing radiation and forcing is used to indicate that the radiative balance is forced from normal state. RF is expressed in Watts per square meter (W m^{-2}). A positive value leads to warming of the system and a negative value to cooling (Forster et al., 2007).
Secondary particles	Particles formed through processes in the atmosphere (Finlaysson-Pitts and Pitts, 2000, Hinds, 1999).
Short-lived climate forcers	Pollutants that have an impact on the climate, but shorter residence times in the atmosphere than CO_2 and will impact the climate over shorter time scales than CO_2. The short-lived climate forcers can have an impact on the regional climate as well through interaction with ice, snow or clouds. Compounds considered as short-lived climate forcers are, for example, particles of black carbon (BC) and particles containing sulphate (Corbett et al., 2010).
Thermophoresis	The movement of particles established due to a force that moves the particles in the direction of decreased temperature (Hinds, 1999). Thermophoresis is reduced with proper isolated sampling tubes and heating of the transfer tubes (Ushakov, 2012).
Volatile compounds	Light hydrocarbons and other compounds that are vapours at room temperature. Some compounds are defined as **semi-volatile** compounds and are absorbed to particle surfaces. Theses compounds can evaporate and desorb easily from the surface when the sample of particles is heated (Kwon et al., 2003).

1 Introduction

Imagine a box of chocolates: some are dark chocolate, some are white chocolate, some are dark chocolate covered with white chocolate and some contain nuts, dried fruits or other decoration. They also vary in shape: some are spherical, some have irregular shapes and some have small spines. Now, imagine that these confections are reduced in size, to a few nanometres (nm, 10^{-9} m) or several micrometres (µm, 10^{-6} m) in diameter. They are so small that we cannot see them, but they are present in the surrounding air. These small chocolates can now be regarded as particles that, together with gases, are present in the ambient air as aerosols[1] and originate from natural and anthropogenic sources. One well-known anthropogenic source is the combustion of fossil fuels. In this thesis, the focus is on the combustion of marine fuels, including both traditional and alternative fuels, and the generated particle emissions.

An increased awareness regarding emissions to the air from ship operations has made the International Maritime Organization (IMO) implement regulations with the aim of reducing these emissions. The regulations target emissions of sulphur oxides (SO_X) and nitrogen oxides (NO_X). Emissions of SO_X are regulated through the fuel sulphur content (FSC) in marine fuel oils. Although particle emissions from ship operations are not yet regulated, they are assumed to be reduced by the lower FSCs in marine fuel oils required by the existing regulations. The strictest limit of FSC exists in sulphur emission control areas (SECAs, also known as SO_X ECAs) since January 2015. There are three strategies to reach compliance with this regulation: make a fuel shift and use low-sulphur marine fuels (FSC <0.1 %m/m), use alternative fuels or use scrubbers. However, there are few studies made that evaluate how these strategies influence the particle emissions.

The particle emissions from the combustion of marine fuels are dominated by very small particles, with a diameter (Dp) less than 50 nm. You may ask why we are concerned with something that is so small that we cannot see it. Additionally, the particles emitted from ships are mainly emitted far away from us, so why study emissions from a source that does not affect us? Particles generated by the combustion of marine fuels should be considered because they have impact on human health and on the climate. Modelling studies have estimated that particle emissions from ships may be responsible for approximately 60 000 premature deaths from lung cancer and cardiopulmonary diseases[2] annually on a global level. Furthermore, approximately 70% of the emissions from ships are emitted within 400 km of land (Corbett et al., 2007) and these emissions can be a dominant source of air pollution in coastal areas (Eyring et al., 2010). The contribution from international ship operations in European waters to the global emissions of particles with a Dp less than 2.5 µm ($PM_{2.5}$) is 15-25%, with local contributions of particles from ships estimated to 20-30% (European Environment Agency, 2013). Furthermore, the annual contribution from ship operations, close to the Danish west coast, to the number concentration of particles with a Dp less than 150 nm is 5-8% (Kivekäs et al., 2014). This thesis focuses on how use of the first two strategies to comply with the SECA regulations (fuel shift and use of an alternative fuel) affect the particle emissions and evaluate how FSC and other fuel characteristics affect these emissions.

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[1] Described further in “Terminology” starting on page xvii.

[2] Heart-lung diseases

1.1 Objectives

The objectives of this thesis are to characterize the particle emissions from marine engines using fuels that comply with the allowed FSC in SECAs and to investigate how the FSC and other fuel characteristics influence particle emissions from ship operations.

The particle emissions are characterized with respect to particle number (PN), particle mass (PM), size distribution by number and mass, chemical content and volatility. Emission factors (EFs) are calculated for the PN (EF_{PN}) and PM (EF_{PM}). In addition, size-resolved EFs for PN and PM have also been calculated.

1.2 Delimitations

This thesis focuses on particle emissions (and to some extent also gaseous emissions), from marine fuels that comply with the current FSC regulations and can be used today in SECAs and at a global level in the future. An in-depth evaluation of the impact of different abatement technologies on the particle emissions is not included. Furthermore, economic aspects and the development of future regulations are not included.

2 Background & Motivations

This section presents the background and motivations for research within the area of particle emissions from ship operations. This section will provide the readers with information to increase the understanding of the subject and why particle emissions from ship operations are important to consider. Information on the impact of particles on human health and climate are presented, as well as current regulations and work with future regulations of particle emissions. Furthermore, information on measurement techniques and instrumentation are included and the section ends with a presentation of previous work done in this field and the motivations for the studies included in this thesis.

2.1 Impact on Human Health

The emissions from ship operations in coastal areas and port cities can be a dominant source of urban air pollution and consequently have an impact on local and regional air quality (Cofala et al., 2007, Eyring et al., 2010). Emissions of particles, NO_X and volatile organic compounds from ship operations, affect the formation of ground-level ozone and have severe impact on human health (Eyring et al., 2010). Various studies, for example Corbett et al. (2007) and Cofala et al. (2007), use modelling to highlight the impact of particle emissions from ships on human health. Furthermore, in 2012, the World Health Organization changed their classification of diesel exhaust gases from "probably carcinogenic to humans" to "carcinogenic to humans" (International Agency for Research on Cancer (IARC) and World Health Organization (WHO), 2012). However, exposure to particle emissions from mobile sources, such as ship operations, is difficult to assess, and improved monitoring systems are needed for this purpose (Delfino et al., 2005). The particles considered here are generated during the combustion of marine fuel oils, so-called primary particles[3], and in the exhaust gas channel and atmosphere, so-called secondary particles[4].

The sizes, i.e., diameter (Dp), of the particles and their chemical content are important properties to consider in assessments of the impact of particles on human health. Several studies emphasize that the smallest particles, i.e., ultrafine particles (UFP) (Dp <100 nm), are most important to consider (Delfino et al., 2005, Pope and Dockery, 2006, Health Effects Institute, 2013). These particles can reach deeper into the respiratory system than larger particles. Larger particles are deposited in the mucus layer present in the upper respiratory tract, i.e., the nose and throat, and can be moved upward in the system with the aid of the cilia[5] and eventually swallowed (Finlaysson-Pitts and Pitts, 2000). UFP reach the lungs and therefore have a higher deposition efficiency in the lungs than larger particles. These particles have the potential to be translocated from the lungs to other organs and tissues via the blood system (Pope and Dockery, 2006, Health Effects Institute, 2013). Studies on both humans and animals emphasize the impact of exposure to UFP on the respiratory and cardiovascular systems, and the observed effects include changes in lung function, increased allergic responses and altered heart rates (Health Effects Institute, 2013). Additionally, a connection between exposure to particles and intestinal diseases[6] is believed to exist (Beamish et al., 2011). UFP dominate the particle emissions from combustion of marine fuel oils. In coastal areas and port cities with dense traffic, particle emissions

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[3] Described further in "Terminology" starting on page xvii.

[4] Described further in "Terminology" starting on page xvii.

[5] Small hairlike projections in the mucus membrane (Finlaysson-Pitts and Pitts, 2000).

[6] Diseases related to the intestines.

from ship operations can be considered a source of air pollution with regard to compliance with European Union (EU) air quality limit values for fine particles (Eyring et al., 2010).

Particles, such as black carbon (BC), can act as carriers of toxic compounds, such as some organic compounds and transition metals that are condensed or adsorbed onto the particle surfaces (Delfino et al., 2005). Known transition metals found in particles from ship operations include vanadium (V), nickel (Ni), iron (Fe), zinc (Zn) and calcium (Ca) (Amann and Siegla, 1981). Vanadium and iron, for instance, are related to the activation of various biochemical processes, may catalyse the formation of reactive oxygen species (Lighty et al., 2000) and may cause respiratory diseases (Lighty et al., 2000, Donaldson et al., 2005). Studies of short-term health effects of particle emissions show a strong relation to BC and indicate that BC can be a better indicator for combustion-derived harmful particulate substances emitted from traffic sources than just using the mass of the emitted particles (Janssen et al., 2012). However, in areas with high levels of primary combustion particles, the effects of $PM_{2.5}$ are expected to be high (Hoek et al., 2012). In addition, non-volatile[7] particles in the form of ash particles that contain metals can be considered toxic (Jayaratne et al., 2012). Volatile and semi-volatile particles[8] can contain compounds, such as dioxins and polycyclic aromatic hydrocarbons (PAH), that trigger biochemical reactions in cells and have carcinogenic characteristics (Biswas et al., 2009, Ning and Sioutas, 2010). The importance of considering both volatile and non-volatile particles in assessments of their impact on human health has been even further strengthened by studies on the biological effects on cells exposed to particles generated from the combustion of heavy fuel oil (HFO) and marine diesel oil (MDO). The particles generated by the combustion of MDO are not less important than the particles from combustion of HFO. However, the biological effects may differ and may be related to the volatility of the particles and adsorbed compounds (Kanashova et al., 2015, Oeder et al., 2015).

2.2 Impact on Climate

Emitted particles to the ambient air can have an impact on the visibility. The visibility is reduced due to scattering of light by suspended particles in the air, resulting in haze (Finlaysson-Pitts and Pitts, 2000). Furthermore, the particles have direct and indirect effects on radiative forcing (RF)[9], with different impacts on the climate (Isaksen et al., 2012, Forster et al., 2007). The direct effects on the RF are scattering and absorption of both shortwave and long wave radiation, which affect the radiative balance. This will result in either heating or cooling, depending on the optical properties of the particles (Isaksen et al., 2012, Forster et al., 2007). Particles containing BC will absorb radiation and cause heating of the atmosphere, with a global and annual mean RF of +0.40 (+0.05 to +0.80)[10] W m^{-2} (BC aerosols from fossil fuels and biofuels). Particles containing organic carbon (OC) and sulphate will lead to cooling due to scattering of the incoming radiation. The global mean RF values are -0.09 (-0.16 to -0.03) W m^{-2} for particles of OC and -0.40 (-0.60 to -0.20) W m^{-2} for particles of sulphate (Myhre et al., 2013, Isaksen et al., 2012, Lack et al., 2011, Lack et al., 2009). The tropospheric lifetime of these three aerosol species is estimated to be approximately 1 week (up to 10 days for BC) (Myhre et al., 2013).

Particles also indirectly affect the climate through effects on the clouds. Particles affect precipitation, the number of clouds and the lifetime of the clouds, as well as radiative

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[7] Described further in “Terminology” starting on page xvii.

[8] Described further in “Terminology” starting on page xvii.

[9] Described further in “Terminology” starting on page xvii.

[10] Global and annual mean RF estimates due to aerosol-radiation interactions between years 1750 to 2011. Uncertainties in brackets.

properties. The size of the particles, together with the chemical composition, mixing state and ambient environment, determine how well a particle can act as a cloud condensation nucleus (CCN) and thereby indirectly affecting the climate (Forster et al., 2007, Isaksen et al., 2012). Among the particles emitted from operating ships, it is mainly the particles containing sulphate that can act as CCNs (Lack et al., 2011). However, particles of BC can act as CCNs when coated, and particles of OC can act as CCNs as well, depending on the size and age of the particles (Myhre et al., 2013).

The net effect of emissions from ship operations on the RF estimates is considered to be negative (-0.408 W m^{-2}), due to a high content of sulphate particles in the emissions compared to other combustion sources and the significant indirect effects of particles emitted by operating ships. However, the uncertainties in this estimate are large (-0.824 to 0.026 W m^{-2}) and important to consider (Eyring et al., 2010). The current regulations of FSC in marine fuel oils (see section 2.3) are believed to reduce this cooling effect (Lauer et al., 2009). Modelling of future scenarios emphasize that the net RF associated with ship operations will change due to changes in the particle emissions from this source. The $PM_{2.5}$ emissions and sulphur dioxide (SO_2) are expected to decrease until 2030 and then increase until 2050, and emissions from ship operations will consequently continue to result in a net negative RF. An increased contribution of BC and OC particles from ship operations in 2020 is also expected (Isaksen et al., 2012). However, the reduction of greenhouse gases such as carbon dioxide (CO_2) are still of major concern in the aspect of tackling the climate change (European Environment Agency, 2013).

Particles of BC also impact the RF by affecting the albedo[11] of snow. BC deposited on snow and ice will make the surfaces darker and reduce the albedo of the surface. This enhances the melting of snow and ice (Isaksen et al., 2012). Furthermore, BC is one of the main short-lived climate forcers[12] emitted by diesel engines. This is of particular interest for the Arctic, because the polar regions are sensitive to the warming effects of BC and other light-absorbing compounds. Increased emissions of these compounds in the Arctic are expected due to increased ship operations in the area and increasing anthropogenic activity in the northern hemisphere, which is increasing the amount of BC transported to the Artic from other areas (Corbett et al., 2010).

2.3 Regulation of Particle Emissions at Regional and International Levels

Particles, PM, emitted from heavy-duty diesel engines have been regulated in Europe since the Euro I standard was implemented in 1992. In 2014, the latest Euro standard, Euro VI, entered into force. This regulation limits particle emissions with respect to both PM and PN. The Euro VI standard is comparable to the US 2010 standard and sets the emission standards to $6.0*10^{11}$ #/kWh for PN emissions during a transient test cycle[13] and $8.0*10^{11}$ #/kWh for a steady state test cycle[14]. The PM emissions are limited to 0.01 g/kWh (The European Commission, 2011, Dieselnet, 2016a). The emission standards originate from the Particle Measurement Programme and consider non-

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[11] Albedo is a measure of the reflectivity of different surfaces on the earth. Ice and snow have a high albedo i.e., reflect a large amount of the incoming solar radiation, while water has a lower albedo, i.e., absorbs more of the radiation (Finlaysson-Pitts and Pitts, 2000).

[12] Described further in "Terminology" starting on page xvii.

[13] World harmonized transient cycle (WHTC), duration of 1,800 seconds with various engine speeds and torques. Requires both hot and cold start (Dieselnet, 2016c).

[14] World harmonized stationary cycle (WHSC), is a ramped steady-state test cycle that includes 13 modes with defined values for engine speed and load, weighting factors and time of duration. Includes hot start of the engine (Dieselnet, 2016b).

volatile particles with a diameter greater than 23 nm (United Nations, 2011). Furthermore, limits on the concentrations of $PM_{2.5}$ and particles with diameters <10 µm (PM_{10}) in the ambient air are included in the established environmental quality standards at the European regional level, as well as at the Swedish national level (Miljödepartementet, 2010, The European Parliament and the Council of the European Union, 2008). However, there are no international regulations that directly control or limit the emissions of particles from ocean-going ships.

2.3.1 Particle Emissions and Regulations within the IMO

The IMO is a specialized agency within the United Nations that is responsible for the prevention of pollution from ships and for the safety and security of shipping (IMO, 2015a). The IMO consists of an assembly, a council and five main committees, of which the Marine Environment Protection Committee (MEPC) is responsible for the prevention and control of pollution from ships. Initially, MEPC was established as a subsidiary body of the Assembly. In 1985, it was raised to full constitutional status (IMO, 2015d).

In 1990, at the 29th session of MEPC, air pollution from ship operations was on the agenda for the first time, with a focus on the emissions of SO_X and NO_X and the future reduction and regulation of these compounds to reduce the environmental impact, i.e., acidification[15]. In 2004, in connection to on-going discussions regarding the regulation of SO_X emissions through a limitation of the FSC, the health risk of particle emissions was raised. In 2005, the relationship between FSC and particle emissions was introduced and the primary motivation for establishment of the regulation began to shift towards the health effects of particle emissions. In 2008, at MEPC 58, the regulation of FSC was adopted as Regulation 14 in MARPOL 73/78 Annex VI (Svensson, 2011). The title of Regulation 14 is 'Sulphur oxides (SO_X) and particulate matter'. However, the regulation does not include any limits on particle emissions; instead they are indirectly regulated by limits imposed on the FSC. The FSC limits are divided into a global level and a level for special areas, the so-called emission control areas (ECAs). The current designated ECAs are the Baltic Sea together with the North Sea and English Channel and the coastal areas around the United States, Canada and United States Caribbean Sea[16] (IMO, 2013). Figure 2-1 shows the allowed FSCs at global level and in SECAs. The European Union Directive 2005/33/EC incorporated Regulation 14 of MARPOL Annex VI into EU legislation. In this directive, the FSC of marine fuel oils used in port areas was limited to 0.10 %m/m sulphur (S) beginning on January 1, 2010. The global limit will be set to 0.50 %m/m S in 2020 without any process of review, which is the case in Regulation 14 of MARPOL Annex VI (The European Parliament and the Council of the European Union, 2005, The European Parliament and the Council of the European Union, 2012)[17]. It is believed that an increased use of marine fuel oils with lower FSCs will reduce the $PM_{2.5}$ emissions by 80% from 2000 to 2020 (European Environment Agency, 2013).

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[15] Described further in "Terminology" starting on page xvii.

[16] The Baltic Sea, North Sea and English Channel are SECAs, while the coastal areas around North America and United States Caribbean Sea are ECAs that consider both SO_X, NO_X and particles (IMO, 2013).

[17] The main directive regarding the sulphur content of liquid fuels, Dir. 1999/32/EC, has most recently been amended by Dir. 2012/33/EU, which concerns the sulphur content of marine fuel oils.

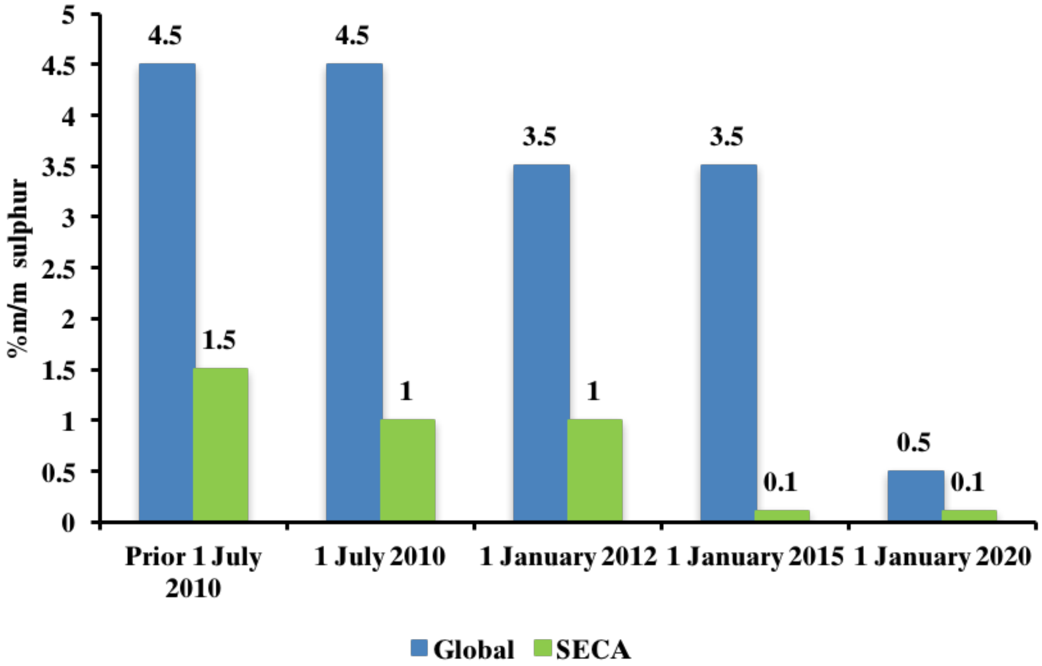

Figure 2-1: Regulation 14 in MARPOL Annex VI, of FSCs in marine fuel oils at the global level (blue) and in SECAs (green). The inserted data labels show the set limits of %m/m S.

The ship traffic in the Artic region is assumed to increase in the future. This assumption, together with the awareness of the impacts of BC emissions (see section 2.2) has encouraged the IMO to investigate BC emissions generated from international ship operations. If necessary, regulations to limit these emissions can be developed. The regulation of BC would reduce the negative impacts on human health of particle emissions as well. Specific discussions about BC and its impact on the climate started in 2008 during MEPC 58 (IMO, 2008). Since 2008, there has been on-going work within MEPC and the sub-committee on Pollution, Prevention and Response (PPR), previously known as the sub-committee on Bulk and Liquid Gases. This work has included the development of a definition of BC emissions from international shipping, the evaluation of measurement methods and the evaluation of control measures (IMO, 2011). During the 2nd PPR session in 2015, a single definition of BC was recommended to MEPC. The definition followed the definition found in Bond et al. (2013)[18] because this definition is independent of the measurement method and supported by the scientific community. Furthermore, the PPR 2nd session concluded that more research is needed in this area, with more measurements to be done to be able to identify the most appropriate methods for measuring BC and possible control measures (IMO, 2015c). The definition of BC from the 2nd PPR session was accepted as the definition of BC generated by international shipping during MEPC 68. However, the Committee noted that there is a need for further measurements of BC to gain experience in the application of this definition and investigate possible measurement methods (IMO, 2015b). During the 3rd PPR meeting in 2016, a draft of a measurement reporting protocol was developed (IMO, 2016).

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[18] This definition describes black carbon as “a distinct type of carbonaceous material, formed only in flames during combustion of carbon-based fuel, distinguishable from other forms of carbon and carbon compounds contained in the atmosphere aerosol because it has a unique combination of physical properties”. These properties include the absorption of visible light at 550 nm, a refractory nature and stability at high temperatures, insolubility in water, organics and other components in atmospheric aerosols and ability to form aggregates of small carbon spherules (IMO, 2015c).

2.3.2 Inland Waterways

The particle emissions from ships used for transport along inland waterways (IWW) are regulated by the EU directive 2004/26/EG, Stage IIIA, and the CCNR2 standards that are regulations set by the Central Commission for the Navigation on the Rhine (CCNR). The limits set in the EU directive entered into force between the 1st of January 2007 and the 1st of January 2012, depending on the engine type, and they regulate the emissions of carbon monoxide (CO), hydrocarbons (HC) together with NO_X and particulate matter with respect to PM. The directive applies to new engines installed on vessels after 2007. The EFs for PM are set to 0.2-0.5 g/kWh and are measured via filter sampling following the procedure described in the Directive. The limits of particulate matter in the EU directive and CCNR2 are similar. However, for NO_X, the limits in CCNR2 are slightly lower than in the EU directive. The limits for IWW are similar to the Euro II standards for trucks, which entered into force in the late 1990s (The European Commission, 2004, The European Commission, 2013, The European Commission, 1997). In the future, the intention is to include a limit on PN emissions in the regulation of emissions along IWW, to reduce the emissions of small particles, similar to the limit imposed by the Euro VI standards on heavy-duty engines. There is also a proposal for new limits on already regulated emissions as well (The European Commission, 2013). Furthermore, the FSC in fuels used by ships operating on IWW has been limited to 10 ppm since January 1, 2011 (The European Parliament and the Council of the European Union, 2009).

2.4 Methods for Particle Measurements

Several techniques and instruments are used to characterize particles by mass, number and the size distribution. Some of them commonly used for measurements of particles are summarised in Table 2-1.

Table 2-1: Summary of particle measurement techniques and instruments presented in this section. Note that the information presented here is general for the instruments and variations between different models may exist.

	Measurement technique			
Name of instrument	**Size**	**Number**	**Size range**	**Temporal resolution**
Engine exhaust particle sizer (EEPS)[a]	Electrical mobility	Electrometer	5.6-560 nm	0.1 seconds to 60 minutes
Dust monitor	Pulse height analyser	Light scatter technology	0.3-20 µm	6 seconds to 60 minutes
Condensation particle counter (CPC)[b]	-	Condensational growth/optical counting	Up to 3 µm	1-60 seconds
Differential mobility analyser (DMA)[b]	Electrical mobility	-	2.5 nm to 1 µm	16-600 seconds
Differential mobility spectrometer (DMS)[c]	Electrical mobility	Electrometer	5 nm to 1 µm or 5 nm to 2 µm	10-60 seconds

[a] Measurements under atmospheric pressure; [b] A combination of a CPC and a DMA are the two working components of the Scanning mobility particle sizer (SMPS); [c] DMS500, measurements under sub-atmospheric pressure.

2.4.1 Electrical Mobility Analysers

Most particles in an aerosol are electrically charged. When these charged particles are placed in an electric field, an electrostatic force acts upon them. The ability of the particles to move in the electric field is the electrical mobility of the particles (Hinds, 1999). The electrical mobility of a particle is related to a number of factors, such as the particle charge (proportionally related), particle diameter (inversely related) and particle shape. Hence, the smaller the particle diameter is, and the higher the number of chargers is on the surface of the particle, the greater is the electrical mobility of the particle (Wiedensohler et al., 2012).

One instrument commonly used to measure particle size distribution is the DMA. A DMA is often connected in line with CPC (described in section 2.4.2), and together they constitute the working components of a Scanning mobility particle sizer spectrometer (SMPS). The DMA is an electrostatic classifier with a bipolar diffusion charger (also called a bipolar neutralizer) that sorts the particles with respect to their electrical mobility. The role of the CPC in the SMPS is to count the particles sorted by the DMA. A known charge equilibrium[19] is applied to the analysed particles before they enter the DMA. This is done by a bipolar diffusion charger that produces positive and negative ions. The DMA consists of a central rod electrode and an outer grounded tube. The charged particles flow from the top towards the bottom of the DMA with a laminar particle-free sheath air flow. Particles with an opposite charge compared to the rod are drawn towards the central rod. For a given voltage of the central rod, particles with a certain mobility will pass through the sample slit located in the bottom of the DMA in the form of a monodisperse aerosol. In the SMPS-system, a range of voltages (up to 10 kV) is applied to the central rod to scan particles of certain mobilities and sizes, which are then counted by the CPC after passing through the slit. Uncharged particles pass through the DMA and are unaffected by the electrical field. An impactor is used to remove particles larger than the upper size limit for the instrument before they enter the system. The quality of the SMPS-system measurements is affected by, for example, the loss of particles by diffusion in the DMA and classifier[20] and the performance of the CPC (Salo, 2011, Wiedensohler et al., 2012, Hinds, 1999). The SMPS-system can be used to measure particles with diameters of up to 1000 nm, with a resolution of up to 167 channels and has a selectable measurement time of 6-600 seconds (TSI, 2012).

Other available instruments that are based on the principle of particles' electrical mobility include the DMS500 and the EEPS (Figure 2-2). These instruments operate according to the same principles as the DMA, but feature some differences. In the DMS500 and EEPS, the particles are unipolarly charged with a mix of ions generated by a unipolar diffusion charger. The charged particles are then led to the measurement region, that has a high-voltage electrode column, and are carried towards the bottom via a sheath air flow. The charged particles are deflected by the electrical field created by the high-voltage electrode column in the centre of the measurement region. The particles move outwards and are collected on electrodes located along the outer walls of the measurement region. Particles with a high electrical mobility, i.e., greater charge and small in size, will strike an electrode at the top of the measurement region, whereas particles with lower electrical mobility, such as larger particles, will strike electrodes located further down. To determine the total particle number concentration, the electrical current is collected from the signals of the charged particles on the series of electrodes (Symonds et al., 2007).

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[19] Boltzmann equilibrium (Hinds, 1999)

[20] Can be corrected for in the software (TSI, 2014)

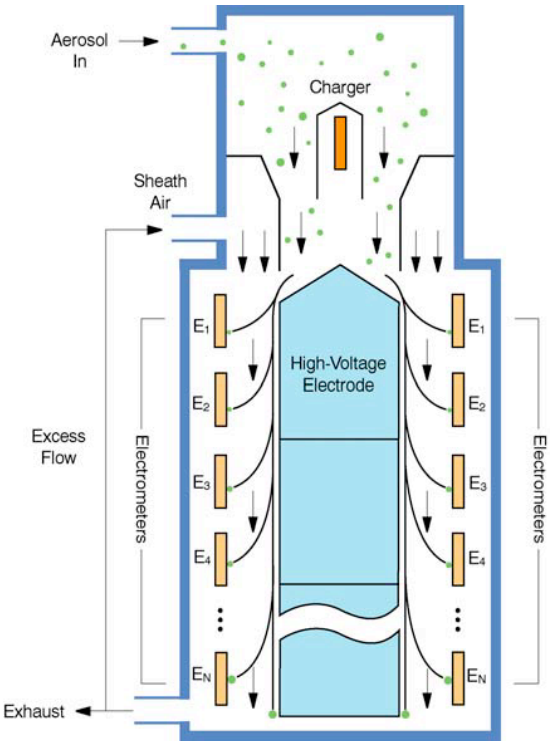

Figure 2-2: Schematic picture of an EEPS (TSI, 2006)

The EEPS measures particles at atmospheric pressure in the size range of 5.6 to 560 nm with a resolution of 16 channels[21] per decade, resulting in a total of 32 channels and a temporal resolution of 10 Hz (0.1 second). The particles are drawn into the EEPS through an inlet equipped with a cyclone with a 1 µm cut. Measurements of the number concentration and size distributions by number are the primary measurements made by the EEPS. The mass concentrations reported by the instrument are based on the number concentration and the assumption that the particles are perfect spheres with a density that is defined in the software (TSI, 2006). The DMS500 measures particles under sub-atmospheric pressure (250 mbar) in the size range of 5-1000 nm, with a temporal resolution of 10 Hz. The instrument has a 2-stage dilution system and a heated line for direct sampling of exhaust particles. The first dilution stage is heated to prevent condensation of water vapour in the instrument. The second dilution stage is a mechanical rotating disc diluter (Symonds et al., 2007, Cambustion, 2010).

The SMPS-system is a widely used instrument for measuring particles in the sub-micron range. However, measurements with the SMPS have low temporal resolution (scanning times of 16 seconds to several minutes) and the chosen temporal resolution affects the measureable size range, as faster scanning time narrows the measurable size range (Levin et al., 2015). For measurements of particles emitted by traffic, instruments with higher temporal resolution and the ability to measure particle concentrations and size distributions are needed, especially for measurements during transient driving cycles (Zimmerman et al., 2015). However, a higher temporal resolution may affect the precision and accuracy of the measurements (Levin et al., 2015). A number of previous studies, such as Jeong and Evans (2009), Asbach et al. (2009), Zimmerman et al. (2015) and Levin et al. (2015) have investigated differences among the results of measurements made with instruments with high and low temporal resolution. Factors that can affect the outcome of measurements with high temporal

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[21] The channels in the aerosol instruments separate the incoming particles into different size bins.

resolution are the morphology of the particles (Zimmerman et al., 2015) and the method of charging the measureable particles. In the case of unipolar charging of the particles, such as in the DMS500 and EEPS systems, the particles may become multiply charged, causing particles of the same size to have different levels of charge and therefore different behaviours in response to electrostatic forces. Consequently, the particles will be collected at different locations on the electrodes on the outer wall of the measurement region. Particles measured by the SMPS can be multiply charged as well (Reavell et al., 2002). However, the distribution of charges among the particles with respect to their size is known and can be corrected for in the software.

2.4.2 Optical Instruments

The optical properties of particles in aerosols are responsible for a number of spectacular atmospheric effects, such as richly coloured sunsets and rainbows. Furthermore, these particles can also cause reduced visibility related to atmospheric pollution. The relationship between light and particles is the basis for measurements of the concentrations and sizes of particles using optical instruments that rely on light-scattering technology. Studies of particles using light-scattering technology started in the late 1800s. The advantages of optical measurements are that they are extremely sensitive, nearly instantaneous and do not require any physical contact with the particles and thereby minimally disturbing the particles. However, the light-scattering effects of the particles can be sensitive to changes in, for example, particle size and shape, which may lead to misleading results (Hinds, 1999). One instrument that uses light-scattering technology to measure aerosol particles is the Dust Monitor. The Dust Monitor measures particles in the size range from 300 nm to over 20 μm, with a size resolution of over 16 channels and with a minimum temporal resolution of 6 seconds. Here, the particles are classified to a certain size based on the intensity of the scattered light associated with the particle. The size of a particle is proportional to the intensity of the detected scattered light. In the instrument, a laser beam illuminates the sampled particles, and the light scattered by the particles is led to a recipient diode via a wide-angle mirror. The detector is located at a right angle to the laser beam. The diode signal passes through a multichannel size classifier and a pulse height analyser, which classify the signals into appropriate channels based on the size (Grimm Aerosol Technik GmbH & Co KG, 2010, Grimm Aerosol Technik GmbH, 2000, Cheng, 2008).

Another type of optical instrument is a CPC, which can be a part of a SMPS-system. CPCs are used to measure the total number concentration of the particle. The particles, enter into the CPC, pass through a volume saturated with the working fluid (water or alcohol, such as butanol or isopropyl alcohol) and then pass through a cooled tube. When the particles are cooled, the working fluid becomes supersaturated and starts to condense onto the particles. Consequently, the particles start to grow and become detectable with optical methods (Hinds, 1999, TSI, 2014, Salo, 2011).

2.4.3 Measurement of Mass Concentrations

Measurements of the mass concentration of emitted particles can be done either through real-time measurements using instruments based on different techniques and with certain assumptions about particle density and shape or by measurements of particles sampled on a filter. To sample particles on a filter, a certain volume of the aerosol is passed through the filter, and the increase in the filter mass is equal to the mass of sampled particles. The sampled particles can represent either the total amount of suspended particles (TSP) or a certain size fraction, such as PM_{10} or $PM_{2.5}$. To determine of the mass concentration of the sampled particles, gravimetric analyses can be made. These analyses are simple, accurate and widely used. In this analyse, the filter has to be correctly weighted before and after sampling. Furthermore, the sampling flow rate and sampling time have to be measured. Particles sampled on filters can be used in other analyses, such as the analysis of the chemical content (Hinds, 1999).

2.4.4 Dilution

The purpose of diluting a raw exhaust gas is to simulate chemical and physical processes that may occur when the hot exhaust is emitted into the cool ambient air (Lipsky and Robinson, 2006, Ushakov, 2012) or to preserve the particles emitted in the exhaust gas in a manner that is as unbiased as possible and in order to estimate the size distribution based on the number of particles in the funnel (Lyyränen et al., 2004). Furthermore, a dilution system is used to dilute the concentrations of particles in the raw exhaust gas to a level that is coherent with the measurement ability of the aerosol instruments and to cool down the exhaust gas (Ushakov, 2012).

The dilution ratio (DR) has an impact on the nucleation and formation of new particles, the number of nanoparticles, and the number of semi-volatile or volatile particles. Consequently, the DR affects the measured PN concentration and number size distribution (Abdul-Khalek et al., 1998, Abdul-Khalek et al., 1999, Lyyränen et al., 2004, Mathis et al., 2004, Ushakov et al., 2014). Low DRs favour nucleation and growth, due to a higher concentration of compounds involved in nucleation (Mathis et al., 2004, Abdul-Khalek et al., 1999). However, DRs and dilution conditions do not affect particles in accumulation mode[22], because these particles mainly consist of carbon agglomerates (Abdul-Khalek et al., 1999, Liu et al., 2007).

2.5 Previous Studies

There are two parallel definitions in measurement standards[23] for the emissions of particles from ship operations: (1) the particles are sampled directly from the funnel, or (2) the sample is diluted and cooled down. Definition (1) includes particles that do not evaporate at 200-<400°C, i.e., non-volatile particles at these temperatures, whereas definition (2) also includes volatile or semi-volatile components. The latter is related to the ISO 8178 standard. However, this standard method is valid for fuels with a FSC content of less than 0.8 %m/m and focuses on filter sampling and results in data on the emitted mass of particles (Lappi et al., 2012).

Previous studies have attempted to quantify particle emissions from ships via measurements of PN and PM. These measurements have been made in three different ways: test-bed engine measurements, on-board measurements and plume measurements. All three types of measurements are useful in the evaluation of emissions from ship operations on human health and climate. These three different methods have both advantages and disadvantages. The advantages of test-bed engine measurements include the ability to study future fuel types and control engine load, etc., but real-world conditions are difficult to achieve. In contrast, real-world conditions are achieved with on-board measurements. However, on-board measurements are often limited to fuel types that can be used in the installed engines and to engine loads set by the crew due to, for example, restrictions in the fairways and ports. Plume measurements result in data on how the emitted aerosol is dispersed in the ambient air. Additionally, plume measurements can be used to determine whether legal requirements are met. At the moment, this is of special interest in SECAs and will likely be of further interest in the future if more regulations concerning emissions from ship operations are implemented.

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[22] Particles with Dp from 80 nm up to 1-2 µm (Finlaysson-Pitts and Pitts, 2000).

[23] Definition (1) can be found in the standards ISO9096, VDI-2066, EN13284-1, EPA17, EPA201a, EPA5 and definition (2) is related to ISO8178:1996 (Lappi et al., 2012).

Some references on particle emissions from ship operations, were published in the 1990s, e.g., the plume measurements of Hobbs et al. (1996) and test-bed engine measurements of Lyyränen et al. (1999). During the 2000s, the number of studies concerning particle emissions from ship operations increased remarkably, and the interest has increased further during the last 10 years. The instrumentation used to primarily measure PN has varied (Table 2-2). The most common instruments presented in Table 2-2 are described further, with measurement techniques, etc., in section 2.4. Measurements of the emitted particle mass have been done using filter sampling. The increase in the number of studies during the last 10 years can be related to the implementation of the FSC regulations in the designated SECAs and an increased awareness of the air pollutants emitted by ship operations. The results from the measurements included in this thesis are compared with the results from some references included in Table 2-2 (see section 8.2) and are further used in section 5.2 to discuss the impact of FSC on particle emissions. Furthermore, several studies with plume measurements have been published with a focus on PN and PM emissions and SO_2 and NO_X emissions from operating ships. Plume measurements have been done using aircrafts and helicopters (Beecken et al., 2014, Chen et al., 2005, Petzold et al., 2008, Lack et al., 2011, Beecken et al., 2015), on land near fairways in port areas (Diesch et al., 2013, Jonsson et al., 2011, Pirjola et al., 2014, Alföldy et al., 2013, Westerlund et al., 2015, Kivekäs et al., 2014) or from ships (Lack et al., 2011, Cappa et al., 2014, Beecken et al., 2015).

Table 2-2: Summary of measurements done both in test-bed engine labs and on-board operating ships. The instrumentation used for PN and PM measurements are included, and new abbreviations are explained below the table. Note that the model of the instruments may vary between the studies.

On-board /Test-bed engine	PN and/or PM measurements	Instrumentation for PN measurements	Method for PM measurements	References
On-board	PN & PM	EEPS and Dust monitor	Filter sampling	Moldanová et al. (2013), Winnes et al. (2014)
On-board	PN & PM	EEPS	Filter sampling	Hallquist et al. (2013a),
On-board	PN & PM	EEPS and OPS	Filter sampling	Fridell and Salo (2014)
On-board	PN & PM	Dust monitor	Filter sampling	Winnes and Fridell (2010), Winnes and Fridell (2009)
On-board	PM		Filter sampling	Moldanová et al. (2009), Agrawal et al. (2008a), Agrawal et al. (2010), Agrawal et al. (2008b), Murphy et al. (2009), Fridell et al. (2008), Cooper (2003), Cooper (2001), Jayaram et al. (2011), Seigneur et al. (2009)
Test-bed	PN & PM	SMPS and CPC	Filter sampling	Petzold et al. (2008), Petzold et al. (2011), Petzold et al. (2010)
Test-bed	PN & PM	SMPS	Filter sampling	Ushakov et al. (2013), Ushakov et al. (2012b), Ushakov et al. (2012a), Kasper et al. (2007)
Test-bed	PN & PM	DMA, CNC, UCPC with SMPS software	Filter sampling	Lyyränen et al. (1999)
Test-bed	PM		Filter sampling	Sippula et al. (2014), Mueller et al. (2015)

OPS: Optical particle sizer; CNC: condensation nucleus counter; UCPC: ultrafine condensation particle counter

2.6 Motivations for the Studies Included in this Thesis

Since January 2015, ships operating in the SECAs have had to use marine fuels with a maximum FSC of 0.1 %m/m. Previously, the limit was set to 1.0 %m/m S. Starting in 2020, the allowed FSC will be 0.5 %m/m at global level (see section 2.3). This reduction will have an impact on particle emissions. However, few studies have focused on operating ships or test-bed engines running on low-sulphur marine fuel oils (see references in Paper I). Furthermore, one of the driving forces behind the regulation of the FSC both in ECAs and at the global level was the goal of reducing particle emissions. The regulation of FSC forces ship owners to run their ships on low-sulphur marine fuel oils, use alternative fuels with a FSC that complies with the regulation or use scrubbers. This thesis focuses on the first two alternatives: use of low-sulphur marine fuel oils (Paper I and Paper III) and alternative fuels, in this case liquefied natural gas (LNG) (Paper II), and the impact of other fuel characteristics, such as content of aromatics, on the particle emissions (Paper IV) (Figure 2-3). Furthermore, because emissions of SO_X and NO_X are regulated in the revised MARPOL Annex VI, interest has shifted towards particle emissions and CO_2.

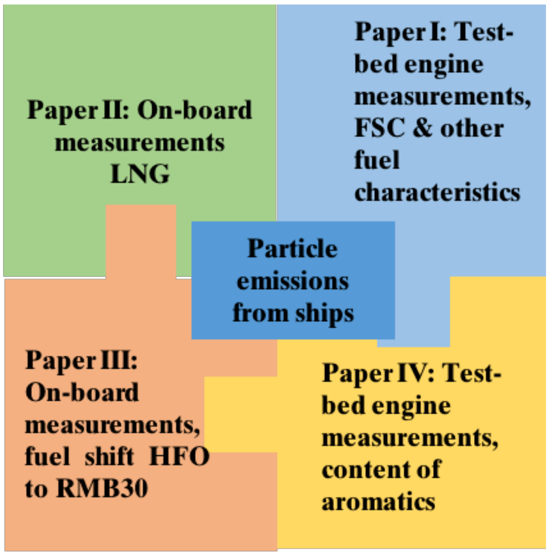

Figure 2-3: Overview of the four studies included in this thesis.

The study presented in Paper I was developed and designed with the regulation of FSC in mind. The two marine fuel oils studied have a FSC that complies with current and future legislation: HFO (0.12 %m/m S) in SECAs and MDO (0.52 %m/m S) at the global level. Emissions from the combustion of Swedish environmental class 1 diesel (MK1, <3 ppm S) and Swedish environmental class 3 diesel (MK3, 3 ppm S) were studied as well. The objective was to gain increased knowledge of the impact of FSC and other fuel characteristics on particle emission. The measurements were done when the engine was operating at lower engine loads, in order to approximate the emissions from ships operating in port areas.

In Paper II, particle and gaseous emissions from a ship using LNG for propulsion was studied. LNG is regarded as a potential future marine fuel, both from environmental and economic perspectives. This may be the first study conducted on-board a ship running on LNG that includes data on the number of particles emitted as well as particle mass and gaseous emissions. This was a unique opportunity for data collection.

The study in Paper III presents results from measurements made on-board the same ship and the same engine before and after January 2015. The two fuel types investigated are normally used for propulsion of the ship and had been used for a period of time before the measurements were made. The two studied fuel types were a HFO with 0.48 %m/m S (used before January 2015), and a low-sulphur residual marine fuel oil (RMB30, 0.092 %m/m S, used after January 2015). The RMB30 oil is a so-called hybrid fuel (described in section 3.2) and is an alternative to marine gas oil (MGO) for ships operating in SECAs. The objective with this study was to investigate how the reduction in FSC affected the particle emissions from a ship operating under normal conditions with normally used fuel types.

Because the FSC for marine fuel oils is regulated, it is interesting to consider which other fuel characteristics that could be changed to further reduce the emissions of particles from ship operations. In Paper IV, the content of aromatics in the fuel was investigated. The content of aromatics was chosen because aromatics are soot precursors in the combustion process (Bockhorn, 1994). Furthermore, few other studies have considered the number and sizes of particles emitted from fuel-blends with various contents of aromatics. Previous studies have mainly focused on the mass of particles emitted. However, no consensus was reached in earlier studies, because some studies showed an increase in PM with aromatic content and others showed no effect on PM with varying aromatic content (see references in Paper IV). The measurements were done on test-bed engines at the Department of Shipping and Marine Technology and at the Department of Applied Mechanics, Chalmers University of Technology. In the studies, MK1 was used as the reference fuel, though it has a low content of sulphur and other compounds that may enhance the formation of particles. To achieve a high content of aromatics, MK1 was doped with a solution of aromatics to levels comparable to those found in marine fuel oils.

There is also interest in studying the impact on BC emissions from marine fuel oils. There is an on-going discussion within the IMO, with the aim of establishing a future regulation of BC emissions from operating ships. The emissions of BC are believed to be related to fuel characteristics other than the FSC (discussed further in section 5.2) (Lack et al., 2009, Lack et al., 2011). Therefore, further research on this should be of interest. The results from measurements of BC emissions have been included in Paper I, in which the FSC of the HFO is lower than the MDO, thereby making it possible to investigate if other fuel characteristics are more important than FSC. The results of the BC measurements are also included in Paper III to describe how the fuel shift towards fuels with lower FSC affects the emissions of BC. Furthermore, this study provides an indication of whether a reduction in FSC is enough to reduce the BC emissions or whether other compounds in the fuel must be considered as well.

The papers included in this thesis include measurements and data on the PN emissions and size distribution by number. During the work on the different papers, the focus has more or less turned towards a focus on the number and sizes, rather than on the PM emissions. This is because particle size is one of the most important properties in the assessments of the impact of particles on human health (section 2.1). Therefore, measurements of the size distribution based on the number of emitted particles are important. Furthermore, the importance of considering PN concentrations is highlighted in Kittelson (1998). Measuring the number and sizes of particles emitted from ship operations is quite a new field, and in contrast to land-based transportation, there remains a lack of knowledge. The EFs (EF_{PN} and EF_{PM}, together with size-resolved EFs) presented in the included papers are useful data in emission inventories, environmental impact assessments and dispersion modelling. Furthermore, the EFs provide an opportunity to compare particle emissions from low-sulphur marine fuel oils and LNG with emissions from marine fuel oils with other properties and emissions from other transport sectors.

3 Marine Engines and Marine Fuels

The most common marine engines installed on-board ships are marine diesel engines that use various marine fuel oils for propulsion. The most common marine fuel oil is HFO due to its low price. However, the current regulation of FSC in SECAs force ship owners to use marine fuel oils with low FSCs (max. 0.1 %m/m S), alternative fuels or scrubbers. One alternative fuel of interest is LNG because it is economically feasible compared to marine fuel oils. The aim of this section is to provide an overview of the marine engines and marine fuels considered in the papers included in this thesis. Furthermore, information on certain fuel characteristics discussed in this thesis are included as well.

3.1 Marine Diesel Engines

Diesel engines are the most common engines or prime movers[24] used to drive ships and other marine structures. The power ranges from 1 Megawatt (MW), for small high-speed engines to 80 MW for large low-speed engines (Woud and Stapersma, 2002). Marine diesel engines are divided into low-speed, medium-speed and high-speed engines, depending on their engine speed at the crankshaft. Low- and medium-speed engines are commonly used as the main engines, whereas medium- and high-speed engines are used as auxiliary engines (Cooper and Gustavsson, 2004). Details about the performance parameters of respective engine types are presented in Table 3-1. One advantage of diesel engines is that they are rather insensitive to fuel quality, allowing low-quality fuels, such as HFO, to be used for propulsion. However, this ability to use low-quality fuel has a negative impact on the emissions of air pollutants from the combustion (Woud and Stapersma, 2002).

Marine diesel engines can be divided into 2- and 4-stroke engines. In general, low-speed engines, such as those installed on tankers, bulk carriers and container ships, are 2-stroke engines. Medium-speed engines, such as those installed on RoRo freight carriers, cruise ships and RoPax-ferries, and high-speed engines are 4-stroke engines (Woud and Stapersma, 2002, Woodyard, 2010c, Woodyard, 2010d). The four-stroke cycle starts with an induction stroke, followed by a compression stroke, an expansion stroke and finally an exhaust stroke. The two-stroke cycle consists of a compression stroke and the power stroke (Stone, 2012). Further explanations of the different strokes can be found in the section on Terminology (starting on page xvii). Furthermore, marine diesel engines are generally turbocharged (Heywood, 1988).

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[24] Prime movers include all machines that convert primary energy, such as diesel fuel, to mechanical energy for use in propulsion systems and electrical systems, on-board a ship, for example. In the combustion process, the chemical energy in the fuel is converted to thermal energy, which is further converted to mechanical energy (Woud and Stapersma, 2002).

Table 3-1: Characteristics of diesel engines, state of the art 2001 (Woud and Stapersma, 2002).

	Diesel engines		
	Low-speed	**Medium-speed**	**High-speed**
Process	2-stroke	4-stroke	4-stroke
Output power range (kW)	80000-8000	35000-500	9000-500
Output speed range (rpm [a])	80-300	300-1000	1000-3500
Fuel type	mostly HFO	HFO or MDO	MDO
Specific fuel consumption (g/kWh)	160-180	170-210	200-220
Specific NO_X emissions (g/kWh)	22-14	18-10	13-7

[a] Revolutions per minute

3.2 Marine Fuel Oils - Fuel Characteristics

Marine fuel oils are fossil fuels produced by refining of crude oil. They are blends of products from a number of processes, and the composition of the blends has an impact on, for example, the combustion characteristics, handling properties and storage stability. During refining, crude oil is processed into a number of hydrocarbon products. Crude oil is a mixture of different hydrocarbons, such as Paraffins and aromatics. Additionally, it contains organic compounds that include sulphur, nitrogen and oxygen, and metals, such as vanadium and nickel. The composition of the crude oil varies depending its origin. The marine fuel oils generated in the refining process are residual fuel oil, commonly referred to as HFO and distillates, which are further divided into MDO and MGO. One of the main differences between the marine fuel oils is the viscosity; HFO exhibits the highest viscosity and distillates exhibit lower (Table 3-2). The residual fuel oil is the least valuable product from the refining process, whereas diesel fuel (including marine distillates) is more valuable and usually the second most produced by volume after gasoline (Aitani, 2004, Hocking, 2005). The price for HFO (FSC >3.5 %m/m) is 195 US dollars/metric tonne and for the MGO (FSC 0,1 %m/m) 390 US dollars/metric tonne (daily price 25th of April 2016 for delivery at Skagen) (Topoil, 2016). Table 3-2 presents the characteristics of the marine fuel oils according to the ISO 8217:2010 standard. The FSC is not included in Table 3-2 because it is regulated by Regulation 14 in MARPOL Annex VI (section 2.3). The fuel oil quality and availability is regulated in Regulation 18 MARPOL Annex. However, this regulation does not specify any fuel characteristics other than sulphur (IMO, 2013).

When the strictest limitation of the allowed FSC in marine fuel oils (see section 2.3) entered into force in January 2015 the expectation was that the shipping sector would start to use MGO to comply with the regulation. However, a number of new hybrid fuels (here also called low-sulphur residual marine fuel oils), with 0.1 %m/m S, were released by several suppliers and are now used for propulsion of ships operating in SECAs. Most of these hybrid fuels are blended products that have some characteristics of distillate products but have higher viscosities than distillates and are more waxy in nature due to their pour point[25]. Thus, heating is required. These fuels are allowed to

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[25] Pour point represents the lowest temperature at which the fuel will continue to flow. Below this temperature the fuel will be waxy and difficult to handle, which means that these fuels should be stored and handled in systems with heating arrangements (Lloyd's Register Marine, 2014).

be used in SECAs as they comply with the FSC limit. However, in California are the regulations somewhat different because the California Air Resources Board has established certain fuel regulations for ocean-going vessels operating in California waters. The California regulations require that the fuel meets the 0.1 %m/m S limit, and also meet the specifications set for MGO or MDO. Therefore, the use of hybrid fuels in this area does not comply with these regulations and exemptions from the California Air Resources Board are needed (Lloyd's Register Marine, 2014). These hybrid fuels are cheaper than MGO, but more expensive than HFO. The price for these hybrid fuels is around 355 US dollars/metric tonne (daily price 25th of April 2016 for delivery at Skagen) (Topoil, 2016).

Table 3-2: Characteristics of marine fuel oils according to ISO 8217:2010 found in Vermeire (2012). Values presented as intervals represent the lowest and highest values found for different types of fuel oil and included in ISO 8217. Some properties are not defined (n.d.) for some of the fuel types.

Characteristics	**Limit (max/min)**	**Marine residual fuel oil (HFO)[a]**	**MDO[b]**	**MGO[c]**
Kinematic viscosity at 50°C (mm^2/s)	max	10-700 (see [a] below)	11.0	6.0
Density at 15°C (kg/m^3)	max	920-1010	900	890
Cetane number	min	n.d.	35	40
CCAI[d]	max	850-870	n.d.	n.d.
Flash point (°C)	min	60.0	60.0	60
Acid number (mg KOH/g fuel)	max	2.5	0.5	0.5
Carbon residue micro method (%m/m)	max	2.5-20	0.30	0.30[e]
Water (volume%)	max	0.3-0.5	0.30	n.d.
Ash (%m/m)	max	0.040-0.150	0.010	0.010
Vanadium (mg/kg)	max	50-450	n.d.	n.d.
Sodium (mg/kg)	max	50-100	n.d.	n.d.
Aluminium plus silicon (mg/kg)	max	25-60	n.d.	n.d.

[a] Includes the residual fuels: RMA10, RMB30, RMD80, RME180, RMG180, RMG380, RMG500, RMG700, RMK380, RMK500 and RMK700. The number after each set of letters represent the maximal viscosity of the fuel oil. In general, RMA10 represents the lowest values and RMK700 the highest. Values for the other residual fuel oil types are located in between. According to Woud and Stapersma (2002), RMA to RMH can be seen as intermediate fuel oils, i.e., residual oil blended with up to 40% distillate oil, and RMH to RML are HFOs.

[b] Named DMB in ISO 8217.

[c] Includes DMA and DMZ in ISO 8217.

[d] Calculated Carbon Aromaticity Index (see section 3.2.1), only used for HFO

[e] Value of carbon residue, analysed with the micro method on the 10% volume distillation residue

Particle formation, primarily soot formation, is related to the fuel composition, i.e., the content of carbon, hydrogen, oxygen and sulphur, and the molecular structure of the hydrocarbons in the fuel, such as the number of carbon-carbon bonds (Tree and Svensson, 2007). Therefore, it is important to have knowledge about various fuel characteristics and the effects they have on the combustion process, ignition qualities and consequently the emissions. The fuel characteristics presented here are those discussed in the included papers and that can be associated with the particle emissions. Some of these fuel characteristics, such as viscosity and sulphur content, are also of special interest to the maritime sector. Furthermore, the carbon residue, content of asphaltenes, cetane number and carbon-to-hydrogen ratio are fuel characteristics used to determine the ignition qualities of the fuel. Additionally, the viscosity, carbon residue, flash point and contents of sulphur, asphaltenes and metals, such as vanadium can determine the quality of a fuel (Woodyard, 2010b).

3.2.1 Aromatics

Aromatics are unsaturated, organic hydrocarbons composed of one or more benzene ring structures with alternating double bonds (Stone, 2012, Heywood, 1988). Aromatics can be divided into monoaromatics, diaromatics and polyaromatics also known as PAHs[26]. Benzene and its derivatives are examples of monoaromatics and are commonly found in crude oil and PAHs are commonly found in diesel fuel oils (Stone, 2012). PAHs can have carcinogenic characteristics, and other aromatics, such as benzene, are toxic to humans (Hart et al., 1999). There are several standard methods used to analyse the content of aromatics in fuels. However, the results of the different methods vary because a molecule may contain several chemical functional groups, making it possible to classify the molecule into different groups of hydrocarbons (Totten et al., 2003).

Aromatics are an important group of compounds because they have an impact on the ignition quality of the fuel and are often the only group of hydrocarbons listed in the specification of diesel fuel. Furthermore, a high content of aromatics in a fuel may have a negative impact on the emissions associated with the combustion of that fuel. The impact on the ignition quality is related to the fact that aromatics have poor ignition qualities and consequently reduce the cetane number (CN) of the fuel. The CN is a measure of the ability of a fuel to autoignite and defines the ignition quality of a fuel (Totten et al., 2003) and seen as the most important characteristic of a diesel fuel (Stone, 2012). A low CN will reduce the ability of the fuel to autoignite, resulting in an increase in the ignition delay period[27] and trouble during engine start-up and operation at low engine loads (Woodyard, 2010b). The increased ignition delay results in an increased rate of heat release during the initial combustion, a higher maximum heat release and a higher peak cylinder pressure (Kidoguchi et al., 2000). This may result in a combustion that is to too rapid and cause diesel knock (Stone, 2012). The CN depends on the content of various hydrocarbons and the structure of them. Straight-chained Paraffins ignite faster under compression, while aromatics have a slower reaction, and will reduce the CN of the fuel. Listed between these compounds are branched Paraffins, Olefins, branched Olefins and Naphthenes (Totten et al., 2003). CN varies between 40 to 55 for commercial diesel fuels (Heywood, 1988).

For marine distillates, such as MDO and MGO, the ignition quality is indicated by the CN of the fuel. The ignition quality of a HFO is more difficult to determine compared to marine distillates because HFOs consist of a mixture of many different compounds. The appropriate index is the Calculated Carbon Aromaticity Index (CCAI), which is calculated and based on the density and viscosity of the HFO (Woodyard, 2010b). Higher CCAI numbers are associated with poor fuel ignition qualities. A poor fuel ignition quality results in reduced engine efficiency, loss of power and higher NO_X emissions compared to fuels with higher ignition qualities. The ignition quality of the marine fuel oils is related to the characteristics of the crude oil and the degree of refinery cracking. In general, large medium- and slow-speed engines (operating below 400 rpm) are less sensitive to the ignition quality of the fuel. High-speed and other medium-speed engines are more sensitive to the ignition quality, which may lead to operational limitations in these types of engines (Totten et al., 2003).

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[26] Monoaromatics are composed by individual benzene rings, diaromatics involve two benzene rings, and PAHs involve three or more benzene rings.

[27] Described further in “Terminology” starting on page xvii.

3.2.2 Ash

Ash represents the content of inorganic impurities and non-combustible material, such as sand, nickel, vanadium, silicon and sodium, found in marine fuel oils. Deposition of ash in the engine and fuel systems can lead to wear and erosion of various parts, and eventually resulting in a reduced performance of the engine (Totten et al., 2003, Woodyard, 2010b)

3.2.3 Carbon Residue

Carbon residue is formed through evaporation and thermal degradation of carbon-containing material, but the residue is not entirely composed of carbon. Instead, it can be seen as a coke and can undergo further changes through carbon pyrolysis. The carbon residue in marine fuels is coked material remaining after the marine fuel has, under controlled conditions, been exposed to high temperatures. The carbon residue is an indicator of the carbon-forming tendencies of a marine fuel. The carbon concentration of marine fuels can reach 18-20 %m/m (Totten et al., 2003).

A high content of carbon residue indicates a high content of asphaltenes, which are high molecular weight hydrocarbons that contain of nitrogen, sulphur and metals, such as vanadium, nickel and iron. Asphaltenes affect the combustion and carbon-forming tendencies of the fuel, and a high content of asphaltenes indicates that the fuel might be difficult to ignite and will burn slowly. A high carbon content in marine fuels results in poor combustion characteristics, such as increased ignition delay and carbon deposits on components in the engine and fuel systems (Woodyard, 2010b, Totten et al., 2003). Furthermore, this might have an impact on the particle emissions, which are related to the combustion conditions and the ability of the engine to completely burn the fuel so that only a small amount or no solid carbon material remains. A higher higher content of asphaltenes in the fuel and consequently greater carbon residue may lead to higher emissions of solid particles (Totten et al., 2003).

3.2.4 Sulphur

Sulphur is a non-metallic element that is chemically bound to marine fuel oils. Sulphur originates in the crude oil and is found in the high-density residual fractions. In the combustion process, sulphur reacts with oxygen in the air and forms SO_2 and sulphur trioxide (SO_3) (Totten et al., 2003). During subsequent reactions, sulphate and sulphuric acid (H_2SO_4) can be formed and take part in the formation of secondary particles (Finlaysson-Pitts and Pitts, 2000). The particle emissions generated by the combustion of marine fuels are assumed to be closely related to the FSC (Totten et al., 2003, Svensson, 2011). The sulphuric acid generated from the sulphur in the fuel can cause wear on the engine system through corrosion. To neutralize the sulphur in the marine fuels and maintain an appropriate total base number[28], an alkaline additive is used in the lubrication oil (Totten et al., 2003).

3.2.5 Viscosity

Viscosity is a measure of the resistance of the fuel to flow and is often presented in the unit centistokes (1 cSt= 1 mm^2/s). Fuels with low viscosity are more fluent compared to fuels with high viscosity. The viscosity decreases when the fuel is heated and increases when the fuel is cooled (Totten et al., 2003, Woodyard, 2010b). Generally, HFOs with higher density have a higher viscosity than marine distillates. The viscosity is also related to the chemical structure, though a fuel with a higher content of aromatics will have a lower viscosity than a fuel with a high content of long-chain-like carbon

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[28] The total base number (TBN) indicates the ability to neutralize the acid compounds in the fuel. TBN is expressed as mg KOH/g of additive or oil sample (Totten et al., 2003)

structures, such as alkanes or Paraffins, which will have a higher viscosity despite similar carbon-hydrogen ratios (Woud and Stapersma, 2002).

The viscosity is one property used as an indicator of fuel quality. However, viscosity alone cannot be seen as an indicator of fuel quality. Regardless, viscosity is used when selecting and purchasing marine residual fuels, such as HFO, due to the restrictions imposed by certain components, such as the injection system of the engine. Marine residual fuels have to be preheated to decrease the viscosity, to enhance proper injection, and to atomize and pump the fuel (Totten et al., 2003, Woodyard, 2010b).

In the combustion process, the viscosity influences on the shape of the fuel spray, which can affect the efficiency of the combustion. A high viscosity can lead to poor atomization and large droplets. The jet of the injected fuel tends to take the form of a solid stream rather than a spray of small droplets. This leads to poor mixing of the injected fuel and air required for combustion, and consequently results in, poor combustion and a loss of power. Even fuels with low viscosity can have negative impacts on the combustion process, due to leakage in the injection pumps and wear on the fuel system (Totten et al., 2003).

3.3 Natural Gas as a Marine Fuel and Dual-Fuel Engines

Natural gas has been used as an energy source in stationary engines for a long time. Interest in using natural gas as a fuel for internal combustion engines has increased during the past decade due to development of viable storage cylinders (Semin, 2008). To be able to use natural gas as the primary energy source for internal combustion engines, conversion and re-design is necessary. There are three types of marine gas engines in use today: dual-fuel engines (DF engines), lean-burn spark ignited engines and high-pressure gas injection engines. The lean-burn spark ignited engines are purely gas-fuelled engines, whereas an injection of diesel fuel is needed for the DF and high-pressure gas injection engines. The main manufacturers of DF engines are Wärtsilä and MAN (Aesoy et al., 2011). Approximately 32 (45%) of the ships running on LNG in late 2015 used DF engines (DNV GL, 2015). For marine applications, DF engines, run on natural gas and liquefied diesel fuels, such as MDO, MGO and HFO (Woodyard, 2010a, Semin, 2008). The natural gas used in DF engines can be either compressed natural gas (CNG) or LNG. LNG is formed when natural gas is cooled to -162°C at atmospheric pressure and liquefied. This process causes a significant reduction in the volume (1/600 that of natural gas) and allows for transportation on ships and trucks. The main component, and also the primary energy carrier, in LNG is methane (CH_4, 87-99 mol%). Other components include other hydrocarbons, such as ethane, propane and butane as well as nitrogen, CO_2 and trace amounts of sulphur (<4 ppmv). The composition, which affects the properties of the LNG, varies depending on the reservoir source of the original gas and the processing history (Mokhatab et al., 2014).

The first LNG-fuelled ships were LNG-carriers that started to operate in 1964 and used the boil-off gas from the LNG cargo tanks as an additional energy source. These ships were equipped with steam-turbines, and the efficiency of these propulsion systems was low. The development of more efficient gas-burning combustion systems started in the 1980s, and the first ships running on natural gas used CNG as the primary energy source. The first ship that used LNG as the primary energy source has been operating in Norway since 2000 (Aesoy et al., 2011). In late 2015, there were approximately 73 ships running on LNG worldwide, with most operating in Norway, and 80 confirmed new builds that will use LNG for propulsion exist (DNV GL, 2015).

LNG is seen as a potential future marine fuel because it represents a way to comply with stricter FSC regulations and limits on NO_X emissions in emission control areas that consider NO_X (NECAs). Furthermore, LNG is cheaper than some marine fuel oils[29] (Burel et al., 2013, Thomson et al., 2015). However, the development has been slow, due to the challenges associated with designing LNG-powered ships. The main challenge is the fuel system (Aesoy et al., 2011). Additionally, the cryogenic tanks, used to store LNG require more space than tanks used to store traditional marine fuel oils and may result in reduced cargo capacity (Gullberg and Gahnström, 2011). Cryogenic tanks are required because LNG is defined as a cryogenic liquid and has to be stored and transported in tanks at temperatures below -162°C (Gullberg and Gahnström, 2011, Brynolf, 2014). Other challenges include safety and regulations for handling LNG (Burel et al., 2013, Aesoy et al., 2011). Furthermore, the availability of LNG in ports and the large investments needed to retrofit existing ships or construct new ships are factors that may slow down the development of LNG as a marine fuel (Burel et al., 2013, Acciaro, 2014, Nikopoulou et al., 2012). However, ships spending most of their time in ECAs (especially ECAs that consider both NO_X and SO_X) may see an economic benefit in the change from HFO-powered ships equipped with abatement technologies, to LNG-powered ships. This because annual machinery costs, including maintenance and the costs of operating abatement technologies, are estimated to be lower for LNG-powered ships than for ships using HFO for propulsion (Elgohary et al., 2014).

3.3.1 Combustion in DF engines and Emissions

DF engines can operate in either gas mode, using LNG or CNG as the energy source, or diesel mode, using fuel oil. DF engines can operate according to the lean-burn[30] Otto principle[31, 32] in gas mode and according to the normal diesel concept[33] when diesel is used for propulsion in diesel mode (Woodyard, 2010a). Natural gas itself is not suited for compression ignition, due to a low CN (Semin, 2008). Therefore, in gas mode, diesel has to be injected in small amounts, as a pilot fuel (1-5% of the total energy) through a common rail system, to ignite the gas (Woodyard, 2010a).

Operation in gas mode reduces the peak temperatures in the combustion process and results in a lower production of NO_X than in conventional diesel engines (Woodyard, 2010a). In general, the NO_X emissions are reduced by 80-90%. The emissions of SO_X are almost eliminated due to the low sulphur content of LNG and can, in principle, only originate from the sulphur in the pilot fuel. CO_2 emissions are also reduced (Mokhatab et al., 2014, Woodyard, 2010a).

The combustion process in gas mode starts with an intake stroke, in which a mixture of gas and air enters the cylinder through the inlet channel. The lean air-gas mixture is compressed as the piston moves up in the cylinder, and when the piston is close to top dead centre the pilot fuel is injected and ignites the mixture. To achieve low NO_X emissions from the combustion process, the amount of pilot fuel injected must be small, normally approximately 1% of the total energy provided to the engine. Higher

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[29] The price for LNG is higher than for HFO, but lower than for MGO. However, it is difficult to get a price due to that many factors have an influence on the price.

[30] Lean-burn means that the mixture of gas and air in the cylinders contains more air than is needed for complete combustion and results in lower peak temperatures and reduced NO_X emissions. Due to optimization of the injection timing and high compression ratio the leaner combustion increases efficiency (Woodyard, 2010a).

[31] Described further in "Terminology" starting on page xvii.

[32] These engines do not have a spark plug, which is normally used in lean-burn gas engines. Instead, the lean air-gas mixture is ignited by the injected pilot fuel (Woodyard, 2010a).

[33] Described further in "Terminology" starting on page xvii.

proportions are used for lower engine loads because the consumption of LNG varies with engine load (see Paper II). To prevent knocking and misfiring, the combustion process has to be controlled, which can be achieved through control of the injection of the pilot fuel and the gas entering each cylinder (Woodyard, 2010a). Control of the amount of pilot fuel injected is important with respect to particle and SO_X emissions. Increasing the amount of pilot fuel injected causes an increase in these emissions (Liu et al., 2013).

In contrast to other emissions are the emissions of CO and HC generally higher from DF engines running on natural gas than from conventional diesel engines. Both emissions are load dependent, with higher emissions at lower engine loads. The low temperatures in the cylinder, combined with the low oxygen concentration in the mixture and a short reaction time enhance the formation of CO under low engine loads (Papagiannakis et al., 2010, Liu et al., 2013). The emissions of unburned HC from LNG are higher, mainly due to three reasons. First, the temperature in the cylinder is too low to complete the combustion of the mixture close to the cylinder walls, leaving a layer of unburned gas. Secondly, the lean conditions affect the ability of the combustion to progress throughout the mixture in the cylinders. Third, small amounts of the mixture can escape into crevices when the mixture is compressed during the compression stroke, and consequently miss the primary combustion process (Liu et al., 2013, Papagiannakis and Hountalas, 2004, Papagiannakis et al., 2010, Sahoo et al., 2009).

The main component (90%) of the unburned HC emissions is methane, and this component is known as the methane slip (Liu et al., 2013). These emissions are important to consider because methane has a higher global warming potential than CO_2 under both short-term (over 20 years) and long-term (over 100 years) perspectives (Myhre et al., 2013). Both the combustion process in the DF engines during gas mode and upstream activities, contribute to the emissions of methane. However, the combustion process represents the greatest contribution. The methane slip of the upstream activities is approximately 1.9 g CH_4/kg LNG, and from the combustion 23.04 g CH_4/kg LNG (Bengtsson et al., 2012). To preserve the climate benefits of using LNG instead of HFO, it is critical to control and limit the methane slip (Brynolf et al., 2013, Burel et al., 2013). Possible strategies to reduce and control the methane slip include improved timing of the injection of the pilot fuel (Sahoo et al., 2009) and use of after-treatment systems, such as oxidation catalysts. However, further research is needed (Hussain et al., 2015).

4 The Route of a Particle from the Engine to the Atmosphere

Particle formation occurs during the combustion process, which takes place inside the cylinders of marine diesel engines. Particles undergo several processes during their time in the engine, exhaust gas channel and plume in the atmosphere. The aim of this section is to provide a brief description of the formation of particles and the different processes that occur. Both marine diesel engines and DF engines are considered.

4.1 In the Diesel Engine and Exhaust Gas Channel

The majority of particles are formed inside the engine, i.e., in the cylinders during the combustion, and are the result of incomplete combustion of the hydrocarbons in the fuel. Some particles originate from the lubrication oil (Heywood, 1988). A schematic illustration of particle formation and growth processes in the cylinders and funnel is presented in Figure 4-1.

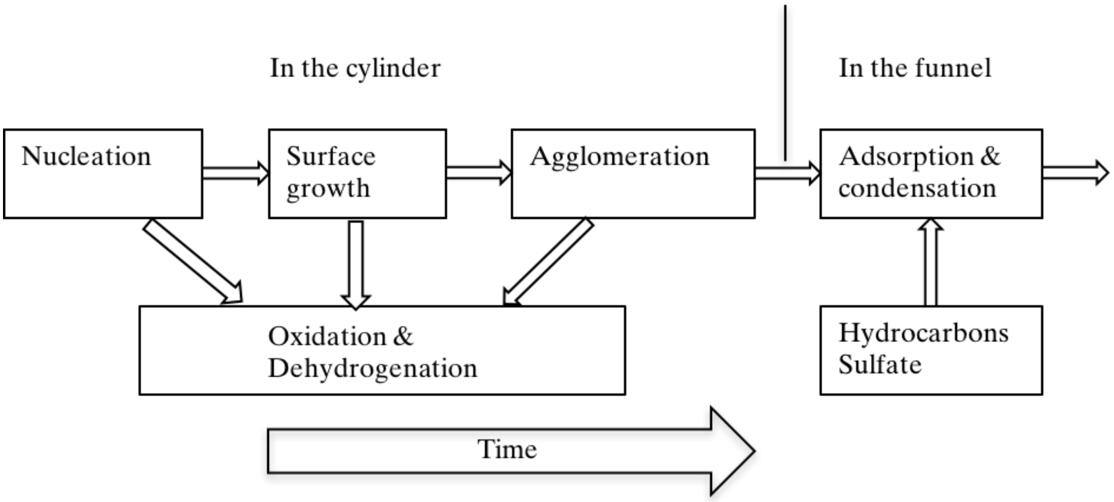

Figure 4-1: A schematic illustration of the particle formation and growth processes in a cylinder and funnel. Adapted from Amann and Siegla (1981).

4.1.1 In the Cylinder

In a 4-stroke engine the formation and growth take place during the expansion and exhaust stroke. In a 2-stroke engine the formation occurs during the power stroke. The formation process starts with thermal decomposition[34] of the large hydrocarbon molecules, the so-called soot precursors, in the fuel after injection of the fuel at the end of the compression stroke (Stone, 2012, Hobbs et al., 1996, Heywood, 1988). Soot particles[35] nucleate from the vapour phase to the solid phase in fuel-rich regions of the cylinder at elevated temperatures and form small spherules (in radii 0.5-5 nm) composed of condensed carbonaceous material (Ono et al., 2015, Omidvarborna et al., 2015). Following formation, these newly formed particle nuclei start to grow, which includes surface growth, and agglomeration (coagulation and aggregation). Surface growth involves the attachment of species in the gaseous phase to the existing particles and results in no changes in PN, whereas coagulation reduces the PN though particle collision that form new particles. Aggregation results in chains and clusters of primary

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[34] Also called pyrolysis, splitting or cracking.

[35] A soot particle is considered to be a solid substance that contains carbon and hydrogen, and is composed of nanoparticles comprising PAHs (Ono et al., 2015, Omidvarborna et al., 2015).

soot particles and an increase in particle size (to 5-50 nm in radius) (Stone, 2012, Hobbs et al., 1996, Heywood, 1988). These process take place under high-temperature conditions in fuel-rich areas of the reaction zone[36] during the diffusion combustion[37]. The available time for particle formation is a few milliseconds (Heywood, 1988, Stone, 2012). The agglomeration process is completed before the exhaust valve opens (Heywood, 1988).

Oxidation, i.e., burning, of soot particles and their precursors occurs during the formation and growth processes of the particles, and results in formation of gaseous species, such as CO and CO_2 (Heywood, 1988). Oxidation starts when the particles enter the fuel-lean zones and continues during the expansion stroke. The amount of soot particles emitted from the cylinder depends on the difference between the formation rate and the oxidation rate during the expansion stroke (Stone, 2012).

At the end of the expansion stroke, the exhaust valve in the cylinder opens and the gases start to rapidly cool, causing the soot particles formed undergo further condensation, adsorption and agglomeration (Hobbs et al., 1996). The exhaust valves remain open during the exhaust stroke and the exhaust gases leave the engine and enter the exhaust gas channel (or funnel). In the two-stroke cycle, the exhaust gas will leave the cylinder at the end of the power stroke (Stone, 2012).

4.1.2 In the Exhaust Gas Channel

In the exhaust gas channel, the exhaust gases continue to cool and become diluted with air. The decreased temperatures do not affect the soot particles. However, it has an impact on the condensation and adsorption of hydrocarbons and other volatile compounds, such as SO_2[38], H_2SO_4 and nitrogen dioxide (NO_2), on the existing soot particles (Heywood, 1988). Depending on the conditions in the exhaust gas channel, the volatile compounds in the emission may undergo transformation and form new particles, both solid and liquid, through nucleation, adsorption or condensation. These newly formed particles are so-called secondary particles (Kittelson, 1998). The transformation of diesel particles in the funnel also depends on the residence time, initial concentration of diesel particles in the exhaust, concentration of volatile compounds and degree of cooling. The transformation results in a decrease in the total PN concentration and an increased PM concentration and average diameter of the particles (Ning et al., 2004).

4.1.3 Marine Applications: Particle Characteristics

Particle emissions from ship operations are found to consist of BC, sulphate, OC, organic matter (OM), elemental carbon (EC), ash, particulate nitrate and other inorganic compounds, and metals from the fuel and lubrication oil (Moldanová et al., 2009, Lack et al., 2009). Metals such as iron, sulphur, calcium, chromium (Cr) and silicon (Si) are related to the diesel fuel and zinc, iron, phosphorus (P) and calcium are related to the lubrication oil (Amann and Siegla, 1981). The trace elements vanadium, nickel and sulphur are found in particles generated by the combustion of HFO (Viana et al., 2009, Lyyränen, 2006).

The proportion of the fuel sulphur emitted as sulphate can range from 1.2 to 3.5% (depending on load) (Lack et al., 2011). Conversion percentages have been reported to be 1-1.3% from on-board measurements (Moldanová et al., 2009, Moldanová et al.,

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[36] Specifically, the flame front

[37] Described further in “Terminology” starting on page xvii.

[38] SO_2 is formed through oxidation of the sulphur in the fuel. Part of the SO_2 is further oxidized to SO_3, upon reacting with water, forms the H_2SO_4 found in emitted particles (Heywood, 1988).

2013) and 1.4% from test-bed engine measurements (Kasper et al., 2007). Plume measurements indicate that 1-4% by mass of the sulphur in the investigated plumes was in form of sulphate (Salo et al., Manuscript in preparation). The low degree of conversion of SO_2 to H_2SO_4 is related to the fact that most diesel engines are designed to retain high temperatures and exhaust gas flow rates in order to reduce the formation of SO_3 to a few percent and avoid temperatures that favour condensation of water. Most particles containing H_2SO_4 are formed when the exhaust is released from the funnel and becomes diluted and cooled in the atmosphere (Lack et al., 2009).

The size distribution by number associated with marine diesel engines is similar to that of other diesel engines used on land, i.e., bimodal in character. Hallquist et al. (2013a) reported a bimodal distribution with a major peak at 12 nm and a minor peak at 30-40 nm from on-board measurements (Hallquist et al., 2013a). Measurements on a test-bed engine showed a major peak at 15 nm and a minor peak at 50 nm (Petzold et al., 2008). Generally, the emitted particles from marine diesel engines are smaller in size (mean diameter of 20-40 nm) compared to land-based vehicles, which mainly emit particles in accumulation mode (Kasper et al., 2007). The size differences are associated with the differences in FSC between marine fuel oils and fuels for land-based vehicles. Furthermore, the mass size distribution also has a bimodal character, with one peak in accumulation mode and one in coarse mode (described in section 4.2). Previous measurements have observed peaks at Dp 0.5 µm and 7 µm (Moldanová et al., 2009), and peaks at 0.1 µm and 10 µm Lyyränen et al. (1999).

4.1.4 Particle Formation and Characteristics - Natural Gas

The main component in natural gas, and consequently of CNG and LNG, is methane. The high content of methane leads to that the soot forming tendencies are lower for combustion of natural gas than for diesel, due to that methane has no carbon-carbon double bonds and a low carbon content (Liu et al., 2013, Tree and Svensson, 2007). However, particles are still emitted from engines using natural gas as energy source. The particles emitted from combustion of natural gas have a non-volatile core, which origin from metals and non-volatile compounds, such as ash, in the lubrication oil (Alanen et al., 2015, Jayaratne et al., 2012, Jayaratne et al., 2008). Furthermore, tracers of elements from the lubrication oil (such as calcium, phosphorus and zinc) can be found in these particles (Yoon et al., 2014). The non-volatile carbon compounds may also exist in the natural gas, and form carbonaceous particles during combustion. The particle grows through condensation of volatile compounds, such as hydrocarbons and sulphur, found in the lubrication oil, natural gas and pilot fuel (if used) (Alanen et al., 2015). The volatile fraction of the particle emissions from combustion of natural gas is significant (Alanen et al., 2015, Jayaratne et al., 2008, Jayaratne et al., 2009, Hallquist et al., 2013b, Jayaratne et al., 2010).

The particles emitted from engines running on natural gas are, on average, smaller than particles emitted from engines running on diesel. Particles with diameters of less than 10 nm dominate the emissions (Hallquist et al., 2013b), and the size distributions peak at 2-5 nm and 6-10 nm (Alanen et al., 2015). Furthermore, the emissions of these small particles from combustion of natural gas can be similar to or higher than those associated with combustion of diesel (Hong and Kwon, 2010). The emissions contain of small amounts of large particles, resulting in a significantly lower mass of particles emitted by the combustion of natural gas relative to the combustion of diesel (Hallquist et al., 2013b, Jayaratne et al., 2010). The number of particles emitted from engines running on natural gas is similar or lower than that of diesel. This variation depends on engine type (compression ignition vs. spark ignition engines), engine load and operational mode (acceleration or cruise) (Jayaratne et al., 2010).

4.2 In the Plume and the Atmosphere

The particles emitted to the atmosphere originate from both natural and anthropogenic sources (Hinds, 1999). They are divided into different modes due to the diameter of the particle. The two main modes are fine and coarse particles. The coarse particles have a Dp >2.5 µm, originate from natural sources and are formed during different mechanical processes. The fine particles have a Dp <2.5 µm and can be further divided into UFP with Dp <10 nm, Aitken nuclei mode particles with Dp 10-80 nm and accumulation mode particles with a size range from Dp 80 nm to 1-2 µm. Fine particles dominate the total number of particles in the atmosphere, as well as the total particle mass (Finlaysson-Pitts and Pitts, 2000). Nanoparticles are defined as particles with Dp <50 nm (Hinds, 1999).

The size distribution by number of diesel exhaust particles is generally bimodal, with a major peak found in the nucleation mode and a minor peak in the accumulation mode. The particles in the nucleation mode consist of both solid particles and volatile particles of organic and sulphur compounds that are formed during dilution and cooling of the exhaust gases. The majority of the particles in accumulation mode are solid agglomerates with adsorbed compounds (Maricq, 2007, Kittelson, 1998). Approximately 90% of particles emitted are in nucleation mode, i.e., nearly all particles emitted from a diesel engine are within the size range of nanoparticles. Particles in accumulation mode represent the major fraction of the emitted particle mass (Kittelson, 1998). Particles formed from the lubrication oil may contribute significantly to the emitted particle mass (Amann and Siegla, 1981).

The primary particles formed in the cylinders are emitted in a coherent plume together with secondary particles formed in the exhaust gas channel. The plume also consists of other air pollutants, such as SO_2 and NO_X, and greenhouse gases, such as CO_2, that formed during the combustion in the engine (Eyring et al., 2010). In the atmosphere, SO_2 and NO_X can contribute to the formation of secondary particles (Finlaysson-Pitts and Pitts, 2000)[39]. The exhaust emissions from ship operations emitted out at sea is emitted to relatively clean parts of the atmosphere (Eyring et al., 2010). The particles and gases in the plume continue to cool and become diluted with the ambient air (Hobbs et al., 1996).

During the ageing of the plume the dominant particle sizes change, which has an impact on the number concentration. The measured diameter[40] varies from 52-70 nm in a young plume, but is approximately 100 nm in an aged plume. The longest life span of particles in nucleation mode is 1 h (Petzold et al., 2006). In an aged plume, the non-volatile particles, such as BC, are the dominant fraction. The secondary particles in nuclei mode, i.e., volatile compounds such as droplets containing H_2SO_4 and hydrocarbons, that formed during the cooling of the young plume are no longer present in the aged plume due to coagulation among particles in accumulation mode and other particles in nuclei mode (Petzold et al., 2008, Petzold et al., 2010, Lack et al., 2009). The non-volatile particles remain in the atmosphere, are transported over long distances and are involved in particle growth and condensation (Hallquist et al., 2013a). The lifetime of BC particles varies between 4 and 12 days (Cape et al., 2012). Particles in the atmosphere are removed through wet or dry deposition[41] (Finlaysson-Pitts and Pitts, 2000).

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[39] SO_2 form secondary particles, primarily through oxidation to H_2SO_4 in the aqueous phase, such as in sea-salt particles and cloud droplets. The NO_X emissions form secondary particles, through reactions between HNO_3 (nitric acid) and sea salt. (Finlaysson-Pitts and Pitts, 2000).

[40] Count median diameter (CMD).

[41] Described further in "Terminology" as Atmospheric deposition starting on page xvii.

5 Factors Influencing Particle Emissions

The content and character of particle emissions emitted to the ambient air depend on several factors related to the engine, fuel and lubrication oil. This section is divided into two parts: the first part describes the factors related to both diesel engines and diesel fuels in general that have an impact on the particle emissions (section 5.1) and the second part (section 5.2) presents the results obtained from measurements conducted on marine engines and fuels.

5.1 Factors Related to Diesel Engines and Diesel Fuels

There are several factors related to diesel engines that can have an impact on the particle formation and consequently the emissions. One factor is the injection timing and rate of the injection. The timing of the injection can be either later than or earlier than the most optimal timing and can consequently have an impact on the ignition delay. An earlier injection reduces the emissions of particles because it causes higher temperatures during the expansion stroke and more time for oxidation of the newly formed particles in the cylinder (Stone, 2012). On the other hand, this causes an increase in emissions of NO_X. In contrast, a later injection results in lower NO_X emissions, but greater particle emissions[42] (Heywood, 1988). The particle emissions can be reduced by improving the diffusion combustion phase, which will reduce the time available for particle formation and enhance the oxidation of soot. Faster injection, increased swirl and a finer spray of the fuel during injection can improve the diffusion combustion phase. A finer spray requires high injection pressures and fine nozzles but leads to a more complete combustion, resulting in lower particle emissions. The formation of particles is strongly related to increased engine loads because a larger amount of fuel is injected. This enhances the formation of soot particles due to the increased time for diffusion combustion, higher temperatures during combustion and reduced oxidation of soot during the expansion stroke. The reduced soot oxidation is due to the lower oxygen concentration and shorter oxidation time following the end of the diffusion combustion. Equipping an engine with a turbocharger also has an impact on the particle emissions. A turbocharged engine generates lower particle emissions, due to higher temperatures during the expansion stroke, which favour oxidation of soot (Stone, 2012).

The content of different compounds in the fuel, including both additives and impurities, has an impact on particle emissions as well[43]. Figure 5-1 presents the different origins of particles formed in the engine and in the funnel. The carbonaceous fraction, such as soot particles, is mainly formed through pyrolysis of the diesel fuel and lubrication oil. The organic fraction is formed through incomplete combustion of the fuel and lubrication oil. The sulphur contents of both the fuel and lubrication oil contribute to emissions of particles containing sulphate. These sulphate particles contribute to the fraction of nucleation mode particles, while soot is primarily found in accumulation mode. Wear together with inorganic compounds in both the fuel and lubrication oil contribute to the inorganic fraction of the particle emissions (Stone, 2012).

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[42] A tradeoff between particle and NO_X emissions exists, and is usually called the diesel dilemma. A decrease in NO_X most often causes an increase in particle emissions (Heywood, 1988).

[43] The measured amount of the different fractions varies with temperature and dilution, which is discussed further in this thesis.

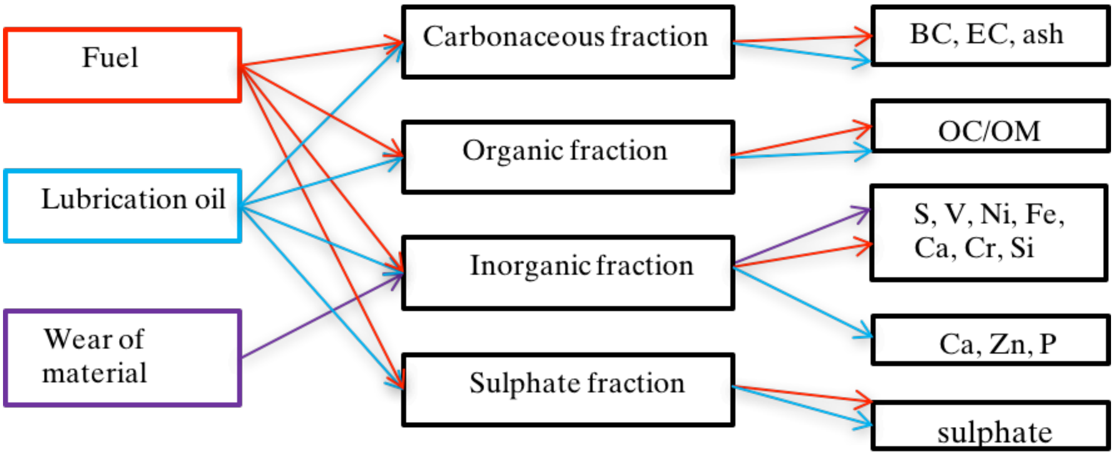

Figure 5-1: Schematic illustration of the contributions of different elements to particle formation and which type of particles they affect. Adapted from Stone (2012).

5.2 Marine Applications

Measurements conducted on-board operating ships, on test-bed engines and in ship plumes emphasize that fuel type, engine load and engine type affect the different types of particles emitted, as well as the PN and PM emissions. The impacts of the different factors on PN, PM and the particle types will be discussed in separate sections here.

5.2.1 Impacts on PN, PM and Particle Size

There is a relationship between the FSC and the PM emitted from marine fuels: lower FSCs result in lower particle emissions (previously discussed in section 2.3) (Figure 5-2). However, no consensus exists regarding whether there is a relationship between the FSC and the number of particles emitted. Some studies emphasize that the relationship between FSC and PN emissions factors is not clear (Beecken, 2015, Lack et al., 2011), while other studies emphasize that PN emissions tend to increase with increased FSC (Alföldy et al., 2013, Diesch et al., 2013). However, Diesch et al. (2013) emphasize that other factors, i.e., other fuel characteristics, engine type, operation mode and exhaust system, should be considered in order to determine which factors that have an impact on the PN emissions, and, to some extent, the PM emissions.

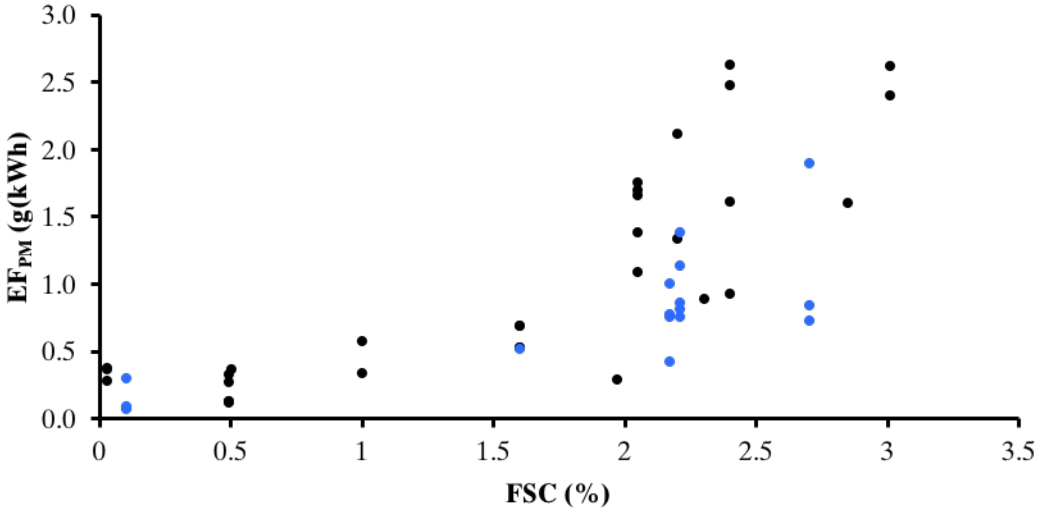

Figure 5-2: Relationship between FSC and emitted particle mass, here as EF_{PM} *in g/kWh. Black dots represent results from on-board measurements (Hallquist et al., 2013a, Moldanová et al., 2009, Moldanová et al., 2013, Fridell and Salo, 2014, Fridell et al., 2008, Winnes and Fridell, 2010, Winnes and Fridell, 2009, Agrawal et al., 2008a, Agrawal et al., 2010, Agrawal et al., 2008b, Murphy et al., 2009) and blue dots represent measurements on test-bed engines (Petzold et al., 2011, Petzold et al., 2010, Mueller et al., 2015, Sippula et al., 2014).*

A previous study emphasized that the FSC, quality of the fuel (with respect to the contents of metals, ash, asphaltenes and organic compounds, such as aromatics) and engine load affect both the PN and PM emissions. Measurements on a 2-stroke test-bed marine diesel engine running on two different marine fuel oils (MDO, 0.155 %m/m S and HFO, 0.6 %m/m S) at various engine loads showed that the emissions of TSP are higher for the HFO than for the MDO, probably due to a higher metal and asphaltene contents in the HFO. At very low loads (1%), the PN and PM emissions from combustion of HFO were higher than for an engine load of 100%. The particle emissions and particle sizes varied with the engine load. For MDO, the PN emitted and sizes of the particles increased with increasing engine load. For HFO, the opposite was found. The PN emissions from combustion of MDO were higher than those of HFO at 100% engine load, but for the opposite was found at 1 % engine load (Kasper et al., 2007). Another study with measurements on a test-bed engine, observed an increase in total PN emissions with decreasing load both for marine fuel oils and biofuels (Petzold et al., 2011).

The engine type, related here to a 2- or 4-stroke marine diesel engines, has an impact on the emitted particle mass. Measurements have indicated that lower PM emissions are emitted by a 2-stroke marine diesel engine than a 4-stroke marine diesel engine operating on the same fuel. Higher particle emissions, both with respect to the PN and PM, were emitted while using HFO than while using MGO (Winnes et al., 2014).

Test-bed engine measurements and on-board measurements reveal that the engine type also affects the number size distribution and the amount of emitted nanoparticles. A 2-stroke engine running on MGO generated a considerably higher amount of nanoparticles than a 4-stroke engine running on the same fuels. The amount of nanoparticles has no relation to engine load. The size distribution by number associated with a 4-stroke engine running on either HFO or MGO exhibits a more unimodal size distribution than that of a 2-stroke engine, which resulted in a size distribution of bimodal character (Ushakov et al., 2012b). Furthermore, engine load, FSC and other fuel characteristics affect size distribution by number of emitted particles. A fuel shift from HFO to a MGO with a lower FSC and ash content causes an increase in the PN emissions and the number size distribution shifted towards smaller particle sizes in the plume (Lack et al., 2011). A shift from a high and stable load to lower engine loads causes a shift in the number size distribution towards larger particles. A shift towards smaller particles was found when transitioning from lower to higher loads (Hallquist et al., 2013a).

5.2.2 Impact on BC Particles

Emissions of BC particles are mainly related to engine load and engine type. Measurements have revealed the dependence on load, i.e., the emissions of BC are higher at lower loads than at higher engine loads (Petzold et al., 2010, Petzold et al., 2011, Lappi et al., 2012, Diesch et al., 2013). The emissions of BC were observed to be stable for engine loads above 40%. Operating at loads below 40% caused higher emissions of BC than for engine loads above 40% (Petzold et al., 2010). Other measurements showed that BC emissions increased when operating at loads below 25% (Lappi et al., 2012, Petzold et al., 2011), independently of fuel type (Petzold et al., 2011). Other measurements indicate a relationship to both engine load and fuel type. For a 2-stroke engine, the BC emissions decreased with decreasing load when running on MDO (0.155 %m/m S), whereas the BC emissions increased with decreasing load when running on HFO (0.6 %m/m) (Kasper et al., 2007).

Measurements of BC particles[44] in plumes from operating ships indicate a relationship to engine type, rather than load. Medium-speed marine diesel engines had higher BC emission factors (in g/kg of fuel burned) than slow-speed marine diesel engines and high-speed marine diesel engines. The measurements also highlight the importance of considering BC emissions in port areas because ships with slow-speed marine diesel engines at dock did not have lower BC emissions compared to operating at sea. An observed relationship between the emissions of CO and BC for medium-speed marine diesel engines suggests that BC emissions are the result of inefficient combustion due to poor maintenance and ageing of the engine (Lack et al., 2008). Marine diesel engines operating outside the tuned engine load without retuning generate higher BC emissions, due to reduced fuel efficiency and conditions other than the ideal conditions. Retuning of the engine, to reduce emissions, is of interest when operating at other loads on a more permanent basis (Lack and Corbett, 2012).

Measurements on marine diesel engines indicate that the emissions of BC are also related to the fuel characteristics. The emissions of BC were inversely correlated with the sulphur content and more associated with other fuel characteristics that enhance formation of BC, such as the contents of ash, large HC molecules and aromatic compounds (Lack et al., 2011, Lack et al., 2009). The contents of these species are higher in HFO than MGO; consequently the use of MGO reduces the formation of BC (Lack et al., 2011).

5.2.3 Impact on Particles Containing Sulphate and Organic Matter

There is a correlation between the FSC and emissions of OM/OC, sulphate and CCN[45]. A lower FSC consequently reduces the amount of sulphate particles in the emission. Additionally, the amount of particles that can act as CCN will be reduced. The emissions of OM are related to FSC and other fuel characteristics. The use of a marine

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[44] In the study by Lack et al., (2008) the BC is included in the light-absorbing fraction of the particle emission, which also includes brown carbon.

[45] Particles that may act as CCN from ship operations are particles containing sulfate. See section 2.2 for further information.

fuel oil with a high FSC increases the consumption of lubrication oil and consequently increases the emissions of OM. The emissions of OM may also depend on the engine type and performance of the engine, which also affect the amount of lubrication oil consumed (Lack et al., 2011, Lack et al., 2009, Diesch et al., 2013).

5.2.4 Summary

Table 5-1 summarizes the different factors that influence particle emissions from operating ships. The results from the references used here indicate that it is difficult to highlight just one factor that influences the particle emissions. Instead it appears to be a combination of different factors that affect these emissions. In addition, some studies presented here report results that are contrary to those of other studies. This further emphasizes the importance of consider this topic in future studies and measurements.

Table 5-1: Summary of the different factors that influence particle emissions from operating ships.

Factor	PN	PM	BC	OM	Sulphate
Reduced FSC	↑↓	↓			↓
Improved fuel quality[a]	↑↓	↓	↓	↓	
Increased engine load	↑↓		↓		
Reduced consumption of lubrication oil				↓	

[a] Change in fuel characteristics other than FSC, resulting in a fuel that is more similar to a distillate than a HFO.

6 Experimental Section

This thesis includes measurements done on test-bed engines and on-board operating ships. Consequently, the measurements have been conducted on various types of engines operating at different engine loads and using different fuel types. The measurements on test-bed engines made it possible to investigate various fuel types, experiment with the concentrations of various fuel compounds and control the engine load and duration of operation at different engine loads. The on-board measurements allowed the investigation of emissions during normal operation of a certain ship running on currently used fuel types.

6.1 The Test-bed Engine Lab

The test-bed engine lab located at the Department of Shipping and Marine Technology, Chalmers University of Technology was used for the measurements presented in Paper I and Paper IV (Figure 6-1). The engine lab is equipped with a 2.4-litre 4-stroke, turbocharged Volvo Penta D3-110 marine diesel engine. The engine has five cylinders, a crankshaft power of 81 kW and a maximum engine speed of 3000 rpm. The fuel system is equipped with a common rail injection system. The engine is equipped with four separate heated fuel tanks, with an option to change between different fuel types during operation and to control the viscosity of the fuel. The engine is connected to a hydraulic brake, which allows operation of the engine at different loads. The test-bed engine was operated at lower engine loads, due to restrictions in the design of the test-bed rig. However, this enabled investigation of particle emissions at engine loads typical for operation in coastal and port areas.

Figure 6-1: The test-bed engine at the Department of Shipping and Marine Technology used for the measurements in Paper I and Paper IV (Photo: Katarina Wignell, Chalmers University of Technology).

6.1.1 Paper I

In Paper I, the particle emissions from four different fuel types were investigated (Table 1, Paper I). The measurements were made during two separate campaigns: the first in March 2012 (Campaign 1) and the second in October 2012 (Campaign 2). The fuels studied were MK1, MK3, HFO and MDO. The HFO was a mixture, by volume, of 50% atmospheric residue 0.7 and 50% MK1. The atmospheric residue 0.7 had to be diluted to reduce its viscosity. The analysed data come from Campaign 2, except for the measurement data on MK3. MK1 was mainly used as a reference fuel, while MK3 was treated as representative of the fuel typically used on IWW. The HFO and the MDO are typical for fuels used on-board operating ships, and the FSC in these two fuels comply with the limits set in Regulation 14, MARPOL Annex VI (see section 2.3). The FSC of the HFO and the MDO were 0.12 %m/m and 0.52 %m/m, respectively. The properties of the lubrication oil used are listed in Table 1 in Paper I.

A test cycle designed according to the operational limitations of the engine was developed. The maximum load and speed were 35% and 1750 rpm. The measurements were conducted at engine loads of 10%, 25% and 35% of the maximum continuous rate (MCR), with an engine speed of 1750 rpm and at idle (700 rpm). To reach stable conditions, each step in the test cycle lasted 30-40 minutes. The whole cycle was repeated twice for each fuel type in order to test the repeatability of the results. An appropriate repeatability was found for the three distillates used, whereas some differences were observed among the results for the HFO.

6.1.2 Paper IV

In Paper IV, the impact of aromatics in fuels on particle emissions was investigated. To increase the content of aromatics in the reference fuels, a fuel additive consisting of aromatics (>93% mono- and diaromatics Caromax28) was used. The reference fuel was MK1, which was chosen due to its low contents of sulphur and other compounds that may influence the formation and growth of particles during and after the combustion. The measurements were made during two campaigns: one in November 2012 and one in March 2014. For the first campaign, the engine was operated according to the test-cycle described in 6.1.1. After this campaign, the hydraulic brake and cooling system of the test-bed engine were replaced. Thereby enabling operation at higher engine loads (50% of the MCR). For the second campaign, a new test cycle was developed, and the measurements were made at engine loads of 50%, 25% and 10% of the MCR with an engine speed of 2000-2010 rpm and at idle with an engine speed of 700 rpm.

Measurements were also done at the test-bed engine lab at the Department of Applied Mechanics at Chalmers University of Technology. The measurements were made in January 2016 and are referred to as Campaign 3 in Paper IV. The aim was to perform in-depth studies of the impact of aromatics on the combustion process, including the rate of heat release. The engine rig was equipped with a 2-litre single-cylinder heavy-duty diesel engine (Volvo D12), with a common rail system and exhaust gas recirculation system. An AVL AMA i60 exhaust measuring system measured the emissions of exhaust gases, i.e., NO_X, CO, CO_2, oxygen (O_2) and HC. Rail pressure, start of injection, and duration of the injection were controlled using ATI Vision software. An Osiris system (from D2T) was used to measure the cylinder pressure and the rate of heat release was calculated using an in-house Matlab code.

In Campaign 1, fuel-blends with concentrations of aromatics of 23 and 30% by volume (%vol) were tested. Measurements with the fuel-blend of 30 %vol aromatics were repeated during Campaign 2. The viscosity of the MK1 used during both campaigns was 2.0 cSt at 40°C, and the flash point ranged from 61-71°C. The ash content of the MK1 during Campaign 1 was <0.01 %m/m and the fuel contained 5-7% rapeseed methyl esters. In Campaign 3, VSD10 diesel was used as the reference fuel. This is a diesel, without biofuel, that meets the EN590 standard. Measurements with fuel-blends with 20%vol and 30%vol aromatics were tested to repeat the previous measurements during Campaigns 1 and 2. During Campaign 3, an ignition improver (Cepro 100, 2-

ethylhexyl nitrate) was added to the fuel-blends to increase the CN and achieve a CN close to MK1. The amount of Cepro 100 added was based on a CN analysis of the fuel-blends by the accredited laboratory Saybolt. The reference fuels, fuel-blends and Caromax28 are presented further in Table 1, Paper IV.

6.2 On-board Measurements

6.2.1 Paper II

In Paper II, the particle emissions from a DF engine running on LNG using MGO (<0.05 %m/m S) as the pilot fuel were studied. The measurements were conducted on-board a cruise ferry operating in the Baltic Sea with daily sailings between Sweden and Finland. The measurements were completed over a period of three days in December 2013. The ship was equipped with four lean-burn DF engines (Wärtsilä 8L DF) with an installed power of 7600 kW per engine. The measurements were conducted on one of the DF engines, operating at different loads. The load on the engine had to be adapted according to the location of the ship, i.e., at berth, manoeuvring or cruising. Measurements at seven different loads were performed. Data on the different measurement conditions for the different engine loads are presented in Table 3, Paper II. For six of these loads, LNG was used for propulsion of the ship, and for one load MGO was used (the properties of these fuels are presented in Tables 1 and 2 in Paper II, respectively). Approximately 1-5%, primarily 1-2%, of the total energy supplied to the engine corresponded to MGO when running on LNG, with higher proportions at lower loads. The engine had to use MGO for propulsion during starting and stopping of the ship. This requirement is set by the classification rules.

6.2.2 Paper III

Paper III considers the impact of the two different fuels with different FSCs on the particle emissions. This study made it possible to compare the particle emissions of a single ship and the same engine, before and after the stricter limitations on the allowed FSC entered into force in SECAs (Figure 2-1). The measurements were made on-board a ship operating in the Baltic Sea during two occasions: Campaign 1 in November 2014 and Campaign 2 in April 2015. During Campaign 1, a HFO with 0.48 %m/m S was used for propulsion, and during Campaign 2, a low-sulphur residual marine fuel oil (RMB30, 0.092 %m/m S) was used (the properties of the fuels are listed in Table S1, Paper III).

The ship was equipped with four Wärtsilä 6L46 engines (main engines), with a total installed power of 23,400 kW. The measurements were conducted on one of the engines, which had an installed power of 5850 kW. The ship has a selective catalytic reduction system installed to reduce emissions of NO_X. The emissions of particles and gases were measured under various engine loads. Information on the operational conditions is presented in Table S3 of Paper III.

6.3 Instrumentation

Similar instrumentation and experimental set-ups were used for the measurements in Papers I-IV. Differences will be discussed throughout the text. Figure 6-2 shows a picture of the experimental set-up in the test-bed engine lab (section 6.1). It was possible to place the aerosol instrumentation close to the exhaust gas channel and the dilution system in the experiments discussed in Papers I, II and IV. For the measurements in Paper III, the aerosol instruments had to be placed one level down from the extracting holes in the exhaust gas channel and the dilution system. Corrections for diffusion losses in the tubes were applied and described further in section 6.4.

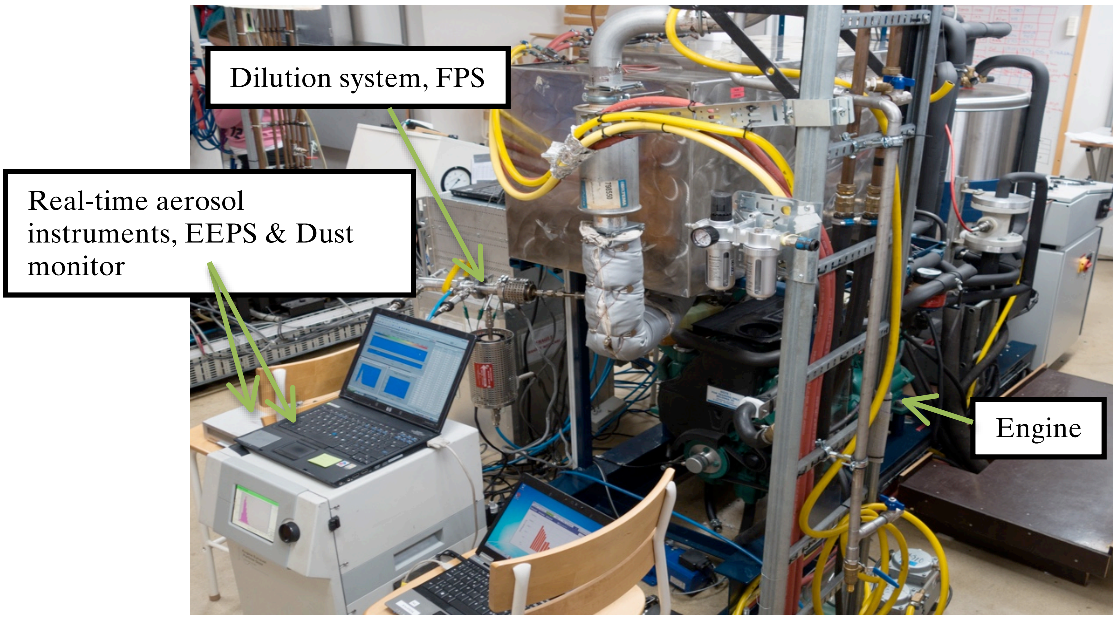

Figure 6-2: Experimental set-up, with instrumentation described in section 6.3, of the test-bed engine at the Department of Shipping and Marine Technology (Photo: Jesper Ingevaldsson, Lighthouse).

6.3.1 Real-time Aerosol Instruments

In the four papers included in this thesis, two different types of aerosol instruments: an EEPS (Model 3090 TSI Inc.) and a Dust Monitor (Model 1.108, Grimm), were used simultaneously to measure emitted particles across a wide size range. These two instruments have high temporal resolutions and are primarily suitable for the on-board measurements when operating conditions can change over short periods of time. The EEPS and the Dust monitor were set to record measurements at temporal resolutions of 1 second and 6 seconds, respectively.

In Paper III, a Multi Angle Absorption Photometer (MAAP, Model 5012, Thermo Scientific) was used to estimate the amount of BC in the particle emissions. The MAAP is an optical instrument that combines measurements of optical absorption and scattering of light to estimate the BC content (Thermo Scientific, 2007).

In Paper IV, particle measurements were done with a DMS500 from Cambustion at the test-bed engine lab at the Department of Applied Mechanics. This measurement instrument has a dilution system included in the instrument. However, during the measurements done in Paper IV this dilution system was not used. Instead, the Fine particle sampler (FPS) described in section 6.3.3 was used.

To study the thermal properties of the aerosols, a thermodenuder (TD, Dekati) was installed upstream of the aerosol instruments, with the ability to bypass it. The measurements were conducted both with and without the TD in order to quantify the amount of non-volatile (solid) particles in the emissions. For the measurements in Papers I-IV the TD was heated to 300°C. During measurements at the Department of Applied Mechanics, a TD developed by the Department of Chemistry and Molecular Biology, University of Gothenburg, was used, and an actual correction for the losses in this TD was done via experimental studies. A TD removes volatile and semi-volatile compounds in the particle emissions by heating the diluted sample. During heating, the volatile and semi-volatile compounds are vaporized. After heating, the particles are led to the adsorber section in the TD, which is coated with active charcoal. There, the sample is cooled using clean pressurized air and the volatile compounds adsorb onto the active charcoal. The vaporized volatile compounds are adsorbed efficiently by the active charcoal due to differences in the diffusion velocities between the non-volatile particles and the vaporized compounds. The non-volatile particles have a much slower diffusion velocity than the vaporized compounds and instead follow the gas flow through the TD (Dekati., 2003).

6.3.2 Filter Sampling

In addition to real-time sampling of the particle emissions, sampling was conducted with filters as well. Filter sampling can be made using different types of filters. In Paper I-IV, three types of filters have been used; Teflon filters (PFTE-filters), quartz filters and polycarbonate filters. For the measurements in Papers I and IV (test-bed engine experiments) only Teflon filters were used. These filters were used for gravimetric analyses of TSP, BC and elemental analysis. The gravimetric analyses were conducted by an accredited lab, and the BC contents were determined with a visible light reflectometer, which is a part of the beta gauge monitor FH62 I-N (ESM Emberline, Germany). The blackness of the sample was determined by measurements of the light reflectance of light (at a wavelength of 0.6 µm) of a sample. The intensity of the reflected light was used to calculate the equivalent BC concentration in the sampled particles (Pettersson et al., 2011, Gagel, 1996). The content of inorganic elements was analysed via energy-dispersive X-ray fluorescence. X-ray fluorescence is a quantitative method that analyses elements from silicon to uranium in the periodic system through measurement of the characteristic energy or wavelengths emitted by the elements (Boman, 2009). The energy-dispersive X-ray fluorescence used in Papers I and IV is in a laboratory at the Department of Chemistry and Molecular Biology, University of Gothenburg, and operates at 50 kV voltage and 25 mA current. The live time used was 1000 seconds.

For the on-board measurements in Papers II and III Teflon and quartz filters were used. The Teflon filters were used for gravimetric and elemental analysis. The latter done with an X-ray fluorescence instrument at an accredited lab. The particles sampled by the quartz filters were analysed to determine the EC and OC contents. The EC/OC analysis is based on a thermal optical method. A 1 cm^2 piece of the sample filter is used. OC is removed first at temperatures of 200-650°C in a non-oxidizing carrier gas, which was helium in this study. Then, EC is removed using a mixture of helium and O_2 at temperatures of 500-850°C. The generated CO_2 is then converted to methane and detected by flame ionization detection. Additionally, in Paper III, particles were also sampled using Polycarbonate filters for electro-microscopy analyses.

6.3.3 Dilution

The dilution system used in Papers I-IV was a fine particle sampler (FPS, Model 4000, Dekati). The FPS was connected directly to the funnel and extracted the raw exhaust gas through a fixed inlet (Apex instruments). The sampling of the raw exhaust gas was performed under isokinetic conditions[46,47]. The raw exhaust was diluted in two steps, primary dilution and ejector dilution. The primary dilution occurs in a perforated tube, in which preheated, clean and dry air (250-315°C) is forced into the tube through small pores. The ejector dilution involves clean air at ambient temperatures, and an ejector

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[46] Described further in "Terminology" starting on page xvii.

[47] The sampling of particles with Dp <2.5 µm occurred under isokinetic conditions, while particles with Dp >2.5 µm might be sampled under anisokinetic conditions, which may affect the results (Hinds, 1999). A previous study found that, for particles in the size range of 12-130 nm, the effect of anisokinetic sampling on the size distribution is thought to be insignificant (Arouca et al., 2010).

is used to draw the sample from the primary dilution sector. The residence time in the system is less than 0.5 seconds according to the manufacturer (Dekati., 2010). Preheated air, with temperatures close to the temperatures of the exhaust gases, is used to prevent condensation of water (Hallquist et al., 2013a), condensation of sulphuric acid and nucleation of new particles (Lyyränen, 2006). Information on the DRs and dilution conditions for the different measurements are presented in the supplementary material of Papers I-IV.

6.3.4 Gaseous Emissions

Measurements of gaseous emissions were conducted in parallel with the real-time measurements of particle emissions in Papers I-IV. The sample of exhaust gas was extracted directly from the funnel with a probe and directly transferred to the instruments. For the measurements made in the test-bed engine lab, presented in Papers I and IV, measurements of nitrogen monoxide (NO), NO_X, SO_2, CO, CO_2 and O_2 were made with an infrared gas analyser (Fuji Electric Model ZRE NDIR-analyser, Fuji Electric Systems Co, Ltd, Japan). In Paper I, the measurements of the gaseous emissions were only made during the second campaign. For the on-board measurements in Papers II and III, SO_2 (Horiba PG-250 NDIR), NO_X (Horiba PG-250 chemiluminescence instrument), CO (Horiba PG-250 NDIR), CO_2 (Horiba PG-250 NDIR), O_2 (Horiba PG-250 galvanic cell) and total hydrocarbons (THC, Bernath Atomic BA 3006 FID) were measured.

The concentrations of NO were measured downstream of the dilution system using a chemiluminescence instrument (TH42i, Thermo Scientific), in order to verify the actual dilution ratio used. The TH42i was connected to the FPS. The values of the actual DR for the different measurements are presented in the supplementary material of Papers I-IV.

6.3.5 Instrumentation Summary

Table 6-1 provides a summary of the instrumentation used in Papers I-IV. The table provides information on which study used the respective instrument, the function of the instrument in the measurements, and the type of data generated by the instrument.

Table 6-1: Summary of the instrumentation used in Papers I-IV.

Instrument	Used in paper no.	Measurement function	Type of data
EEPS	I-IV	Real-time aerosol measurements	The concentration of PN, PM and size distributions by number and mass for particles in the size range of 5.6-560 nm. Used in calculations of EFs.
Dust monitor	I-IV	Real-time aerosol measurements	The concentration of PN, PM for particles in the size range of 0.3 to over 20 µm. Used in calculations of EFs.
MAAP	III	Real-time aerosol measurements	Content of BC in aerosol
DMS500	IV	Real-time aerosol instrument	The concentration of PN and size distribution by number.
TD	I-IV	Study thermal properties of the particle emission	Makes it possible to study the proportion of non-volatile particles in the emissions.
Filter sampling	I-IV	Sampling of particles	Mass of TSP, content of BC, EC/OC and other elements. Used in calculations of EFs. Polycarbonate filters for electro-microscopy studies (Paper III).
FPS	I-IV	Dilution system	Used dilution ratio and data on dilution conditions
Gas instruments	I-IV	Measurements of the concentrations of NO, NO_X, SO_2, CO, CO_2, O_2 and THC.	Concentrations of different gases in the exhaust gases. Used in calculations of EFs and measurements of actual DR.

6.4 Data Analysis and Particle Size Statistics

Data from real-time measurements and filter sampling were corrected for the actual DR. Measurements with the TD were corrected for losses of particles according to the instructions of the manufacturer. Losses of non-volatile particles in the TD can occur in the adsorber section due to diffusion and can vary with the length of the adsorber section. The data from the real-time aerosol measurements with the heated tube, in Paper I, were also corrected for the calculated losses within the tube. The losses were greatest for the smallest particles. Correction factors for each size channel of the EEPS were derived from the data gathered from the measurements with and without the heated tube. Processes that might occur in the heated tube include diffusion[48] and thermophoresis[49] (Ushakov, 2012). These processes were further discussed and investigated, did not account for the total loss of particles that actually occurred in the tube. Other processes believed to be responsible for the particle losses in the heated tube include coagulation and settling of large particles. In Paper III, long tubes were used to transport the particles between the FPS and the real-time aerosol instruments. The FPS and the aerosol instruments were located on two different floors, and the conductive tubing used was approximately 7 metres long for the EEPS and Dust monitor and approximately 9 metres for the MAAP. When the thermodenuder was used, the total length of the conductive tubing was approximately 9 metres for the EEPS and Dust monitor. To correct for the potential diffusion losses in the tubes, the equation developed by Gormley & Kennedy, and presented in Willeke and Baron (1993) for the fraction passing through the tube via laminar flow was used, resulting in size-resolved correction factors for the sizes measured by the instruments. The greatest losses (16-18%) were associated with the smallest particle sizes measured. For the larger particles, the losses were less than 1%. The temperatures and pressures at the time of the measurements were used.

The particle emissions were analysed with respect to the PN, PM, size distributions by number and mass, volatility and chemical content. EFs and size-resolved EFs were calculated for PN and PM, and EFs were also calculated for the various measured gases. Operational data, such as fuel consumption and engine load, were used in the calculations of the EFs. These data were either recorded from readings on the control panel in the engine room of the operating ships (Papers II and III), or from own readings on the control panel in the test-bed engine lab (Papers I and IV). EF_{NOX} was calculated according to the IMO NO_X Technical Code and corrected for ambient temperature and humidity as described therein (IMO, 2009). In calculations of EFs for PM from the real-time instrument measurements, unit density was assumed. However, the densities of particles generated by the combustion of diesel fuels differ from unity and are dependent on the particle size and content of condensable compounds, such as sulphate[50]. Previous studies have found that the density decreases with increasing particle size, with densities of 0.8-1.2 g/cm^3 for particles approximately 50 nm in diameter and 0.4-0.8 g/cm^3 for particles approximately 300 nm in diameter. Smaller particles (approximately 50 nm) are more compact than larger particles, which tend to be irregularly shaped agglomerates, thereby explaining the differences in density (Barone et al., 2011, Ahlvik et al., 1998, Park et al., 2003, Virtanen et al., 2002, Olfert et al., 2007).

The size distributions by number and mass are presented using data collected with the EEPS and the Dust monitor in the papers included in this thesis. In Paper IV, data from the DMS500 measurements are presented as well. A lognormal distribution is commonly used in the presentation of aerosol size distribution because it matches the observed size distributions and can cover a wide range of values. Most aerosols are polydisperse, with particles of different sizes ranging from several nm up to several µm, and the distributions often exhibit a skewed shape (Hinds, 1999). To handle a wide range of values, a logarithmic scale can be also used for the vertical axis (Finlayson-Pitts and Pitts, 2000).

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[48] Described further in “Terminology” starting on page xvii.

[49] Described further in “Terminology” starting on page xvii.

[50] The sulphuric acid formed from the sulphur in the fuel can condense on existing particles, which can increase the density of particles emitted by the combustion of fuels with a higher FSC (Olfert et al., 2007, Park et al., 2003).

7 Results

This thesis includes studies from both on-board measurements and test-bed engine measurements (Figure 2-3). The on-board measurements consider two strategies that can be used for compliance with the FSC regulations in SECAs: fuel shift and use of an alternative fuel. The newly built ship in Paper II uses LNG for propulsion, whereas the ship studied in Paper III, shifted from HFO to a low-sulphur residual marine fuel oil (RMB30). The test-bed engine measurements consider the impact of FSC and other fuel characteristics on the particle emissions (Paper I), with a thorough study of how the content of aromatics in the fuel affects the particle emissions (Paper IV). When these studies are taken together, the aim is to provide information on how these strategies will affect the particle emissions and how the FSC together with other fuel characteristics should be considered with respect to particle emissions from ship operations.

7.1 Particle Emission Before and After 2015

The strictest FSC limit in SECAs was implemented in January 2015 (see section 2.3). This has forced ship owners to use low-sulphur marine fuel oils (max. 0.1 %m/m S), alternative fuels or scrubbers to comply with the regulation. To further illustrate the particle emissions from operating ships in SECAs before and after 2015, example emission calculations have been made. The calculations are based on a scenario in which a ship is operating between Stockholm and Mariehamn, i.e., in the Baltic Sea SECA. The ship is operating at lower engine loads (38-50%) for approximately 4 hours and higher engine loads (80-90%) for approximately 2.5 hours. These assumed periods of time come from data gathered during the on-board measurements in this thesis. The used fuel types are based on the studies made in Papers II and III. The emission factors are presented in Table 7-1.

Table 7-1: EFs for PN, PM and TSP for the different fuel types: HFO (0.48 %m/m S), RMB30 (0.092 %m/m S) and LNG (<3 ppm-mol S) for particles in the size range of 5.6-560 nm and for the total particle emissions and the non-volatile fraction. One standard deviation is shown in parenthesis.

		EF_{PN} (10^{14} #/kWh)		**EF_{PM} (10^{-2} g/kWh)**		**EF_{TSP} (g/kWh)**
Fuel type	**Engine load**	**Total emission**	**Non-volatile fraction**	**Total emission**	**Non-volatile fraction**	**Total emission**
HFO	85%	3.4 (0.4)	3.4 (0.2)	2.1 (0.1)	1.7 (0.2)	0.49
	50%	3.9 (0.2)	3.7 (0.1)	2.2 (0.2)	1.8 (0.1)	0.30
RMB30	82%	3.5 (0.1)	3.4 (0.1)	0.5 (0.1)	0.4 (0.1)	0.24
	38%	3.2 (0.1)	3.1 (0.09)	1.0 (0.1)	0.8 (0.1)	n.a.
LNG	90%	0.035 (0.02)	0.012 (0.004)	0.023 (0.01)	0.014 (0.006)	0.0022
	40%	0.023 (0.007)	0.010 (0.003)	0.018 (0.006)	0.015 (0.004)	n.a.

Figure 7-1 presents the number of particles emitted per trip for the different fuel types. The combustion of HFO, with a FSC that complies with the SECA limits before 2015 resulted in the highest PN emitted during a trip, both for the total emissions and the non-volatile fraction. The main difference between HFO and RMB30 is found for the emissions at lower engine loads, with somewhat higher emissions for HFO. At high engine loads, the PN emissions are similar (red in Figure 7-1). The use of LNG for propulsion of the ship resulted in the lowest emitted PN per trip, and the PN emissions were reduced by 99% compared to HFO and RMB30.

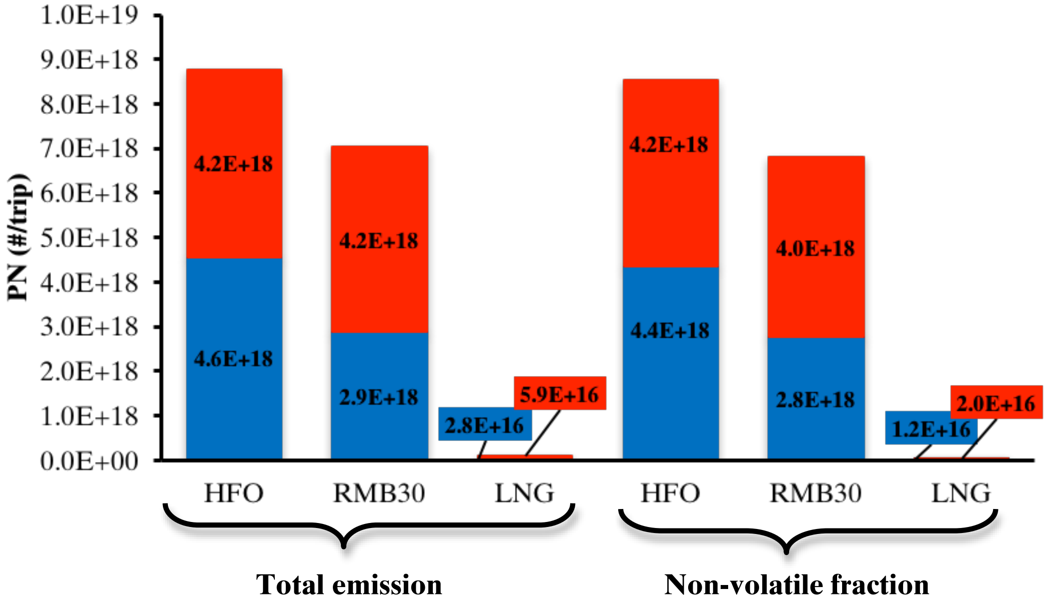

Figure 7-1: Number of particles (PN) emitted in the size range of 5.6-560 nm during a trip from Stockholm to Mariehamn with blue symbols representing operation at low engine loads and red symbols representing operation at high engine loads.

The PM emitted during a trip decreased considerably when the ship changed from HFO to RMB30, and decreased even further following the switch to LNG (Figure 7-2). The emitted particle mass was reduced by 72% for the total emissions and the non-volatile fraction, when the ship changed from HFO to RMB30. The use of LNG for propulsion reduced the total particle emission and the non-volatile fraction by 99% compared to HFO and 96% compared to RMB30. The fuel shift from HFO to RMB30 had no impact on the emissions of BC but did reduce the emissions of most inorganic elements in the emitted particles. Only the emissions of zinc and iron were similar or higher for RMB30, due to the similar contents in the fuel and lubrication oil. The emissions of inorganic elements when the ship used LNG for propulsion were related to the lubrication oil and pilot fuel.

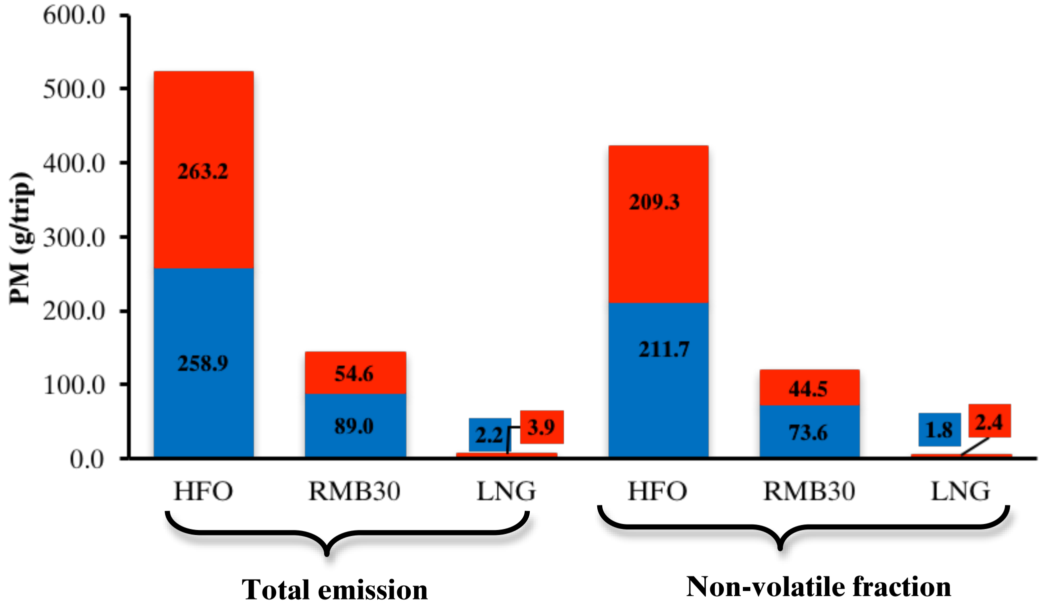

Figure 7-2: Mass of particles (PM) emitted in the size range of 5.6-560 nm during a trip from Stockholm to Mariehamn with blue symbols representing operation at low engine loads and red symbols representing operation at high engine loads.

The fuel shift from HFO to RMB30 resulted in a change in the sizes of emitted particles, both for the total particle emissions and for the non-volatile fraction. The combustion of HFO, during high engine loads, resulted in a peak at 34 nm, whereas the combustion of RMB30 resulted in a peak at 19 nm (Figure 7-3a). The emission of particles with Dp <25.5 nm was higher for RMB30 than for HFO. The combustion of HFO resulted in higher emissions of particles between 25 and 165 nm. For particles larger than 165 nm, the emissions were of a similar level for the two fuel types. Similar trends were observed for the particle emissions at lower engine loads (Figure 7-3b). Compared to HFO and RMB30, the use of LNG for propulsion reduced the emissions of particles of all sizes, except for particles with Dp of approximately 6-9 nm. The origin of the emitted particles from the various fuel types is discussed further in respective paper.

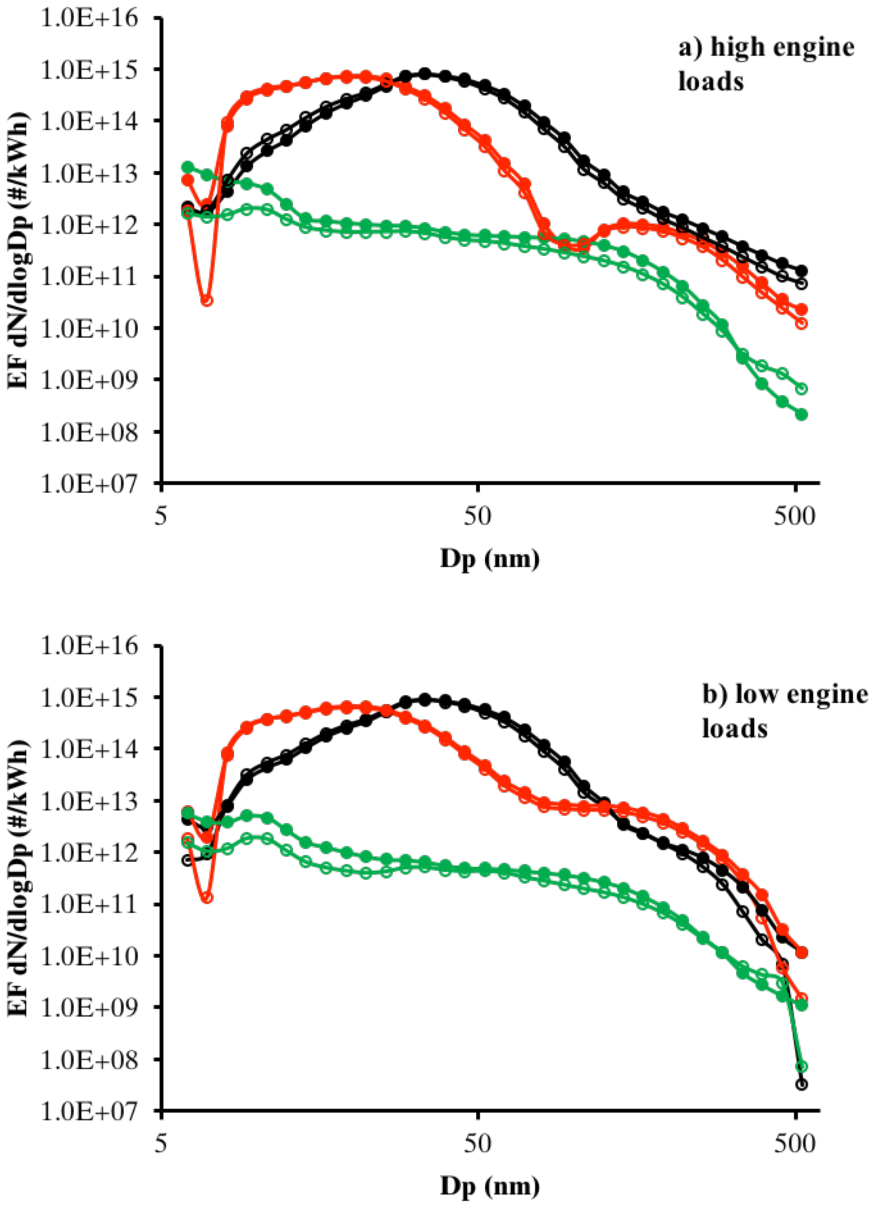

Figure 7-3: Size-resolved EF_{PN} for HFO (black), RMB30 (red) and LNG (green) for a) high engine load and b) low engine loads. Filled symbols represent the total particle emissions and unfilled the non-volatile fraction. Note: both axes use a logarithmic scale.

The gaseous emissions of SO_X, NO_X, CO, CO_2 and THC are also of interest and Figure 7-4 shows the emissions of NO_X and THC. The EFs for the various fuel types are presented in Table 4 in Paper II (LNG) and Table 1 in Paper III (HFO and RMB30). The total emissions of SO_X were considerably reduced when the ship shifted from HFO to RMB30. The use of LNG for propulsion reduced the emissions even further[51] and also reduced the emissions of NO_X considerably compared to use of HFO and RMB30. The EF_{NOX} associated with LNG was below the set values in the regulation of NO_X emissions in NECAs (see Paper II for more information). However, the use of LNG for propulsion resulted in higher emissions of CO and THC compared to HFO

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[51] During the measurements made in Paper II, interference occurred between SO_X and CH_4 in the instrument. Due to the very low sulphur content in LNG and the low FSC of the pilot fuel, the assumed emissions of SO_X are very low.

and RMB30, which is important to consider with respect to the impact on the climate of various fuel types (discussed further in Paper II and section 3.3). Furthermore, the calculated emissions of CO indicate that RMB30 may emit more CO than HFO at lower engine loads and that use of this fuel led to more incomplete combustion. However, exactly identical engine loads could not be compared (approximately 40% engine load for RMB30 and 50% for HFO), which may affect the results.

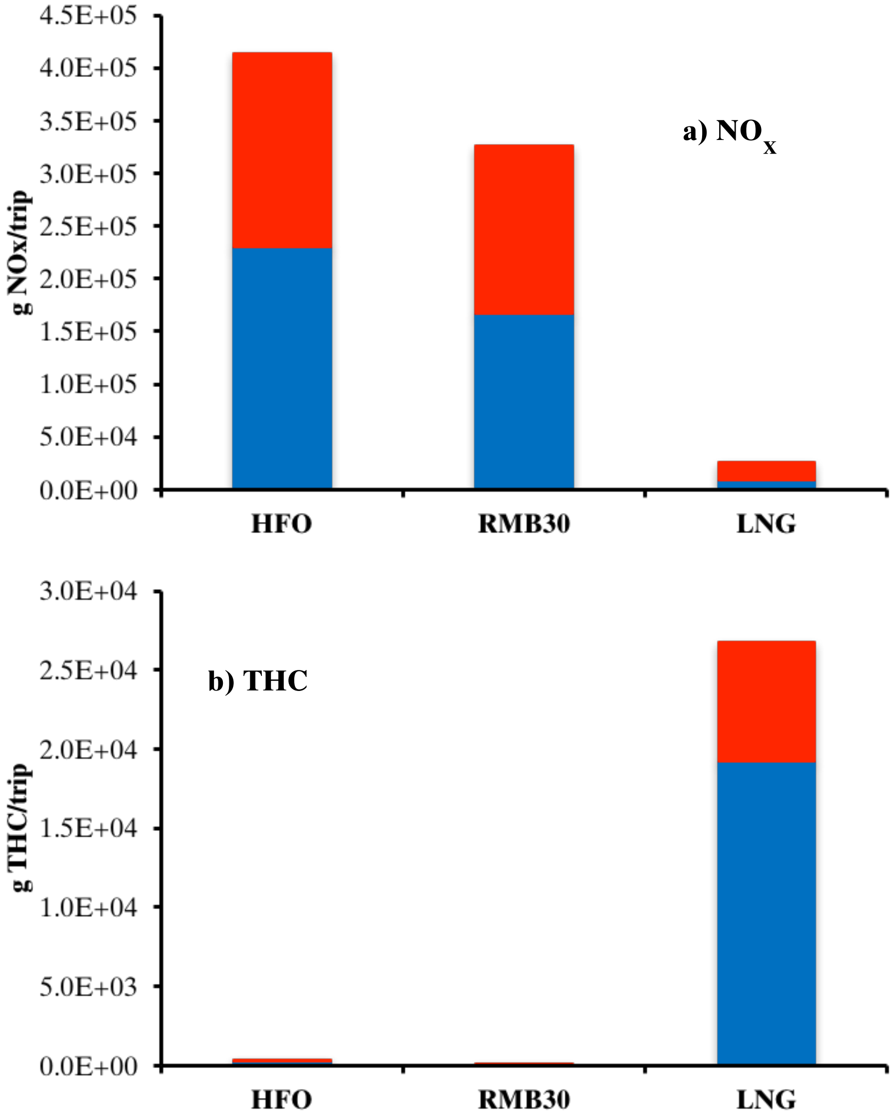

Figure 7-4: Emissions of a) NO$_X$, and b) THC emitted during a trip from Stockholm to Mariehamn with blue symbols representing operation at low engine loads and red symbols representing operation at high engine loads.

7.2 Impact of Fuel Characteristics on the Particle Emissions

With a regulation of the FSC of marine fuel oils in SECAs and at the global level in the near future, it is important to consider how other fuel characteristics than FSC affect the particle emissions from ship operations. Table 7-2 presents the EFs for PN and PM for different fuel types investigated during measurements in the test-bed engine lab (Paper I). The HFO used had a lower FSC than the MDO (0.12 %m/m S and 0.52 %m/m S, respectively). This difference makes it possible to study how other fuel characteristics may affect the total particle emissions and the non-volatile fraction. The combustion of HFO resulted in the highest EFs with respect to both PN and PM.

In general, with few exceptions, the combustion of MDO resulted in EFs that were lower than those of HFO but higher than those of MK1 and MK3. Furthermore, independent of fuel type, the EFs increased with decreasing engine loads. This increase is believed to be related to more incomplete combustion and reduced temperatures in the engine at lower engine loads. These conditions enhance the formation of new particles (nucleation) from compounds in the fuel and lubrication oil. Reduced engine loads also favour the increased growth of existing particles. Examples of growth processes include adsorption of compounds on existing particles and agglomeration (see section 4.1).

Table 7-2: EFs for PN, PM and TSP for MK1, MK3, HFO and MDO for various engine loads. Both the total particle emission and the non-volatile fraction are included. A 95% confidence interval is presented in parenthesis.

		EF_{PN} (10^{16} #/kg fuel)		**EF_{PM} (g/kg fuel)**		**EF_{TSP} (g/kg fuel)**
Fuel type	**Load (%)**	**Total emission**	**Non-volatile fraction**	**Total emission**	**Non-volatile fraction**	**Total emission**
MK1	35	0.02 (0.004)	0.02 (0.003)	0.03 (0.005)	0.03 (0.004)	0.09
	25	0.05 (0.009)	0.05 (0.005)	0.06 (0.004)	0.05 (0.003)	
	10	0.2 (0.03)	0.2 (0.02)	0.2 (0.01)	0.2 (0.007)	
	0	0.4 (0.1)	0.2 (0.02)	0.2 (0.02)	0.2 (0.009)	
MK3	35	0.03 (0.002)	0.03 (0.001)	0.05 (0.004)	0.05 (0.005)	0.06
	25	0.05 (0.002)	0.05 (0.002)	0.08 (0.005)	0.08 (0.004)	
	10	0.08 (0.003)	0.09 (0.003)	0.1 (0.006)	0.09 (0.005)	
	0	0.4 (0.01)	0.5 (0.01)	0.2 (0.02)	0.2 (0.02)	
HFO	35	0.7 (0.01)	0.5 (0.02)	2.6 (0.1)	1.3 (0.3)	0.47
	25	60 (0.18)	0.6 (0.01)	2.6 (0.4)	1.9 (0.1)	
	10	21 (0.07)	0.6 (0.009)	0.8 (0.05)	0.9 (0.05)	
	0	133 (0.57)	1.4 (0.01)	2.0 (0.08)	0.8 (0.04)	
MDO	35	0.3 (0.1)	0.1 (0.05)	0.04 (0.01)	0.03 (0.007)	0.06
	25	0.2 (0.001)	0.3 (0.001)	0.03 (0.004)	0.03 (0.004)	
	10	2.3 (0.005)	2.2 (0.003)	0.05 (0.006)	0.04 (0.004)	
	0	1.5 (0.02)	1.5 (0.01)	0.3 (0.02)	0.3 (0.02)	

Figure 7-5 presents the size-resolved EF_{PN} values for the total emissions and non-volatile fraction, for MK1, HFO and MDO during operation at 35% engine load. For HFO and MDO, the emissions, both the total and non-volatile fraction, were dominated by nanoparticles (85-88% for HFO and 94-98% for MDO). For MK1 approximately 60% of the emitted particles were in the size range of nanoparticles. The two marine fuel oils investigated showed a pronounced peak at 10 nm, and generated higher emissions of particles with Dp <22 nm compared to combustion of MK1. One explanation for this difference is the difference in FSC because some of these particles were of volatile character (Figure 7-5a). However, other fuel characteristics should also be considered because a similar difference between the fuels is observed in the non-volatile fraction as well (Figure 7-5b). In terms of particles with Dp >22 nm, the combustion of MK1 and MDO resulted in similar emissions of particles of various sizes, whereas the combustion of HFO resulted in a different trend with higher emissions of particles with Dp >52 nm. HFO showed a peak at 100-120 nm, whereas MDO and MK1 showed a peak at 45-50 nm. This indicates that other fuel characteristics than FSC have an impact on the emission of these particles and that it is important to consider these as well. Examples of fuel characteristics that should be considered include the viscosity, the contents of aromatics, carbon residue, ash and metals.

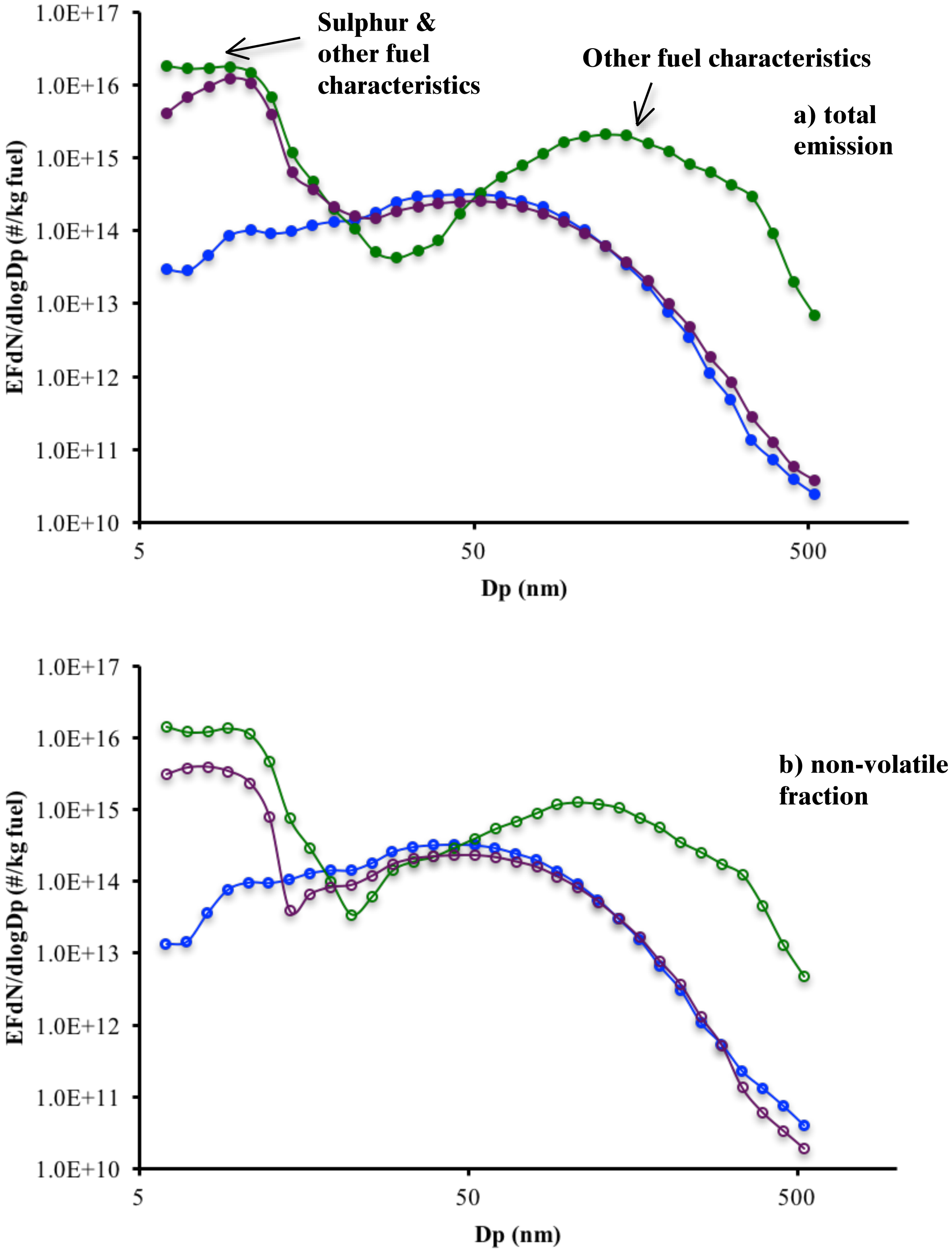

Figure 7-5: Size resolved EF_{PN} for a) total particle emissions and b) non-volatile fraction for MK1 (blue), MDO (purple) and HFO (green) at 35% engine load. Note: both axes use logarithmic scales.

7.2.1 Impact of the Content of Aromatics

As highlighted above and in the litterature, e.g., Bockhorn (1994), a compound that affects the particle emissions, especially the formation of non-volatile soot particles, is aromatics. This was investigated further in Paper IV, in which MK1 was used as a reference fuel and was doped with an aromatic mixture to achieve higher concentrations of aromatics in the fuel. The two investigated aromatic concentrations were 23 %vol and 30 %vol, which are within the same range as the concentrations of aromatics in marine fuel oils. The hypothesis for the study in Paper IV was that an increased content of aromatics will increase the particle emissions. However, the hypothesis was rejected, except for operation at idle. Similar trends were observed for both test-bed engines used in the study. The increased content of aromatics in the fuel reduced the CN of the fuel and thereby likely increased the ignition delay, which led to a longer premixing time and reduced formation of particles in the combustion process.

Data for EF_{PN} for the fuel-blends (MK1 doped with aromatic mixture) and the reference fuel were compared to the EFs for HFO and MDO from Paper I. The content of aromatics was <4.8 %vol in MK1, 7.7 %vol in HFO and 18.1 %vol in MDO. EF_{PN}, both the total emissions and the non-volatile fraction, were lower for the fuel-blends compared to those for the other three fuels at high engine loads, despite a higher content of aromatics in the fuel-blends. The main difference between the particle emissions was for particles with Dp between 5.6-20 nm. With respect to these particles, the combustion of HFO and MDO generated considerably higher emissions compared to the fuel-blend with a higher content of aromatics (Table 3 in Paper IV). When operating at idle, the fuel-blends resulted in emissions that were higher than those of MK1 but lower than those of HFO and MDO. However, the emissions of non-volatile particles were more at the same level for HFO, MDO and fuel-blends.

The study made in Paper IV and the comparison with marine fuel oils emphasize that the content of aromatics may affect the particle emissions. However, other fuel characteristics seem to have an impact as well. This was further strengthened by the studies made in Paper IV in which an ignition improver was added to the fuel-blends. The ignition improver increased the CN of the fuel-blend to a CN similar to that of MK1. However, the particle emissions did not increase to a level similar to that of MK1 (Figure 3 in Paper IV).

8 Discussion and Considerations

This chapter is divided into two different parts. The first part (8.1) presents methodological considerations regarding dilution, the aerosol instruments used in Papers I-IV, filter sampling vs. real-time measurements and on-board measurements vs. measurements in test-bed engine lab facilities. In the second part (8.2), the results presented in section 7 and Papers I-IV are compared to previous studies in this field and are discussed, with respect to regulations (both in the maritime sector and for land-based transportation) and the impacts on human health and climate.

8.1 Methodological Considerations

At present there are no international regulations directly limiting the particle emissions. However, the FSC regulations are assumed to reduce the emissions of particles, and there is an on-going work within the IMO to establish a legal framework to regulate BC emissions (see section 2.3). The work involved with the BC legal framework includes, among others, the issue of evaluating of measurement methods appropriate for this case. The best ways to measure particles and to compare data from different measurements using different instruments based on different measurement techniques were discussed during the time as PhD-student. The calculated EFs found in references originate from measurements conducted with different experimental set-ups and conditions. Furthermore, the dilution method of a sample may have a significant impact on the measured particle emissions.

The measurements done in the included papers of this thesis consider both the total particle emissions and the non-volatile fraction. To study the non-volatile fraction, a TD was used. By using a TD, it is possible to investigate the characteristics of particle emissions under high-temperature conditions that are similar to the parts of the exhaust gas channel that are closest to the engine and result in an estimation of the non-volatile fraction of the particle emissions. The measured non-volatile fraction includes BC, but it is not possible to specify the concentration of BC in the emissions. For analysis of BC, other methods are used and provide a better estimate of the amount of BC in the emissions (Petzold et al., 2013).

The emission standards for particle emissions from heavy-duty diesel engines considers non-volatile particles with Dp >23 nm (United Nations, 2011). However, with respect to ship operations and the fact that the marine fuel oils used have a considerably higher FSC than fuels used for other transport sectors, even in SECAs, measurements of only the non-volatile particles do not result in a true estimate of the emissions. Both the non-volatile and volatile fractions of the emissions are important to consider because both affect human health and the climate. Measurements of the non-volatile fraction, which includes BC, is valuable in the evaluation of the effects of ship operations on climate and are critical to the on-going work on the regulation of BC emissions. Measurements of the total particle emissions result in information on the characteristics of the emitted aerosols, which is useful in dispersion modelling and impact assessments. However, it is important to understand that the results from these two types of measurements will differ and that the two fractions are affected by different factors, such as dilution conditions.

8.1.1 Dilution

The method of dilution (DRs and dilution conditions) of a sample may have a significant impact on the measured particle emissions. As presented in 2.4.4 the purposes of dilution are varied. The purpose of the dilution in the studies included in this thesis was to make the particle emissions measurable and to study the particle number size distribution in the funnel and the particle emissions that are emitted to atmosphere. Therefore, the lowest DR possible was chosen. Furthermore, the aim was to use same DRs and dilution conditions when measurements were repeated, which was the case in Papers I, III and IV. However, instrumental limitations, such as the measureable ranges of particles and of NO[52], required changes to the planned set-up of the DRs and conditions. The instability of the dilution system (here the FPS) also influenced the plans and required adjustment to the current conditions and situations.

The same dilution system, the FPS, was used for all on-line measurements presented in this thesis. The raw exhaust was diluted in two steps by the FPS, first with preheated air with a temperature close to that of the exhaust gases and second with air at ambient temperature. Even if preheated air was used for dilution, a considerable amount of nanoparticles was observed in the number size distribution. The impact of the DR on the measured PN concentration and number size distribution has been reported in several papers (Abdul-Khalek et al., 1998, Abdul-Khalek et al., 1999, Lyyränen et al., 2004, Mathis et al., 2004, Ushakov et al., 2014). To investigate the effect of the DR and dilution conditions on the particle measurements with a marine application, DR tests were made in the test-bed engine lab used in Papers I and IV and during Campaign 1 of the on-board measurements presented in Paper III. In Paper III, high DRs (97-111) had to be used during the measurements to accommodate the limitations of the instrument measuring NO after the FPS. However, tests with low DRs (19-21) and low primary dilution temperatures were made. During the tests in the test-bed engine lab, a number of DRs were tested both with and without a TD heated to 300°C. Both tests resulted in similar trends and estimates the effects of the chosen DR on the particle emissions. There is a clear effect of DR on particles in nucleation mode (Dp approximately 10 nm). These particles were mainly of volatile character because a major proportion of them disappeared when the sample was drawn through the TD (Figure 8-1a). Furthermore, the concentration of particles in nucleation mode was reduced when the DR was increased (Figure 8-1b) because low DRs favour nucleation and growth (Mathis et al., 2004, Abdul-Khalek et al., 1999). The temperature of the primary dilution gas and DR had no impact on the non-volatile fraction. Both tests show that there was little to no influence of DR on particles in accumulation mode, which is similar to the findings reported by Abdul-Khalek et al. (1999) and (Liu et al., 2007). Furthermore, these results are in line with previous studies on the impact of DR on particle emissions from marine fuel oils and marine diesel engines made on-board an operating ship by Hallquist et al. (2013a).

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[52] The measurable range of NO for the chemiluminescence instrument (TH42i, Thermo Scientific), used for verification of the DR, is 0-20 ppm.

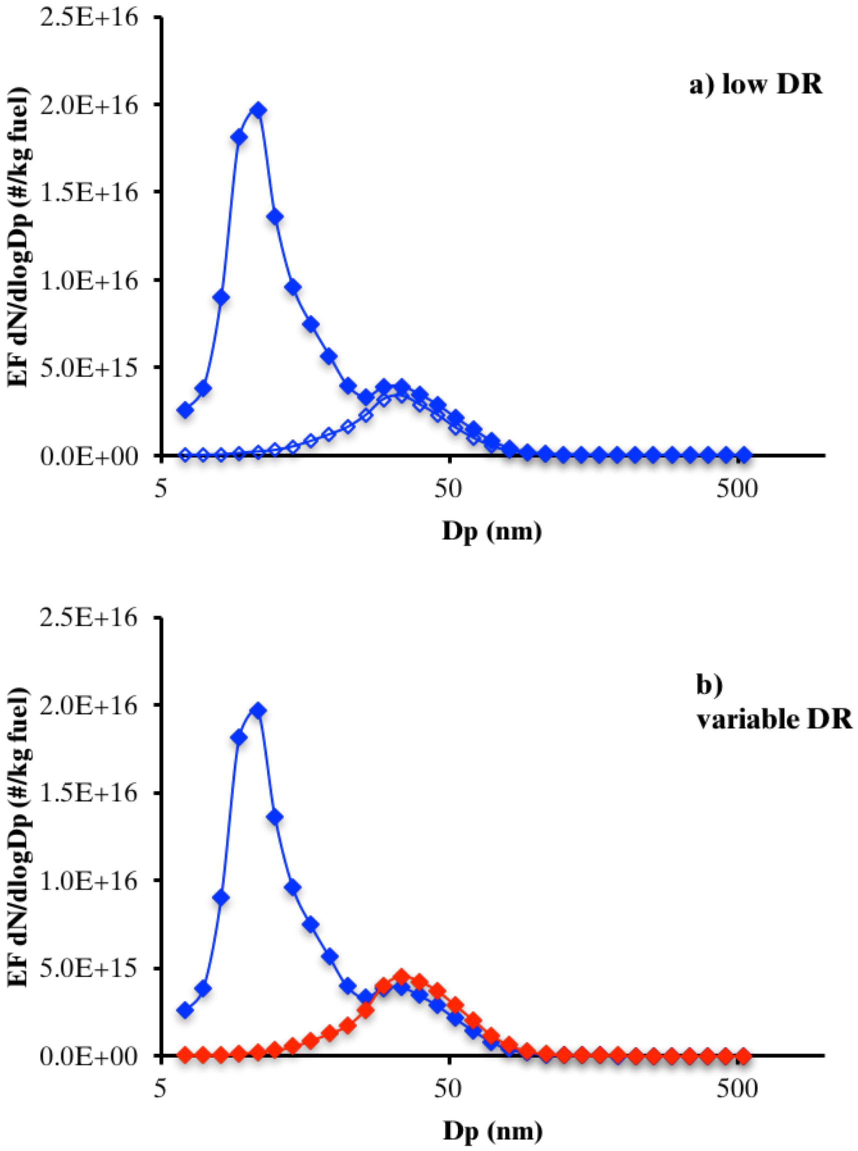

Figure 8-1: Impact of a) a low DR, low dilution temperature and use of TD and b) variable DR on the measured size distribution of emitted particles from a ship operating at 50% engine load. The blue line represents the case of low DR and low DR temperature. The red line represents high DR and high primary dilution temperature. Filled symbols represent the total particle emissions and unfilled the non-volatile fraction.

Because marine fuel oils have high contents of sulphur and heavy hydrocarbons, which are compounds that enhance nucleation of volatile and semi-volatile particles (Liu et al., 2007), it is important to consider DRs and dilution conditions when evaluating the results from these types of particle measurements. This is important for particle emissions from engines running on natural gas as well (Jayaratne et al., 2012, Alanen et al., 2015). As discussed above, the DRs and dilution conditions affect the nucleation and amount of volatile and semi-volatile particles measured and, consequently the results. The effect of using high DRs was observed in the measurements in Paper III, where there were small differences between the total particle emissions and the non-volatile fraction. Consequently, the amounts of volatile compounds in the emissions were likely higher than measured, which would have been more clear if lower DRs were used.

8.1.2 Aerosol Measurements

The measurements done during the studies in this thesis have included both real-time measurements, mainly with the EEPS and Dust monitor, and filter sampling. As described in section 2.4, the method for classifying of the particles differs between the EEPS and Dust monitor. The EEPS classifies the particles according to their electrical mobility, while the Dust monitor is an optical instrument that classifies the particles with light scattering technology (TSI, 2006, Grimm Aerosol Technik GmbH & Co KG, 2010). Furthermore, the instruments measure particles in different size ranges. However, there is an overlap in the measureable sizes of these two instruments, and this overlap can be used for comparison of the two techniques. The overlap includes particles in the size range of 300-560 nm. In a comparison of the particles in this size range, the Dust monitor tended to produce higher particle concentration results in the overlapping range (see example in Figure 2 in Paper III). The purpose of using the Dust monitor was to gather data about the amount of larger particles (Dp >300 nm) in the emissions, not to compare EF_{PN} or EF_{PM} calculated from the measurements with the two respective instruments. This would be misleading because the instruments measure different size ranges. It is important to consider the differences between instruments in comparisons of data from different measurements and when compiling data for emission inventories and impact assessments.

During the completion of this PhD, the accuracy and reliability of the EEPS, compared to instruments with lower temporal resolution, have been subjects of discussion. The EEPS was used in the papers presented in this thesis to better understand the emission of smaller particles and the size distributions. Furthermore, the EEPS was developed to measure of particle emissions from different combustion sources for which a high temporal resolution and a wide measurable size range are needed. The SMPS can be used to measure emissions of smaller particles and the size distribution as well. However, it has a lower temporal resolution, and the selected temporal resolution affects the size range of the measured particles (Levin et al., 2015). In Jeong and Evans (2009), a correction of the data from instruments with high temporal resolutions is suggested. This method is further developed in Zimmerman et al. (2015) and can be applied to diesel-generated particles as well. In the studies made in this thesis, this data correction could not be done because this method requires that measurements with both EEPS and SMPS are made in parallel.

Another aspect to consider in a discussion about aerosol measurements is the issue of the particle mass calculated from measured PN with real-time instrumentation versus the particle mass sampled by filters. As shown in Table 2-2, filter sampling is frequently used for particle measurements in marine applications. The data presented in Papers I-IV in this thesis suggest that dissimilarities exist between the EF_{PM} based on the real-time measurements and the EF_{TSP} calculated from filter sampling. In general, EF_{TSP} values are higher than the corresponding values of EF_{PM}. The differences may depend on the assumed density of particles when calculating PM from PN (Kasper et al., 2007). The density used for the real-time instrument measurements was set to unity. However, previous studies have shown that the density differs from unity and decrease with increasing particle size (Barone et al., 2011, Ahlvik et al., 1998, Park et al., 2003, Virtanen et al., 2002, Olfert et al., 2007). Furthermore, differences between the sampling methods, evaporation of volatile species (Kasper et al., 2007) and DR will affect the results as well (Lipsky and Robinson, 2006). However, sampling of particles on filters provides the opportunity to perform more types of analyses (e.g., chemical composition, such as inorganic elements and EC/OC) on the particles emitted than is possible using real-time instruments.

8.1.3 Reflections on Future Measurements

A major question in future studies of particle emissions from ship operations is 'How should measurements on-board ships be made?'. This question is particularly interesting with respect to the on-going work on the development of BC emission regulations (2.3), which includes an evaluation of the possible applicable methods for conduct measurements on-board operating ships. Currently, the accepted method for conducting measurements of particle emissions on operating ships is ISO 8178 (see section 2.5). From a marine perspective, this standard has some disadvantages. First, the acceptable FSC is in most cases greater than 0.8 %m/m in marine applications. In designated SECAs, the ships have to use marine fuels with a FSC of less than 0.1 %m/m, but the global cap is considerably higher. Second, the standard does not consider the number or the sizes of the emitted particles. As discussed throughout this thesis, these data are important in health impact assessments. Third, this standard includes both volatile and non-volatile particles. The volatile particles are sensitive to the sampling conditions (i.e., dilution and engine load) and fuel type, resulting in poor repeatability of the measurements. Therefore, only non-volatile particles are considered in the regulations of PN emissions from land-based vehicles (United Nations, 2011). As discussed earlier, it is interesting to consider both fractions in marine applications. However, because the volatile fraction is more sensitive to dilution conditions and is related to the FSC, among other factors, it is not an easy task to develop a standard for particle emission measurements from ship operations that are repeatable, highly accurate, understandable and to a certain degree easy to perform.

As mentioned above, the dilution, instrumentation and sampling technique have an impact on the outcome of the measurement and their repeatability and accuracy. Use of a dilution system results in an uncertainty in the measured data but is essential for some aerosol instruments. In discussions of instrumentation and sampling technique (real-time vs. filter), it is difficult to rule out one technique in favour of the other. Measurements with both filter sampling and real-time instruments result in a more complete understanding of the particle emissions and increase the amount of data that can be collected from the measurement process. The real-time measurements provide data on the number size distribution, which are important when considering impacts on health. The analyses of particles sampled by filters result in information on the chemical content (BC, EC, OC and inorganic compounds), which is valuable in evaluating the impact of particles on health and climate (see section 2.1 and 2.2).

Another question to consider is 'What types of measurements are most useful when evaluating and controlling particle emissions from ships?'. In this context, the measurement 'types' refer to test-bed engine measurements, on-board measurements and plume measurements and 'controlling' to future regulations of particle emissions from operating ships. The measurements done in this thesis consider two types of measurements, whereas in other studies all three types of measurements were used (section 2.5). However, the different types of measurements have both advantages and disadvantages (discussed in section 2.5). In test-bed and on-board measurements, the DR used can move the studies in two different directions, depending on the aim with the study. Plume measurements result in data on how the emitted particles disperse in the ambient air. However, these measurements will not generate data on the properties of the particle emissions in the funnel and have a limited ability to relate the emissions to operating conditions. In an evaluation of the impact on health and climate from particle emissions from operating ships, results from all three types of measurements are of interest and provide a broader view of the actual emissions and their dispersion in, for example, coastal and port areas.

Considering the regulation aspect, some type of international standard method should be developed and applied to measurements conducted on-board operating ships. This standardized method should include measurements of both PN and PM. A combination of measurements on test-bed engines and marine diesel engines on-board operating ships would be valuable in the development of a standard method. However, if the particle emissions from operating ships become regulated, how are authorities able to determine that the regulations are being followed? Is it possible to perform measurements in the plume by airplane, from boats or on land next to fairways and use these data to calculate EFs for particle emissions in the plume? Alternatively, will it only be possible to use on-board measurements?

8.2 Discussion of Results and Implications

The aim with this thesis is to characterize the particle emissions generated by the combustion of marine fuels that comply with the allowed FSC in SECAs and to investigate how the FSC and other fuel characteristics influence particle emissions from ship operations. The results presented in Papers I-IV and in section 7 are summarised in Table 8-1.

Table 8-1: Summary of the results presented in this thesis and included papers.

	Factor	PN	PM	BC	OC
Paper I	Reduced FSC	↑↓	↑		
	Changed fuel characteristics^a	↓	↓	↓	
	Increased engine load (idle vs. 35%)	↓	↑↓		
Paper II	Use of LNG^b	↓	↓		
Paper III	Reduced FSC	↑↓	↓		
	Changed fuel characteristics^c	↑↓	↓	→	↓
	Increased engine load	↑↓	↓	↓	↑↓
Paper IV	Increased content of aromatics	↑↓	↑↓	→	
	Increased engine load (idle vs. 35-50%)	↓	↓		

^{a}Change of other fuel characteristics than FSC, including reduced ash content, carbon residue, some metals and viscosity; ^{b}Includes reduced FSC and change in fuel characteristics; ^{c}Change of other fuel characteristics than FSC, including reduced ash content, carbon residue, aromatics, some metals and viscosity.

As demonstrated in Figure 5-2, a correlation between FSC and PM emissions exists. In Figure 8-2 (an updated version of Figure 5-2), the values of EF_{PM} presented in Papers I-III are compared with values reported in the literature. The data from the on-board measurements in Paper III (orange circles) are somewhat lower or similar to previously reported values. The values of EF_{PM} from measurements on the test-bed engine reported in Paper I (blue circles) are in line with the on-board measurements, but somewhat lower than other test-bed engine measurements. The increase in EF_{PM} with decreasing FSC can also be related to other fuel characteristics because the HFO used in Paper I had a lower FSC than the MDO used. Figure 8-2 indicates that the impact of FSC on EF_{PM} levels out for FSCs below 1.0 %m/m. However, the reduction of the allowed FSC at the global level from 3.5 %m/m S to 0.5 %m/m S in 2020 will result in a considerable reduction in the EF_{PM} (from approximately 2.5 g/kWh to less than 0.5 g/kWh). The EF_{PM} associated with the use of LNG as the primary energy source (green circle) is considerably lower than the EF_{PM} associated from other traditional marine fuel oils. Furthermore, the EF_{PM} for LNG (0.0022 g/kWh) is lower than the EF_{PM} for MK1 (0.02 g/kWh), MK3 (0.014 g/kWh) and the acceptable EF_{PM} value for trucks in the Euro VI-standard (0.01 g/kWh). The EF_{PM} for the HFO and RMB30 is similar to the accepted value for IWW (0.5 g/kWh for the largest cylinders).

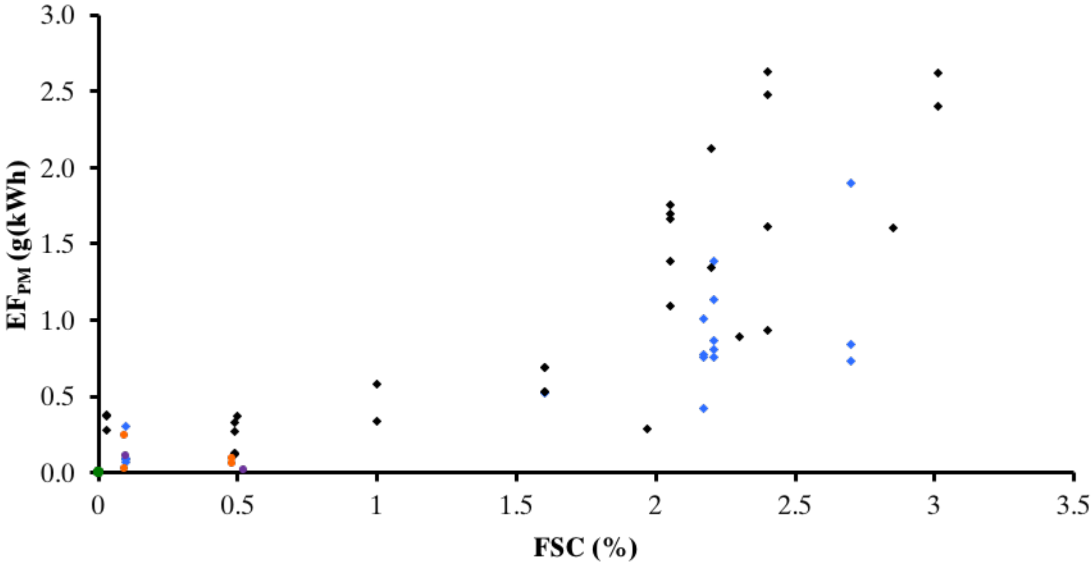

Figure 8-2: Comparison of EF_{PM} values from measurements in Paper I (purple circles), Paper II (green circles) and Paper III (orange circles) with values from references based on on-board measurements (black diamonds) (Hallquist et al., 2013a, Moldanová et al., 2009, Moldanová et al., 2013, Fridell and Salo, 2014, Fridell et al., 2008, Winnes and Fridell, 2010, Winnes and Fridell, 2009, Agrawal et al., 2008a, Agrawal et al., 2010, Agrawal et al., 2008b, Murphy et al., 2009) and test-bed engine measurements (blue diamonds) (Petzold et al., 2011, Petzold et al., 2010, Mueller et al., 2015, Sippula et al., 2014).

Based on the data provided in Table 5-1, the emissions of BC were expected to be related to fuel characteristics other than the FSC. However, the fuel shift from HFO to RMB30 showed no significant impact on the BC emissions. Instead, these emissions were more closely related to the engine load. The engine load also exhibited an impact on the PN and PM emissions as well. A reduced engine load can result in an increase in PN emissions, which may be related to increased incomplete combustion in association with reduced engine load and changed combustion conditions. The reduced temperature in the exhaust gases at low engine loads can result in enhanced formation of new particles from unburned fuel and lubrication oil. These compounds can also condense on existing particles (Kittelson, 1998). These processes emphasize the importance of considering particle emissions from ship operations in port areas and while the ships are docked.

Tables 5-1 and 8-1 show that there is no clear correlation between FSC and PN emissions and that a reduced FSC does not necessarily result in reduced PN emissions. Furthermore, a change in other fuel characteristics may not result in reduced PN emissions either. As indicated in Diesch et al. (2013), there are several factors, such as engine load and engine type, that can have an impact on PN emissions from ship operations, which may explain why this correlation is weak. Furthermore, few studies have done measurements on PN emissions from marine fuel oils with various FSC. In this thesis, the focus is on marine fuel oils with FSCs that comply with Regulation 14 in MARPOL Annex VI. The poor correlation between PN emissions and FSC, for fuels with low FSCs (less than 1 %m/m), may be because the sulphate particles only contribute to a limited fraction of the total particle emissions. Further removal of sulphate particles via an even lower FSC will have a limited impact on the particles emitted (Beecken, 2015).

In this investigation focused on compliance with the FSC regulation, the use of LNG for propulsion was the only strategy that resulted in a significant reduction in the PN emissions and consequently reduced emissions of harmful particles (which was one driving force behind the implementation of the regulation). However, particles are still emitted from DF engines that use LNG as the primary energy source, and these particles are small in size. For the smallest particles (Dp <10 nm), the emissions can be even higher than from the combustion of diesel fuels (Hong and Kwon, 2010). As presented in section 2.1, the size of the emitted particles is one of the main properties to consider with respect to impacts on human health. In Paper II, the suggested origin of the particles is the lubrication oil used, similar to the findings in Alanen et al. (2015) and Yoon et al. (2014). Additionally, the combustion of the pilot fuel used in DF engines generates particles. The origin of particles associated with traditional marine fuels is different and, as shown, a reduction in FSC and changes in other fuel characteristics do not necessarily reduce the PN emissions. The fuel characteristics discussed in Papers I, III and IV are the viscosity and contents of ash, carbon residue, metals, and aromatics. However, the results presented in Paper IV indicate that the content of aromatics may not play a crucial role.

The Euro VI standard regulates the PN emissions from heavy-duty diesel engines with the accepted value set to $6.0\text{-}8.0*10^{11}$ #/kWh for non-volatile particles with Dp >23 nm. A future regulation of PN emissions for IWW within the EU is expected to be similar (see section 2.3). Table 8-2 shows EF_{PN} values for the non-volatile fraction from measurements reported in Papers I-III. The values are presented for the whole size range measured by the EEPS[53] and for the fraction with Dp >23 nm. The ratio of EF_{PN} for particles with Dp >23 nm to EF_{PN} for the whole size range is also included. The data in Table 8-2 indicate that the use of LNG as a marine fuel resulted in EF_{PN} values that were less than the values in the Euro VI standard and a possible future limit for IWW. The EF_{PN} values for the other fuels are considerably higher. Even the EF_{PN} values for MK1 and MK3, which are diesel fuels used for land-based transport and along IWW, are higher than the Euro VI standard. Therefore, factors other than just the choice of fuel affects the PN emissions. Furthermore, data on the percentage of the EF_{PN} for particles with Dp >23 nm relative to the EF_{PN} for the whole size range indicates that the particle emissions from RMB30 and LNG are dominated by particles with Dp <25 nm. Thus, a major portion of the particle emissions will be excluded from the measurements if a future regulation includes a lower size limit similar to the Euro VI standard. This would consequently make it difficult to properly assess the impacts on human health.

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[53] EF_{PN} presented for the size range 5.6-560 nm can be seen as EF_{PN} for all particles emitted because only a few large particles are emitted and have no significant impact on the data presented here.

Table 8-2: EF_{PN} values for the non-volatile fraction of particle emissions divided into two size ranges, 5.6-560 nm and 25-560 nm, and the percentage of particles with Dp 25-560 nm compared to Dp 5.6-560 nm for the investigated fuels in Papers I-III.

		EF_{PN} (#/kWh) non-volatile fraction		
Fuel type	**Engine load (% of MCR)**	**Dp 5.6-560 nm**	**Dp 25-560 nm**	**% of EF_{PN} 5.6-560 nm**
$HFO^{paper\ III}$	85	$3.4*10^{14}$	$2.7*10^{14}$	80
	50	$3.7*10^{14}$	$3.0*10^{14}$	81
RMB30	82	$3.4*10^{14}$	$9.4*10^{13}$	28
	38	$2.6*10^{14}$	$9.5*10^{13}$	37
LNG	90	$1.2*10^{12}$	$3.7*10^{11}$	32
	40	$1.0*10^{12}$	$3.0*10^{11}$	31
MK1	35	$5.1*10^{13}$	$3.8*10^{13}$	75
MK3	35	$6.5*10^{13}$	$4.1*10^{13}$	63
MDO	35	$7.7*10^{14}$	$4.3*10^{14}$	55
$HFO^{paper\ I}$	35	$1.7*10^{15}$	$1.6*10^{14}$	9.4

As mentioned before, the reduction in harmful particles was a driving force for the implementation of the FSC regulations at the global level and in designated SECAs. However, the results in Paper III indicate that the strategy of using low-sulphur residual marine fuel oils similar to RMB30 will not reduce the number of particles emitted (here especially at higher engine loads). The findings also emphasize the importance of measuring and regulating both PN and PM emissions. Furthermore, the emitted particles tend to be smaller than those produced by a HFO with low FSC. This indicates that the positive effects on human health from implementation of the FSC regulation may not be as large as expected. Paper I presents results that indicate that an HFO with a lower FSC than a MDO generates higher PN emissions, despite its lower FSC. Therefore, reduced FSCs likely will not be the only solution for reducing emissions of particles from operating ships, and other fuel characteristics need to be considered.

9 Concluding Remarks

The objectives of this thesis are to characterize the particle emissions from marine engines using fuels that comply with the allowed FSC in SECAs and to investigate how the FSC and other fuel characteristics influence particle emissions from ships. Two strategies used to comply with the FSC regulation and investigated here, are a fuel shift to a low-sulphur residual marine fuel oil and use of an alternative fuel, here LNG.

The results presented in this thesis indicate that the particle emissions in SECAs are dominated by nanoparticles, independent of the fuel type used. Use of LNG results in considerably reduced particle emissions compared to traditional marine fuel oils. A fuel shift from HFO to RMB30 has no or little effect on the PN emissions and the emissions are dominated by even smaller particles. However, the PM emissions were reduced.

The FSC primarily affect particles with a Dp <50 nm, whereas other fuel characteristics affect particles in all sizes. Furthermore, reducing the FSC is not the only solution for reducing emissions of particles from ships. Other fuel characteristics need to be considered. However, the content of aromatics may not be the next factor to consider.

The results also indicate that it is important to consider both PN and PM emissions in measurements of particle emissions from ships and in possible future regulation of these emissions. However, the results also indicate that dilution conditions, such as DR and which particles to measure (size and non-volatile fraction vs. total emission) have to be considered in the design of measurement standards in regulations.

The FSC regulation is a step in the right direction towards reduced particle emissions, if alternative fuels, such as LNG, or marine fuels, more similar to distillates, is used. Furthermore, the positive effects on human health from implementation of the FSC regulation may not be as large as expected if not other fuel characteristics are considered as well.

10 Future Work

This thesis is a part of the initial work on particle emissions from ship operations. The regulation of FSC has opened for more research within this field and some of these new topics are presented here and can be seen as a possible continuation of this thesis.

One interesting subject is more measurements of emissions generated by the combustion of various hybrid fuels and other marine fuels, such as MDO and MGO that comply with the FSC regulation in SECAs. There are a number of hybrid fuels on the market today, and they have different fuel characteristics, which consequently impact the emissions. Additionally, one batch of a given hybrid fuel can differ from another batch of the same fuel. Future projects designed to examine this subject could test different hybrid fuels in test-bed engine lab facilities and on-board operating ships. It would be especially valuable to perform measurements using MDO or MGO on-board the ship studied in Paper III.

Another subject is the investigation of emissions from alternative fuels. One alternative fuel of interest is methanol. Currently, one ship uses methanol as the primary energy source, and probably there are more to come. It would be interesting to make more measurements of LNG-related emissions on-board other ships with other types of gas engines and additional measurements of the methane slip are needed.

As the FSC has been regulated and reduced, in some years even at the global level, it is interesting to investigate how other fuel characteristics and the lubrication oil affect the particle emissions and which factors govern the formation of particles generated from different types of fuels and lubrication oils. It would also be interesting to study how different engine parameters, such as timing of injection, affect the emissions. These studies can be done in test-bed engine lab facilities, and the results can be valuable and increase the understanding on how the engine, operating parameters, fuels and lubrication oils affect the emissions.

For land-based transportation, diesel particulate filters are used to reduce the particle emissions. This is not yet standard practice for marine transportation due to a number of reasons, including high FSCs and pressure drops in the exhaust gas channels that reduce the performance of the diesel particulate filters. Tests of different diesel particulate filters with different marine fuels is a very interesting field of future studies that could provide information about whether the use of diesel particulate filters is a potential solution in the marine transportation sector.

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Maria Zetterdahl
Gothenburg, April 2016

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