Soot particles from shipping: Analysing emission factors

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Nicklas Mauritzson

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Abstract

Emissions of air pollutants from shipping in Europe result in about 50 000 premature deaths every year. Soot particles, also called black carbon, are particularly hazardous to human health when inhaled. The adverse health effects are especially a danger in coastal areas, but the particles can travel further away with the wind. These soot particles also have an effect on the climate. Fresh soot particles are known to be ineffective cloud condensation nuclei for cloud droplet formation, whereas aged soot particles with condensed inorganic sulphuric acid on the particle surface may act as effective cloud condensation nuclei. This leads to changing properties of clouds, thereby changing the cloud reflection of incoming solar shortwave radiation. The particles can also deposit on surfaces of snow and ice, where they have a warming effect. The snow and ice melts, causing a reduced amount of reflected sunlight.

The aim of this study was to calculate the emissions of soot particles from ships in Gothenburg. The amount of soot emissions from ships was compared to the amount of fuel used. This was done by calculating the emission factor for soot and its absorption coefficient. Calculations of the emission factors in ship plumes were made on five selected days. The initial data was gathered over a period of a month outside Gothenburg harbor in the fall of 2014. The field station containing the measurement instruments was located 500 meters downwind from the shipping lane. Plumes were just over a minute old when they reached the field station.

A sliding percentile-based method was used in order to separate plumes from background concentrations of CO_2 and soot particles. Subsequently, the emission factors were calculated. The total number of analysed ship plumes was 228. Some of which are the same ships arriving and leaving the harbor. When plumes were present, the amount of CO_2 rose above the background levels with a minimum of 2 ppm. Plumes could increase with as much as 35 ppm.

The emission factor for black carbon, or soot, was estimated at 0.57 (± 1.40) grams of black carbon per kilogram of fuel. This is an average number for the shipping fleet connected to Gothenburg, which should be able to be applied to the entire shipping fleet travelling in the SECA area in Europe. Additionally, it is not entirely certain how lower fuel sulphur content affect the emissions of black carbon. There are no identical studies done so far which makes it difficult to reach a conclusion whether the emissions of black carbon particles have decreased or not. When looking at individual ships, no clear difference could be observed. Oil tankers and cargo ro-ro's usually emits the most black carbon but also include vessels with lower emissions. All passenger ships have different emission factors.

Not many studies have been done on the subject. It is therefore important to further study this in order to fully understand the effects on soot particles when reducing sulphur.

Sammanfattning

Emissioner av luftföroreningar från sjöfarten i Europa leder till cirka 50 000 förtida dödsfall per år. Sotpartiklar i synnerhet är farliga för hälsan vid inandning. De negativa hälsoeffekterna är framförallt en fara vid kustområden, men partiklarna kan färdas längre avstånd med hjälp av vinden. Dessa sotpartiklar har även en effekt på klimatet. De är ineffektiva som molnkondensationskärnor för molndroppsbildning, medan åldrade sotpartiklar med kondenserat sulfat på ytan möjligen kan agera som effektiva molnkondensationskärnor. Sotpartiklarna förändrar molnens reflektion av inkommande kortvågig solstrålning. Partiklarna kan också deponeras på ytor av snö och is där de har en värmande effekt. Effekten blir att snö och is smälter bort vilket minskar mängden reflekterat solljus.

I denna studie undersöktes mängden sot som avges från fartyg i förhållande till mängden bränsle som används. Detta gjordes genom att beräkna emissionsfaktorn för sot och dess absorptionskoefficient. Beräkningar av emissionsfaktorer från fartygsplymer gjordes på fem utvalda dagar. De ursprungliga mätdata samlades in under en period av en månad utanför Göteborgs hamn under hösten 2014. Fältstation med mätinstrumenten var belägen 500 meter nedvind från sjöfartsleden. Plymerna var drygt en minut gamla när de kom fram till fältstationen.

En glidande percentil-baserad metod användes för att separera plymerna från bakgrundshalterna av CO_2 och sot. Därefter beräknades emissionsfaktorerna. Det totala antalet analyserade fartygsplymer var 228 stycken. En del utav dessa är samma fartyg som både anländer och lämnar hamnen. Skeppsplymer identifierades som en stigning av CO_2 med minst 2 ppm. Plymer kunde öka med så mycket som upp till 35 ppm.

Emissionsfaktorn för sot beräknades till 0,57 (± 1,40) gram sot per kilogram bränsle. Detta är ett medelvärde för skeppsflottan i kontakt med Göteborg, vilket bör kunna appliceras på hela skeppsflottan som färdas i SECA-området i Europa. Dessutom är det inte helt säkert hur lägre svavelhalt påverkar utsläppen av sot. Det finns inga identiska studier som gjorts hittills, vilket gör det svårt att nå en slutsats huruvida utsläppen av sotpartiklar har minskat eller inte. Ingen tydlig skillnad kunde inte heller observeras för enskilda fartyg. Tankfartyg och lastfartyg avger oftast mest sot men har även några individuella fartyg med lägre utsläpp. Alla passagerarfartyg har varierande emissionsfaktorer.

Det är inte många studier som gjorts på detta ämne. Därför är det viktigt att vidare studera detta för att till fullo förstå effekter på sot partiklar vid en reduktion av svavel.

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1 Introduction

This chapter contains a short introduction to the background leading to this study, and existing problems surrounding the issue. Aim and objectives, and disposition are presented at the end.

1.1 Problem definition

A gas containing solid or liquid particles is called an aerosol. The air that we breathe is an aerosol, which can contain many solid or liquid aerosol particles (Hinds, 1999). These aerosol particles can remain suspended in the atmosphere for long periods of time, depending on the size of the particles. The size of particles range from 1 nm in diameter to 100 μm in diameter. Both the properties and concentrations of particles vary with size and mass. Particles are naturally formed from for example sea salt through the breaking of waves, or windblown dry dust (Barry and Chorley, 2003). Anthropogenic sources include mechanical grinding as well as various combustion sources, such as vehicle engine combustion and power plant combustion.

Particles in the atmosphere have a considerable effect on human health (Sarnat et al., 2001). Air pollution is accompanied with health effects such as increased mortality, respiratory and cardiovascular diseases. It is estimated that anthropogenic particles originated from other countries are the cause of 3500 premature deaths per year in Sweden (Forsberg et al., 2005). Local sources of particles in Sweden have been estimated to be the cause of 1800 premature deaths per year.

Not only do these particles affect the health of breathing organisms, such as humans, but they also have an effect on earth's climate. The effects of aerosols are divided into two: direct and indirect effects (Haywood and Boucher, 2000). Direct effects include scattering and absorption of radiation, both solar and terrestrial. Indirect effects include an influence on the properties of clouds as well as precipitation.

One important source of anthropogenic particles is ship emissions. There are about 80 000 merchant ships across the world (Equasis, 2013), many of which use fuel with worse quality than vehicles on land (Lack et al., 2009). Fuel quality and emissions aren't strongly regulated over the open sea. The chemical composition of particles from ship emissions is most likely dominated by sulphur and organic matter, and slightly lower black carbon content. Especially black carbon is of significance due to its hazardous properties when inhaled. Black carbon, or soot, is carbon particles with tar impregnated into them. They form during the combustion of carbonaceous material. In Europe, ship emissions are responsible for an estimated 50 000 premature deaths every year (Brandt, et al., 2011).

The chemical and size dependant composition of particles from ship emissions have not yet been properly measured and observed to this day. Therefore, there is a lack of knowledge in this particular field. This is especially evident for the difference in emissions between different ship types, as well as how regulations affect particle emissions, and the chemical composition of particles. How these emissions affect climate and human health has not been properly investigated either.

1.2 Aim and objectives

The aim of this study is to take a closer look on measured ship emissions. There is a Sulphur Emission Control Area (SECA) in Europe that regulates the allowed sulphur fuel content. The last implemented ship emission regulation was in 2010, with a maximum limit of 1 % sulphur in the ship fuel. In 2015

this will be further reduced to 0.1 %. In this study the emissions of black carbon particles from the shipping fleet will be quantified, and potential differences between ship-types will be investigated.

The objectives of this study were to answer the following:
- How large are the emissions of black carbon particles, or soot, per kilogram burnt fuel?
- How do the emissions of black carbon differ between ship-types?

1.3 Disposition

This chapter (1) was an introduction to the thesis. In the following chapter (2) a background about aerosol particles will be presented. Chapter 3 contain a background specifically about ship emissions. The experimental section is presented in chapter 4, and the methods of calculation in chapter 5. Chapter 6 is both the result and discussion. Finally, chapter 7 contains the reached conclusions. References is located at the very end.

2 Aerosol particles

This chapter contain a background regarding aerosol particles, effects, source and origin, and processes.

2.1 Definition and size classification of aerosol particles

An aerosol is defined as solid or liquid particles contained in a gas (Hinds, 1999). How the solid or liquid aerosol particles behave in the atmosphere depends on their chemical composition and the size of particles, ranging from 1 nm in diameter to 100 μm.

Airborne particles usually consist of sulphates, nitrate, acids, ammonium ions, metal compounds, water, crustal materials, or carbonaceous compounds (Areskoug, 2000). The composition and properties of aerosol particles are influenced by environment, time of suspension, and weather conditions (Hinds, 1999). Several different aerosol processes change the shape and chemical composition of the particles during their lifetime. How long aerosol particles remain in the atmosphere depends on both specific properties of the aerosol particle as well as the meteorological surroundings. Particles can remain suspended in the atmosphere from hours to weeks.

Particles are divided into different modes, depending on size intervals (Seinfeld and Pandis, 2006), Figure 1. First off in the lower end of the size spectrum is the nucleation mode and Aitken mode. The nucleation mode consists of particles up to 30 nm in diameter (Please note that other size limits of the nucleation mode are also found in the literature). Particles in this size range are formed through gas-phase reactions. During fossil fuel or biomass combustion, these particles can be formed when the emissions are cooled down in the atmosphere, some tens of seconds to several seconds after the emissions. Nucleation mode particles might also be formed several hours or days after the emissions of sulphuric containing gases and organic carbon compounds from combustion of biogenic forest emissions. The Aitken mode consists of particles within the range of 30 nm up to 0.1 μm in diameter, believed to form from either primary sources or growing nuclei mode particles via coagulation or condensation (further discussed in section 2.3 and 2.4). Being so small, the particles in the nucleation mode and Aitken mode make up about 5 % of the total mass of airborne particles. The next particle mode is called the accumulation mode, which is consisting of particles between 0.1 and 1 μm (historically, the upper size limit was often set at 2.5 μm diameter), which originate mainly from

growing Aitken-mode particles and cloud processing, but to some extent also from primary emissions. The accumulation particles usually remain in the atmosphere the longest of all modes, due to particle removal mechanisms not being very strong in this specific size interval. Finally, there is the coarse mode, consisting of particles above 1 μm in diameter. Particles of this size are mainly generated mechanically.
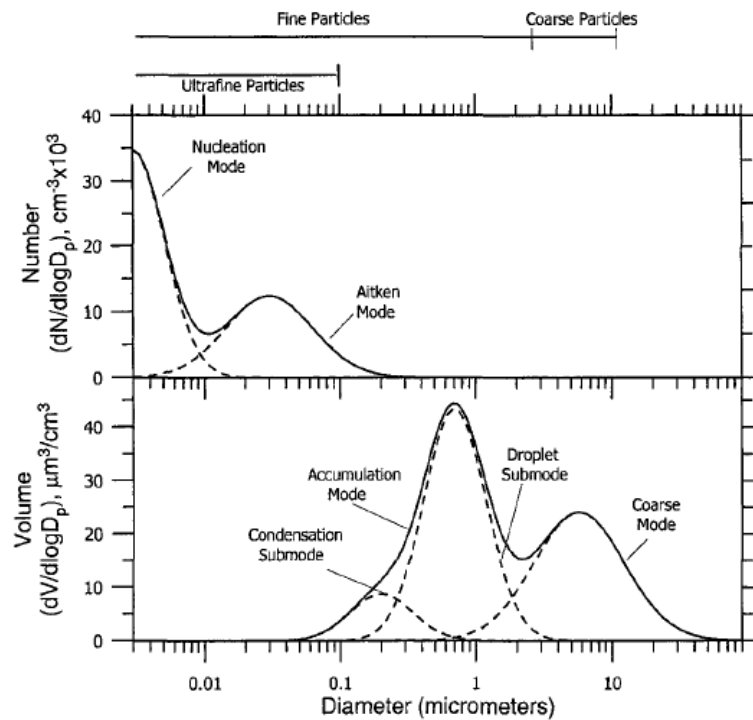

Figure 1: Typical atmospheric particle distributions in number and volume, as well as the different modes. Retrieved from Seinfeld and Pandis, 2006.

2.2 Effects

The atmospheric aerosols do not only affect the chemistry and physics of the atmosphere itself, but it also affects the climate, the biosphere, and public health. (Seinfeld and Pandis, 2006). They have an influence on energy, scattering and absorbing radiation from both the sun and the Earth. They affect both the abundance and distribution of atmospheric gases, such as greenhouse gases. They affect the circulation in the atmosphere. Aerosol particles have crucial impacts on the hydrological cycle, being involved in the processes of cloud formation and precipitation.

On another note, one lesser crucial effect is the reduced viewing distance, often occurring when it is humid (Hinds, 1999). This is caused by the light scattering on airborne particles, effectively changing the atmospheric visibility and making it difficult to see distant objects clearly. When it is humid outside water vapour get absorbed or adsorbed to particles, increasing their volume and their ability to scatter light.

2.2.1 Climate effects

Aerosol particles have an impact on the radiative forcing of the Earth's atmosphere system (Houghton et al., 2001). A positive radiative forcing is defined as the surplus of energy trapped in the Earth's atmosphere system in response of an anthropogenic disturbance. An example of positive forcing is the absorption of terrestrial radiation by human-emitted greenhouse gases, leading to a

warming of the surface of Earth, known as the global warming. A negative forcing can happen due to an increased reflection and scattering of solar radiation due to anthropogenic activities, thereby cooling the surface of Earth.

The radiative effects of aerosol particles are divided into two categories; direct and indirect effects (Houghton et al., 2001). Direct effects are caused by the particles absorbing and scattering solar and terrestrial radiation. Particles also have indirect effects on the radiation. They change the radiative properties and precipitation patterns of clouds when they act as cloud condensation nuclei and ice nuclei. These effects are, like health effects, also dependant on the specific properties of aerosol particles, such as chemical composition, structure, and particle size. The various atmospheric particle processes, discussed in section 2.4, are affecting aerosol particle properties. Due to the difficulty in observing these processes in the atmosphere, adding the highly variable nature of both weather conditions and atmospheric composition, it is difficult to predict the climatic feedback effects from aerosol particles, be it natural or anthropogenic in origin. It is even hard to specify whether the net effect is a positive or negative feedback.

For example, an increase in aerosol particles can result in an increase of cloud condensation nuclei and ice nuclei in the atmosphere (Houghton et al., 2001; Pöschl, 2005). This can lead to a variety of effects for the properties and nature of ice, water, clouds, and precipitation in the atmosphere. Effects such as: altered precipitation efficiency in clouds-- because of an increase in smaller cloud particles; or bigger glaciers-- because of more ice nuclei. The indirect effect on cloud formation is particularly interesting. Clouds have a significant effect on climate, like reflecting solar radiation amongst other properties (Kristensson and Martinsson). The increase of anthropogenic particles released into the atmosphere results in these particles partaking in the formation of clouds. However, these particles increase the number concentration of cloud droplets, making cloud droplets smaller due to the water getting distributed amongst a higher number of droplets. This means an increase in total cloud surface area, which is followed by an increase in scattering of light. The smaller droplets also result in clouds having a longer lifetime. This is because the smaller droplets are effectively delaying the formation of precipitation. This could result in more clouds overall, which would further increase the scattering of incoming solar radiation.

According to the 2013 IPCC report (Intergovernmental Panel on Climate Change), the consensus on the aerosol direct effect is that the anthropogenic radiative forcing compared to pre-industrial times at the year 1750 is currently negative, but with an error bar that extends all the way into a positive forcing (Figure 2, denoted "Mineral dust, sulphate, nitrate, organic carbon, and black carbon"). The indirect effect of aerosol particles is estimated to be even lower. But, here the uncertainty is even larger due to the difficulty of quantifying aerosol-cloud climate interactions (Figure 2, denoted as "Cloud adjustments due to aerosols").
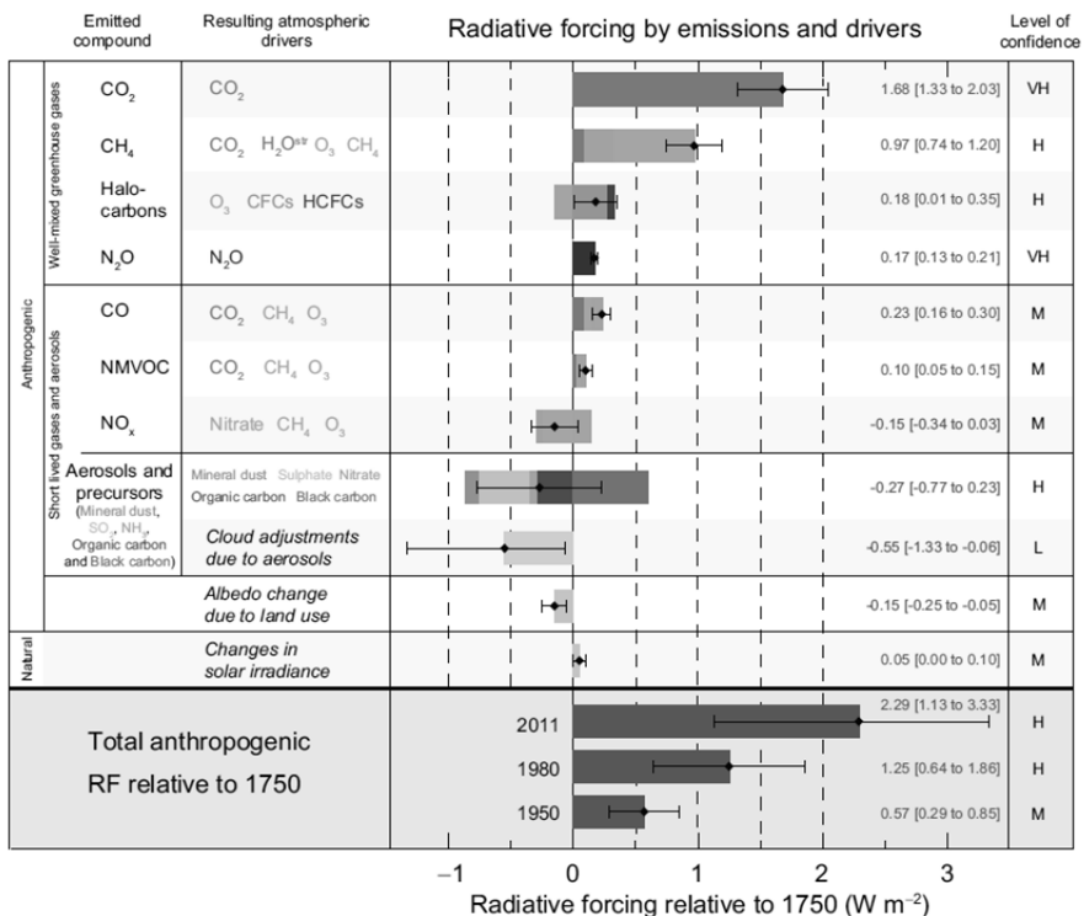
Radiative forcing by emissions and drivers

Emitted compound	Resulting atmospheric drivers	Radiative forcing relative to 1750 (W m⁻²)	Level of confidence
Anthropogenic — Well-mixed greenhouse gases			
CO_2	CO_2	1.68 [1.33 to 2.03]	VH
CH_4	CO_2 H_2O^{str} O_3 CH_4	0.97 [0.74 to 1.20]	H
Halo-carbons	O_3 CFCs HCFCs	0.18 [0.01 to 0.35]	H
N_2O	N_2O	0.17 [0.13 to 0.21]	VH
Short lived gases and aerosols			
CO	CO_2 CH_4 O_3	0.23 [0.16 to 0.30]	M
NMVOC	CO_2 CH_4 O_3	0.10 [0.05 to 0.15]	M
NO_x	Nitrate CH_4 O_3	-0.15 [-0.34 to 0.03]	M
Aerosols and precursors (Mineral dust, SO_2, NH_3, Organic carbon and Black carbon)	Mineral dust Sulphate Nitrate Organic carbon Black carbon	-0.27 [-0.77 to 0.23]	H
	Cloud adjustments due to aerosols	-0.55 [-1.33 to -0.06]	L
	Albedo change due to land use	-0.15 [-0.25 to -0.05]	M
Natural	Changes in solar irradiance	0.05 [0.00 to 0.10]	M
Total anthropogenic RF relative to 1750	2011	2.29 [1.13 to 3.33]	H
	1980	1.25 [0.64 to 1.86]	H
	1950	0.57 [0.29 to 0.85]	M

Figure 2: Estimated radiative forcing in comparison with year 1750. Retrieved from IPCC, 2013.

All of the effects above have impacts on a global scale, effectively altering temperature, atmospheric cycles, oceanic cycles, hydrological cycles, distribution of radiation, and can bring about an increase of more extreme weather conditions.

2.2.2 Human health effects

Aerosol particles also have an impact on human health (Nel, 2005; Pöschl, 2005; Samet et al., 2001). This is especially evident for anthropogenic sources such as traffic exhaust, as well as finer particles no matter the origin. Epidemiological studies show that the increase in particle mass concentrations correlate with several negative health effects like increased mortality, respiratory, allergic, and cardiovascular diseases. However, the exact mechanisms behind all of these effects are not entirely understood.

With decreasing particle size, the particles become more dangerous (Oberdorster et al., 2004). The small size allows the particles to reach deep inside the human body when inhaled, getting inside the bloodstream or getting transported to the brain through nerves. Ultrafine particles, around 100 nm in diameter, are considered to be very detrimental to human health. Most of the ultrafine particles in urban areas originate from local traffic. The deciding properties whether particles actually have a negative impact on human health however, are not entirely known.

When it comes to allergic diseases and air quality, even less is known (Zhang and Anastasio, 2003; Pöschl, 2005). However, the finer particles coming from traffic are thought to be one of the factors causing the overall increase of allergies. The allergens in urban air are composed of 5 % of protein

molecules, from biological particles. For example, a study from 2005 show that the pollen of birch trees go through increased nitration when in contact with increased levels of nitrogen oxides (NO_2) or ozone (O_3), in urban locations (Franze et al., 2005). These nitrated proteins trigger immune reactions, enhancing the effect of allergic diseases. This is thought to be the reason why birch pollen is such a powerful allergen. Effectively decreasing overall pollution could thereby bring about a reduction in cases of allergies and airway inflammations. It is imperative that aerosol components, gaseous or particulate, as well as chemical reactivity and aging are fully understood in order to control these emissions for the purpose of human well being.

2.3 Particle sources

The particles in the atmosphere originate from many sources (Barry and Chorley, 2003; Kristensson and Martinsson). The means of which the particles are formed is generally divided into two categories:

- Primary particles, formed directly at the source
- Secondary particles, formed through gas-to-particle conversion

These two categories are not always easy to distinguish. Particles formed minutes to hours after its release into the atmosphere are generally called secondary particles. However, particles can be formed through gas-to-particle conversions within a few seconds after being emitted from the exhaust pipe of a vehicle. These particles are often referred to as primary, even though they are secondary by nature.

Generally the primary particles sources are dust generated particles, sea-salt spray particles, grinding of material, different combustion sources (including cars, power plants, ships, wood burning, etc.), and biological particles like pollen or plant spores. Secondary particles consist of organic or inorganic gases converted into particles through condensation or nucleation, for example condensation of sulphuric acid. However, condensation is not the formation of new particles but it results in an increase of mass concentration of particles (Kristensson and Martinsson). Unlike nucleation, condensation is not a true aerosol source process and will be further discussed in section 2.4.1.

2.3.1 Mechanically generated particles

Wave-breaking is the forming of aerosol sea spray particles (Kristensson and Martinsson). When waves break and whitecaps form, gas bubbles rise up from under the surface and break. The breaking of the bubble creates small film drops which burst into the atmosphere. When the drops are airborne the water starts to evaporate so as to equalize with the surrounding relative humidity, leading to the droplets becoming aerosol particles. The newly created aerosol particle will contain material from the ocean surface, which is some form of organic matter and sea salt.

Wind-blown dust starts off with the wind picking up larger particles of about 100 µm in diameter. These particles are too heavy to be suspended in the air for long periods of time but they will bounce around causing particles of other sizes to move about. When particles of small enough size, like 20 µm, gets airborne they can remain suspended for long periods of time. This is called saltation. Deserts and even agricultural fields can be large contributors of these sorts of particles.

Vehicle abrasion is the forming of particles due to the grinding resulting from contact between vehicle wheels and a surface. Vehicle abrasion also includes the particles created from the braking of

vehicles, which leads to deterioration of the brake block. The vehicle abrasion particles can be generated from train wheels and automotive tires. When trains brake the deterioration of steel wheels leads to emissions of metal particles, which can cause negative health effects for the people nearby. The braking of automotive tires results in emissions of mostly organic coarse-mode particles. The road itself is also grinded, emitting asphalt dust-containing particles. When these grinded asphalt particles get re-deposited to the road they can be grinded even further. Vehicle abrasion has a strong impact in northern countries during winter, such as Sweden. The use of studded tires during winter causes more grinding of the asphalt than usual. When the snow melts and the roads dry up, large amounts of particles become airborne and released into the atmosphere.

Grinding of material is the final mechanically generated particle type, which produces different particles depending on the grinded material. Road surface abrasion above is one such example. However, grinding includes plenty of other examples such as construction activity or stone-crushing.

2.3.2 Primary combustion particles
Diesel exhaust particles are examples of combustion particles (Kristensson and Martinsson). Different particles are formed this way. The first type is a soot core (or black carbon) surrounded by absorbed organic compounds, which is formed in the engine. These are at or below 100 nm in diameter. The second is organic and sulphur compounds that condense behind the exhaust pipe, creating particles of 10 to 40 nm in diameter.

Biomass combustion is another source of combustion. It includes forest fires, and anthropogenic biomass combustion. While the particle types and the chemical composition are similar between the sources, the emission strength varies. Larger particles are emitted from biomass combustion than vehicle combustion exhaust. Biomass combustion release more ash, levoglucosan, and in some cases less soot particles than diesel combustion.

2.3.3 New particle formation
New particle formation, otherwise known as nucleation, is a significant source of atmospheric aerosol particles (Kristensson and Martinsson). This formation of new nanoparticles results in a high number concentration of aerosol particles ranging from 1 and 2 in diameter. The production occurs through several gas-to-particle conversions from both natural and anthropogenic sources, although natural sources remain the largest contributor of nucleation. New particle formation is therefore generally considered as a secondary particle source, however it can also be perceived as a source on its own. There are five different theories, or processes, regarding the formation of new nanoparticles. These five nucleation processes are divided into two, heterogeneous and homogeneous. The heterogeneous nucleation process is when gas molecules interact with other clusters of different molecules. Meanwhile, the homogenous nucleation process is instead an interaction between identical molecules, resulting in a formation of clusters.

2.3.4 Natural and anthropogenic emissions
On a global scale the mass emissions of particles from natural sources are larger than anthropogenic sources (Hinds, 1999). Natural source emissions vary depending on geographical location (Areskoug, 2000). For example, around Sahara there are sandstorms blowing up large amounts of larger particles, while there's no such big natural source in Sweden. Anthropogenic emissions, although small compared to the total natural amount, are concentrated in the small industrialized areas of

Earth (Hinds, 1999). In these areas of civilization, anthropogenic sources remain the largest contributors to high mass concentrations.

For number emissions of particles, less is known about how much contribution is coming from natural versus anthropogenic sources. Also, anthropogenic emissions contribute relatively much to the number concentrations in all different environments.

2.4 Atmospheric particle processes

Airborne particles can be subjected to different processes, which bring about chemical and physiological changes and interactions, some of which can be seen in Figure 3 (Pöschl, 2005). The particles can undergo changes in size, structure, and composition due to such processes as: coagulation, chemical reaction, restructuring, and gas uptake. The lifetime of the atmospheric particles can also be shortened due to these processes.
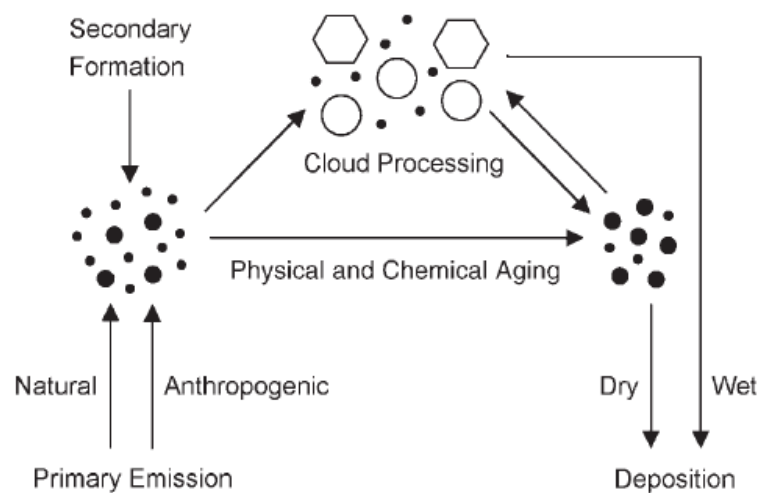

Figure 3: Atmospheric cycling of aerosols. Retrieved from Pöschl, 2005.

2.4.1 Condensation

Particles can grow through condensation. This is a process where gas molecules condense onto particles, increasing their size (Kristensson and Martinsson). This process is also called secondary formation. The change in size is dependent on the balance between condensation contra evaporation. Some organic compounds that contribute to condensation come from sources such as: oceanic biota, pack-ice processes, combustion, and from oxidation products of monoterpenes and isoprenes emitted from coniferous and deciduous forests.

Different chemical compounds have different volatility in the atmosphere, meaning that there are compounds that are very volatile, where little mass is condensing on particles, for example carbon dioxide (CO_2). There are also compounds with intermediate volatility that can exist in high concentrations both in the particle and the gas phase. Finally, there are compounds which have very low volatility, that are predominantly found in the particle phase, for example sulphuric acid.

2.4.2 Coagulation

Coagulation is when two particles collide, turning into a larger aerosol particle (Hinds, 1999). For example, in a plume with a high particle number concentration, coagulation will effectively alter the

number concentration as well as the size of particles. The mass concentration in the plume will be unaffected.

The smallest particles, in the nucleation mode, are mainly lost through coagulation with larger particles due to smaller particles having a larger number concentration, and since coagulation is effective between the smallest and largest particles (Seinfeld and Pandis, 2006). This can be seen as a process where the smallest particles disappear, while the larger particles are basically unaffected (due to the low mass of the smallest particles). Because of this, smaller particles usually have a shorter lifespan. In a combustion engine exhaust where the number particle concentration is high, the size distribution can change within seconds. Particles in the accumulation mode are growing either through coagulation with particles in the nucleation mode, through condensation, or through cloud activation. The coagulation process in the accumulation mode is a very slow process.

2.4.3 Cloud activation / Cloud Condensation Nuclei (CCN)

In order for clouds to be able to form, atmospheric aerosols are an essentiality (Seinfeld and Pandis, 2006). Particles that can turn into cloud droplets are called cloud condensation nuclei, or CCN. These particles are activated by interacting with a supersaturation of water vapour. A CCN usually exists in the atmosphere for about a week, residing a few hours in a cloud and thereafter a few days outside clouds before eventually being removed from the atmosphere due to precipitation. A CCN have a specific point where they turn from a stable state into an actual cloud droplet. However, this specific point depends on the amount of water supersaturation, the condensation of water vapour being what controls the size of the CCN.

Supersaturation occurs when clean air is cooled below dew-point, in which the relative humidity is above 100 %, causing water vapour to condense on CCN (Barry and Chorley, 2003). As the water vapour is condensing on the cloud droplets, the supersaturation is gradually decreasing, slowing down the radical growth rate of the cloud droplets.

2.5 Aerosol particle sinks

Aerosol particles won't stay afloat in the atmosphere forever (Seinfeld and Pandis, 2006). Sooner or later they return to the Earth through either of two sinks: wet deposition or dry deposition.

Wet deposition includes every way in which particles can reach the Earth's surface through getting scavenged by atmospheric hydrometeors, like snow or rain (Seinfeld and Pandis, 2006). This is the main sink of atmospheric aerosol particles. Wet deposition is then divided into two different ways of scavenging: in-cloud scavenging, where particles are scavenged in the cloud activation process, and below-cloud scavenging, where particles are scavenged by falling rain droplets during precipitation.

Dry deposition is when particles and gaseous species fall down to Earth's surface without the use of precipitation (Seinfeld and Pandis, 2006). It is instead through convective transport, diffusion, and adhesion to the surface of the Earth (Pöschl, 2005). In essence, dry deposition of particles and other species depend on several factors, for example the structure of surrounding terrain and ground surface, how much turbulence there is in the atmosphere affects how long it takes for particles to reach the surface. The size, shape, and density of particles affect whether they will be picked up by the surface.

3 Ship emissions

This chapter contain a background about ship emissions, related health and climate effects, regulation of ship emissions, a method of quantifying emissions, and the impact of various factors regarding engine and fuel.

3.1 The shipping fleet and its emissions

One source of particles, in which the focus of this study lies, is ship emissions. As of 2013 there are about 80 000 merchant ships cruising on the world's oceans (Equasis, 2013). In the year 2001 the entire shipping fleet had a total fuel consumption of 280 million metric tons (Mt) (Eyring et al., 2005). In 1950 the total ship fuel consumption was at 64,5 Mt. Ships of various size and purpose are using different types of engines such as large slow-speed diesel (SSD) engines or medium-speed diesel (MSD) engines (Lack et al., 2009). Furthermore, the regulations regarding fuel-quality and emissions are both miniscule and erratic. For this reason, neither the engines nor the fuel quality have improved considerably on the course of decades, in comparison to engines of trucks and cars (Fridell et al., 2007). The fuel itself, residual oil, contains high amounts of sulphur and polyaromatic hydrocarbons, both of which have an effect on the formation of larger particles. When the fuel goes through combustion, sulphur dioxide (SO_2), and particulate matter are emitted as a result (Mellqvist, 2014). Particulate matter includes primary soot particles, and secondary inorganic sulphate particles (SO_4^{2-}). The sulphate particles form when sulphur dioxide goes through atmospheric oxidation.

The particle composition of ship emissions consists mostly of sulphate, organic matter, and black carbon (Lack et al., 2009). However, the percentage of these varies with fuel sulphur content, engine type and combustion efficiency. The amount of particulate matter emitted from ships in the year 2001 was at 1.67 Tg, compared to the 2.1 Tg emitted from road traffic (Fridell et al., 2007). NO_x emissions are estimated to be 6.87 Tg N per year (Corbett and Koehler, 2003). Sulphur emissions are estimated to be 6.49 Tg S per year.

There have been little studies done on ship emissions regarding size distribution of particles (Fridell et al., 2007). There is also a lack of information regarding how size distribution and emissions are affected by fuel quality, engine load, and aftertreatment.

3.2 Health effects caused specifically by ship emissions

Ship emissions, and the chemical reactions that follows, creates and emits ozone and particles (Kivekäs et al., 2014). Both of these pollutants affect the human respiratory system during inhalation and have a negative effect on human health.

As previously stated in section 2.2, particulate matter have certain impacts on human health, such as asthma or premature mortality (Nel, 2005; Pöschl, 2005; Samet et al., 2001). With ships emitting a considerable amount of particles, they contribute to those negative health impacts. Considering that about 70 % of all international shipping is carried out within 400 km of land, this is a significant source of impact (Corbett et al., 1999; Eyring et al., 2009). Furthermore, major shipping ports are usually surrounded by large human populations.

It is estimated that 60 000 premature deaths every year are caused by shipping-related emissions of PM 2,5. A majority of these mortality cases arise in Europe and Asia (Corbett et al., 2007). According to a newer study by Brandt et al. (2011) however, a death toll of around 50 000 is expected in Europe alone. The biggest impact being in coastal regions, especially those near the larger shipping routes. In

Europe alone, international ship emissions were estimated to be responsible for 7 % of the total health costs from air pollution in year 2000 (Brandt et al., 2011). That is 58 billion Euros per year. At this rate it is estimated that health costs regarding ship emissions will continue to increase, reaching 12 % of Europe's total health costs from air pollution. However, in light of new policies and measures of regulation such as SECA being implemented (see section 3.3), this number is expected to decrease rather than increase.

Sulphur dioxide in ship emissions is one component causing both health problems as well as environmental impacts (Kalli et al., 2015). Fine particles (PM 2,5) are considered notably dangerous to human health, which have a correlation with the amount of sulphur present in ship fuel. Reducing the sulphur dioxides would be a very cost-efficient way to reduce the related negative health effects.

3.3 Climate effects caused specifically by ship emissions

The contribution of shipping emissions to climate change is rather complex (Fuglestvedt, 2009). The emissions contain CO_2 which is a known greenhouse gas, contributing to the global warming. There is also sulphur dioxide (SO_2) which instead has a cooling effect. This cooling is achieved by SO_2 being oxidized into sulphate (SO_4^{2-}) which form particles that scatter incoming solar radiation or cloud condensation nuclei which participate in cloud formation (Bieltvedt Skeie et al., 2009; Fuglestvedt, 2009). Ships emit nitrogen oxides (NO_x) which increase ozone (O_3) while also reducing methane (CH_4), two additional greenhouse gases. Adding up all of the above factors, some studies estimate that we get a negative net global mean radiative forcing (Eyring et al., 2009; Bieltvedt Skeie et al., 2009; Lack et al., 2011). Radiative forcing is the altered equilibrium between the Earth's outgoing radiation and incoming solar radiation (European Environment Agency, 2003). A negative radiative forcing causes climate cooling through scattering of light, while a positive forcing causes climate warming through absorption of light. If the sulphur in ship fuel was to decrease, the climate effects of shipping would go from cooling to warming (Fuglestvedt, 2009; Lack et al., 2011). However, it should be mentioned that the residence time of sulphate is a few days and the climate response is decades whereas the effect of CO_2 lasts centuries (Eyring et al., 2009). In essence, shipping emissions have two opposite effects: a cooling effect in the short-term, and a warming effect in the long-term (Fuglestvedt, 2009). Whether reducing sulphur dioxide is a good short-term action regarding Earth's climate remains a topic of research. According to the European Environment Agency (2003) shipping will continue to result in a negative radiative forcing until 2020. In a more recent study it is estimated that the cooling effect will last until the year 2050 (Lund et al., 2012). However, should we refrain from reducing shipping emissions for the sake of climate; the result would be a negative impact to human health and ecosystems due to air pollution (European Environment Agency, 2003).

A recent study from 2013 investigated the potential climate and air quality trade-offs, when adjusting the sulphur in ship fuel (Partanen et al., 2013). They compared the health- and climate effects of 2013 with two different simulations. *Simulation 1*. where sulphur in fuel was restricted to 0.1 % in a specific area of emission control, while the sulphur content was at 5.4 % everywhere else. *Simulation 2.* like *simulation 1.* sulphur in fuel was restricted to 0.1 % in areas of emission control, but instead the sulphur content was at 0.5 % everywhere else. The result showed that not implementing sulphur reductions in the ship fuel would lead to tens of thousands of deaths per year. Furthermore, if sulphur would only be restricted in coastal waters, the pollution would still travel from the open sea and inflict damage upon human health throughout the continents due to the long-range

transportation. The cooling effect would simply not be worth the cost, even if ship emissions were to be manipulated and controlled.

Sulphur dioxide and nitrogen oxides have other effects, not just cooling. These two are acidifying agents, having a negative impact on ecosystems on both land, lake, and ocean through acidification (Kalli et al., 2015). Nitrogen oxides (NO_x) form nitric acid (HNO_3) and sulphur dioxide (SO_2) form sulphuric acid (H_2SO_4). However, these two compounds don't contribute to acidification as much as CO_2 globally. The acidification is at its most hazardous near coastlines, where sensitive biota exists.

Yet another indirect effect of ship emissions is the emitted black carbon, which deposits on areas of ice and snow (European Environment Agency, 2003). This will cause those surfaces to reflect less solar radiation. With less reflection, the snow and ice will instead absorb more solar radiation, resulting in faster melting. With shipping lanes being relatively near the Arctic this is indeed a problem. The exact mechanics of how black carbons affect snow and ice is not entirely certain.

The radiative forcing effect of black carbon on ice and snow is twice as high as CO_2 in changing global temperature (Hansen and Nazarenko, 2004). The black carbon could be a contributing factor to global warming during the past 100 years, thinning and melting ice and snow in the northern hemisphere. Reducing the black carbon emissions should return the reflective properties to ice and snow, reducing global warming by a small amount. It's estimated that black carbon could be the cause of one fourth of the Earth's global warming. However, greenhouse gases remain the biggest cause of global warming the last 100 years and will continue to do so the next 100 years to come.

3.4 Regulation (SECA)

In 2013 the European Commission formed a strategy into EU's policy, with the purpose of reducing ship emissions. The strategy is made up from three steps:

- Monitoring CO_2 emissions from large ships in EU ports, proposed to start 1 January 2018;
- Greenhouse gas reduction goals;
- Further measuring and the inclusion of market-based measures.

While there have been no major global market-based measures as of yet, there are so called Emission Control Areas (ECA). These areas limit NO_x, SO_x and particulate matter emissions, mainly through limiting the maximum amount of sulphur content allowed in fuel (International Maritime Organization, 2015). These limits have been progressively changed over the last years, as can be seen in table 1 from International Maritime Organization. The EU sulphur directive states that all ships in EU waters are required to use 0.5 % from 2020 and onwards.

Outside an ECA established to limit SOx and particulate matter emissions	Inside an ECA established to limit SOx and particulate matter emissions
4.50 % m/m prior to 1 January 2012	1.50 % m/m prior to 1 July 2010
3.50 % m/m on and after 1 January 2020	1.00 % m/m on and after 1 July 2010
0.50 % m/m on and after 1 January 2020*	0.10 % m/m on and after 1 January 2015

Within an ECA ships must be using fuel with sulphur content no higher than 0.10 % m/m as of the year 2015. Changing of fuel to higher sulphur content must be done outside the ECA. Figure 4 below illustrate the different changes in sulphur fuel content between SECA areas and the world.
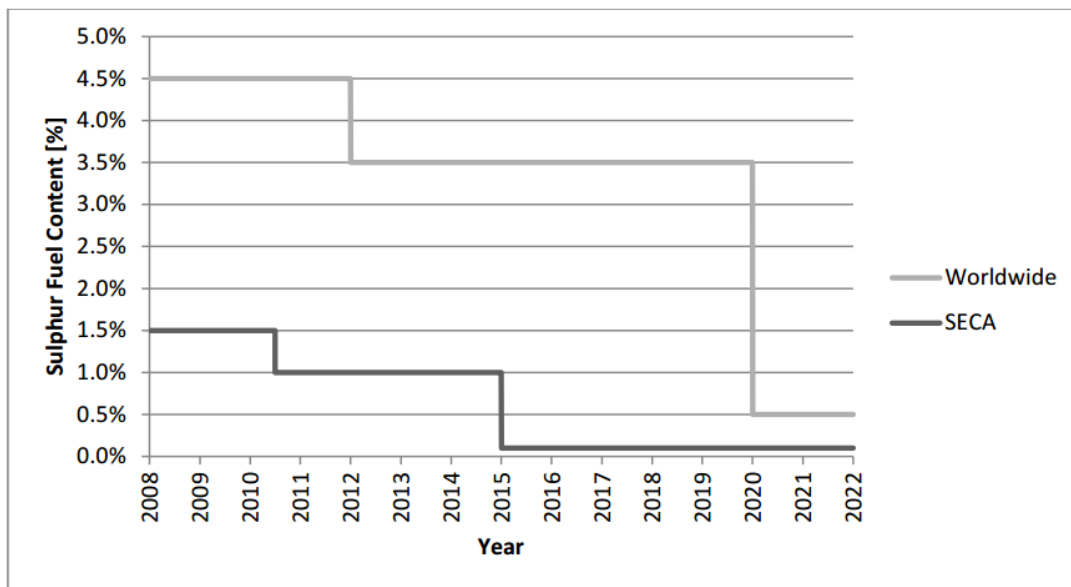

Figure 4: Regulation of Sulphur Fuel Content [%] in the world and SECA areas. The Worldwide cap in 2020 may be postponed until 2025, depending on fuel availability. Retrieved from Mellqvist et al., 2014.

The map below (Figure 5) shows the Sulphur Emission Control Area (SECA) in Europe, which is only controlling the amount of sulphur in fuel, not NO_x. In North America and the Caribbean there is an ECA controlling both sulphur and NO_x. The European SECA includes the Baltic Sea, the North Sea, and the English Channel.
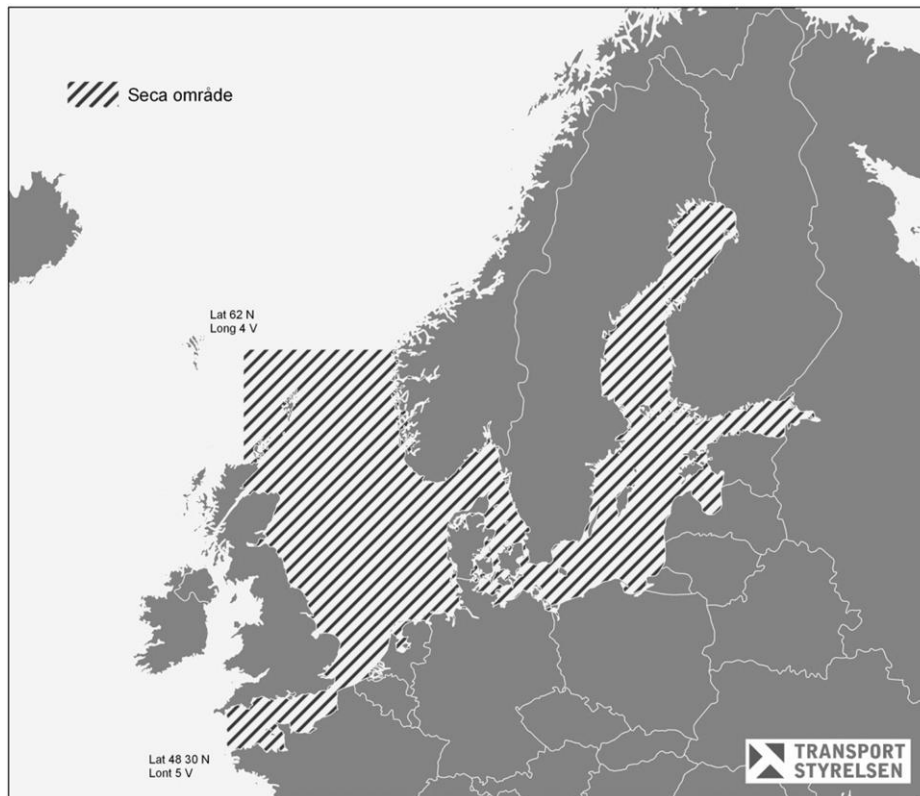
The enforcement within this area is carried out by Port State Control (PSC) authorities (Mellqvist et al., 2014). The PSC have the right to inspect ships in their harbours or inland waters. Should it become necessary, they can also detain ships in the harbours or inflict civil penalties. The exact enforcements are decided by each country, but are relatively similar. If the ships are outside internal water, they can only be inspected if there is suspicion of the ship breaking regulations. If the ships are located on international waters, no inspection can be carried out. However, a complaint can be filed to the flag state.

There is a significant price difference between fuel of high (1 %) and low (0.1 %) sulphur content (Mellqvist et al., 2014). It is therefore an economic advantage in using fuel of high sulphur content. Enforcer actions are needed in order to avoid this. PSC authorities do inspections and while some inspections are easy and straightforward others are not. It is easy to check the most recent used fuel quality of ships. However, it is harder to prove if ships have been using fuel with high sulphur content during part of their journey in the SECA. Because this is so difficult to control there is a need to form a measurement system for effective fuel control. There is however voluntary indexes, such as Environmental Ship Index (ESI) and Clean Shipping Index (CSI), which ships can partake in to establish themselves as being more environmentally friendly. Both the indexes demand that ships improve air

emissions, but the CSI is more demanding by including use of chemicals, waste treatment, and treatment of discharge water.

The indexes can be used by ports as a means of identifying and compensating those who strive to be more environmentally friendly. For example, as an alternative measure the port of Gothenburg did a campaign for cleaner fuel during 2011 - 2014. Ships that used cleaner fuel in port water would receive financial compensation. The campaign was funded via the port charge. In 2015 they are offering port discounts for ships with ESI (with score above 30 p) and CSI. A further discount is given to ships using liquefied natural gas (LNG) as fuel.

3.5 Quantitative emissions / Emission Factors

An emission factor is a value that represents the relationship between the amount of pollution released into the atmosphere, and the activity related to the release of that specific pollutant (Environmental Protection Agency, 2014). This value can then be used in emission comparisons. In the case of this study, that specific activity is ship engine combustion. Emissions factors are expressed as weight of the pollutant divided by a unit weight, volume, distance, or duration of the activity. For example, how much grams of black carbon is released into the atmosphere per kilogram of combusted ship fuel. There is however some external conditions influencing emissions, like the fuel content or varying parameters concerning combustion.

3.6 Effect of using specific engines, fuel-type, and engine load

There are many factors that affect the emissions of ships. Such factors as type of engines, the used engine load, type of fuel, fuel quality, etc. Some examples of differences is presented below.

Petzold et al. (2004) measured the exhaust gas of single-cylinder test bed engine operating on different load conditions. The fuel used contained a high sulphur content of 3.45 wt. %. The result was that particles emitted from ships mainly are composed of sulphate and sulphate-bound water. For example, the exact composition of particles with an engine load of 25 % was: black carbon (7 %), organic matter (18 %), sulphate (38 %), sulphate-bound water (30 %), and ash (7 %).

A study done by Anderson et al. (2015) indicate that both sulphur content and the quality of the fuel should be considered when setting regulations for particle emissions. These are fuel quality factors such as viscosity, metal content, flash point, and carbon residue. Furthermore, there was no clear relationship between emitted particulate matter and engine load in this study. The study was conducted on a test-bed engine operating at low engine loads, while using different fuels of low sulphur content. A reduction in sulphur and the use of high quality fuel is going to decrease emitted nanoparticles. As previously stated, these nanoparticles are of importance in aspect of climate and human health.

Winnes and Fridell (2009) conducted field emission measurements on a 4500-kW four-stroke main engine on a product tanker. Two different fuels were tested, heavy fuel oil (HFO) and marine gas oil (MGO), the latter having lower sulphur content than the former. Sulphur dioxide (SO_2) in HFO was the only gas being exceedingly different between the two fuels. Particulate matter and sulphur dioxide emissions are higher in HFO. However, a change from HFO to MGO did not reduce the levels of particles below 2 μm in diameter. These are of the particle size that poses the largest threat to human health. Nevertheless, a switch in low sulphur content fuel will still decrease the total amount of particle emissions, positively impacting health effects related to ship emissions. The reached

conclusion in this study is that reducing sulphur alone is not going to be enough to minimize negative health effects.

Lack et al. (2009) did a study on particle emissions from more than 200 ships. Generally, the particle composition is determined by factors such as fuel sulphur content, engine type, vessel activity, and maintenance. The emission of black carbon was found to have a strong correlation to engine type, its combustion efficiency, and maintenance. The emission of sulphate (SO_4^{2-}) was dependent on fuel sulphur content. The emission of organic matter was a function of both engine type and the fuel sulphur content. The reached conclusion is that fuel type and ship activity have a contribution to the composition and mass of emitted particulate matter. Strong correlations were found between fuel sulphur and organic matter, SO_4^{2-}, cloud condensation nuclei, particle water uptake, and particle single scatter albedo. All of these parameters are of importance on climate, thereby directly linking the type of fuel used with the radiative effects of shipping particle emissions. Lack et al. (2009) also found that the mechanisms of particle formation inside the engine during combustion are what dictate particle size, no matter the type of engine. The size of particles can increase with distance after emission, due to condensation of sulphuric acid upon larger particles.

Tian et al. (2014) investigated the evolution of ship emitted aerosol particles. They found that the processes of dilution and coagulation had a major influence on particle distribution and cloud condensation nuclei activation properties. The impact on cloud condensation nuclei was dependent on the supersaturation threshold. Dilution and coagulation reduced the particle number concentration during the first hour of emission. Furthermore, coagulation altered the mixing state of particles during the initial 1-2 minutes. This resulted in internal mixtures of black carbon and sulphate.

In another study by Lack and Corbett (2012), they found that black carbon emission factor increases when the ships engine load decreases. Absolute emissions of black carbon are increased by up to 100 % at low engine loads, considering the average emission factor for black carbon in combination with the reduced speed and fuel consumption. Improving the fuel quality can reduce emissions of black carbon by 30-80 % potentially. It is suggested that more research is needed for the exhaust scrubbing systems which can likely remove black carbon with various efficiency dependent on the sulphur content in fuel.

In another study done by Lack et al. (2011) they measured emissions of gas and particulate matter on a large ship before and during a fuel switch before entering regulated waters. The ship also reduced speed when entering the regulated area. The ship was using HFO (containing 3.15 % sulphur and 0.05 % ash) before gradually blending it with MGO (containing 0.07 % sulphur and <0.01 % ash). They measured drastic reduction in emission factors (>90 %) of sulphur dioxide, particulate matter, particulate sulphur, and cloud condensation nuclei. Black carbons emission factors got reduced by an average of 41 %, and particulate organic matter got reduced by 70 %.

4 Experimental

This chapter contain the experimental specifics. It presents the measurement location, and the measurement instruments.

4.1 Measurement site

The data used in this study was compiled from a field station outside the harbour of Gothenburg, in southern Sweden (latitude 57° 41' 01.0" N, longitude 11° 48' 17.0" E). The measurements took place during autumn, between the 12th of October and the 14th of November 2014. Five days were chosen based on good data availability, wind direction, and sufficient wind speed. Out of these five days 228 ship plumes were of sufficient duration and quality. The weather information was gathered from the website [http://rl.se/], which is a privately owned site hosting public weather data gathered from measurement stations and airports. A proper wind direction is from within the measurement window (B) in Figure 6.

The field site, A in Figure 6, is located at a distance of about 500 meters downwind from ship plumes. However, ships don't travel exactly like the map suggests (i.e. the dotted line), and normally tend to travel closer to the southern isles, depending on traffic. As such, the exact distance may fluctuate a little above 500 meters during different times. The ship plumes are usually a little more than a minute old when they reach the field station.
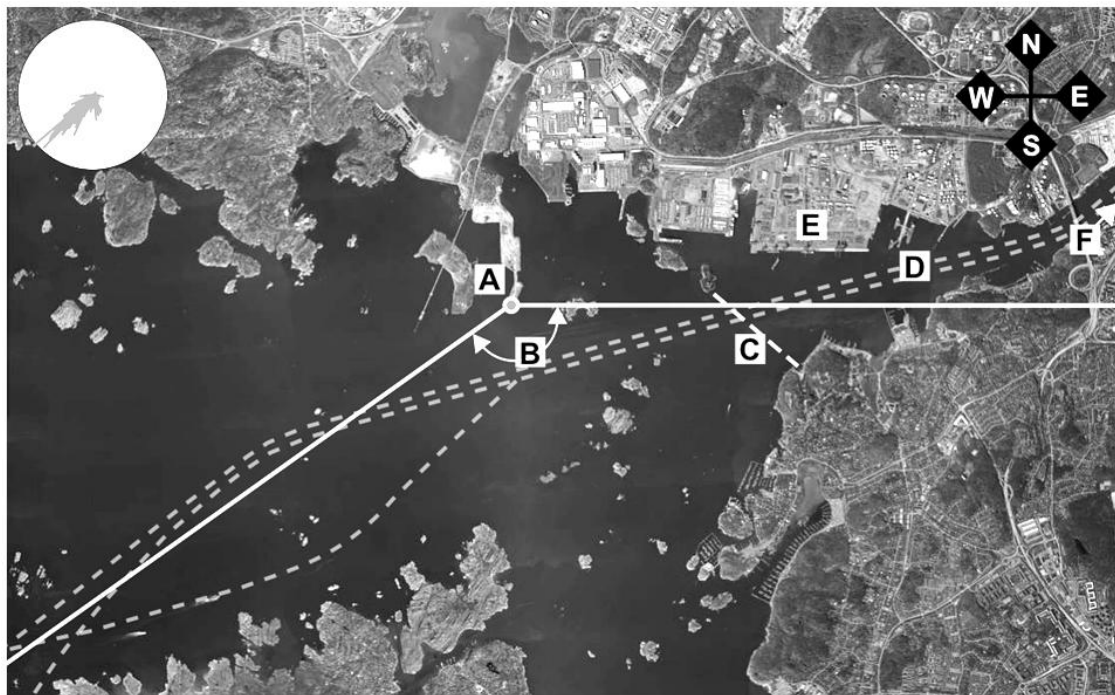
A. Measurement location
B. Measurement window
C. Port speed zone
D. Shipping lane
E. Cargo port
F. Inner Harbor

Figure 6: Geographical overview of the measurement location, using Google maps.

The field station containing all the instruments was located very close to the shore, just a few meters away (Figure 7). Between the station and the coastline there was nothing but flat ground. The inlet on top of the field station was 11 meters above sea level. Behind the field station, closer to the mainland, there was a wind turbine. Sometimes wind turbine maintenance technicians would arrive on the nearby road. However, this should not have any effect on the particle concentrations when the winds were blowing from the sea.

4.2 Instruments

The field station contained several instruments measuring various air qualities and other parameters. The air was first collected through an inlet on the roof. The inflow rate was set at 4,77 m/s, or 124 m^3/h. As of yet, the particle transmission as function of particle aerodynamic diameter has not been calculated for the inlet. The instrument setup is shown in the Figure 8 below. The instruments were continuously being calibrated when needed. The collected data used

Figure 7: A picture of the field station located outside the harbour of Gothenburg.

in this study was produced using two different instruments; CO_2 and MAAP. The CO_2 monitor had a time resolution of 1 second with an accuracy of about 0.2 ppm, while the MAAP had a time resolution of 1 minute.
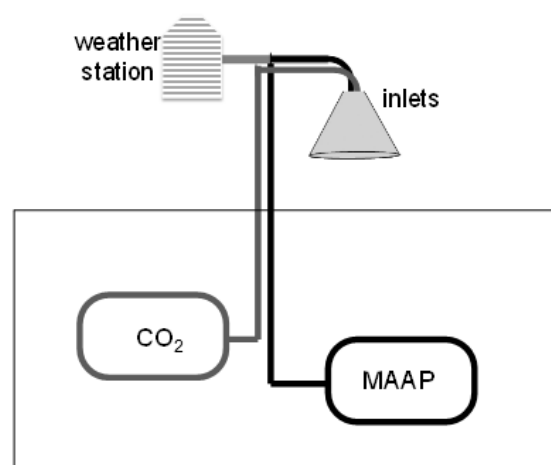

Figure 8: A schematic over the CO_2 and MAAP, the instruments that produced the data used in this study. The field station contained several other instruments measuring other parameters.

4.2.1 Multi-Angle Absorption Photometry

Soot, or black carbon, was measured using a Multi-Angle Absorption Photometry (MAAP 5012). The measurement is based on aerosol optical absorption (Nordmann et al., 2009). The wavelength used by the MAAP is in the same wavelength interval where black carbon is the main absorber. The mass concentration of black carbon is calculated by measuring the opacity at this wavelength due to soot particles collected on a particle filter. The MAAP measures absorption coefficients but returns values as mass concentration of black carbon.

Specifically, mass concentration of black carbon is calculated using the following equation:

$$mBC = \frac{\sigma_{ap}^{637\ nm}}{Q_{BC}} \tag{1}$$

mBC is the mass concentration of black carbon, measured in $\mu g/m^3$. $\sigma_{ap}^{637\ nm}$, or sigma, is the optical absorption coefficient, measured in inverse Mega meters (1/Mm). The absorption coefficient is calculated by measuring the radiation transmitted through and scattered back from a particle-loaded filter (Müller et al., 2011). Q_{BC} is the specific absorption coefficient of black carbon, which is 6.6 m^2/g.

The wavelength used by the MAAP is supposed to be 670 nm according to the manufacturer, but in reality it is 637 nm (Müller et al., 2011). Because of this, the MAAP software is calibrated to a wavelength of 670 nm when it should in fact be 637 nm. Hence, since light absorption is about 5 % higher at a wavelength of 637, this is adjusted by multiplying with 1.05:

$$\sigma_{ap}^{637\ nm} = mBC \times Q_{BC} \times 1.05 \tag{2}$$

However, equation (1) for mBC is valid only for pure black carbon particles (Müller et al., 2011). In the case of this study, the measured aerosols contain not only black carbon that absorbs light at 637 nm, but might contain other light absorbing compounds as well, or the specific absorption coefficient of black carbon might be different then what the manufacturer is providing. This means that the actual amount of black carbon particles, measured in µg/m3, might not be correct. As a safety precaution, it is important to always present the light absorption coefficient alongside the mass concentration of black carbon, since this property should be sufficiently preserved independent of which type and shape of particle is absorbing the light.

As stated before, the MAAP is measuring using a filter (Müller et al., 2011). Particles are gathered on the filter, where they will absorb a certain amount of light, reducing the transmission of light through the filter. The results are thereafter compared to another filter without particles, leaving the resulting difference in light transmission as the measured light absorption of the used particles. There will most likely be some particles or compounds that scatter incoming light. This issue is resolved by measuring reflected light from two different angles. The scattered light caused by the filter is taken into account through calibration of measurements. The MAAP also take into consideration the potential of particles stacking on top of each other, the so called filter loading effect, and is properly calibrated for this. An illustration of the technical measuring setup can be seen in the schematic in Figure 9.
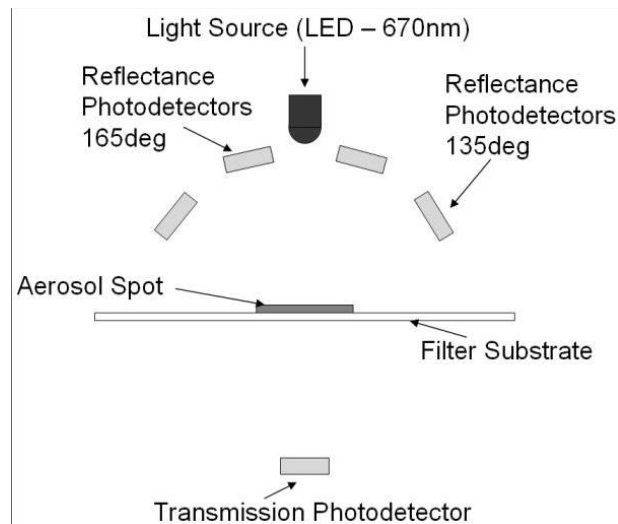
4.2.2 CO_2

The CO_2 was measured using infrared sensors (Vaisala, 2012). The instrument sends IR radiation through the measured gas to a detector. The detector have a filter preventing wavelengths other than the measured gas's. The intensity of the light is converted into a gas concentration value. The CO_2 readings, given in ppm, increase as the concentration of CO_2 molecules increases.

4.2.3 Other instruments

Two additional instruments were used to measure the soot concentration, a Photo Acoustic Soot Spectrometer (PASS-3), and Soot Particle Aerosol Mass Spectrometer (SP-AMS). In the end, the data from these were not used, see chapter 5.4

In essence, the Photo Acoustic Soot Spectrometer (PASS-3) is also used to measure the light absorption coefficient in three wavelengths, and the black carbon concentration (The University of Manchester, 2015b). However, unlike the MAAP, this instrument measures aerosol particles suspended in the air rather than on a filter. The PASS-3 uses a photo acoustic technique to measure the optical absorption coefficient, aerosol scattering coefficient, as well as total extinction of the aerosol particles.

A Soot Particle Aerosol Mass Spectrometer (SP-AMS) measures particles containing black carbon (Onasch, 2012). Using two lasers, the instrument measures mass of refractory black carbon (rBC), the chemical composition and mass of the compounds surrounding the black carbon core, particle size and morphology.

5 Data analysis

This chapter contains the methods of identifying ships, defining ship plumes, and calculations of emission factors. Limitations is presented at the end of the chapter.

5.1 Identifying ships

As ships came passing by, their Maritime Mobile Service Identity (MMSI) was registered. This is a series of unique digits almost every ship sends out using a radio signal, in order to identify

themselves. The MMSI-numbers of specific ships can then be used to get information such as ship type, deadweight, size, etc. This was done through the website [www.marinetraffic.com]. The website is hosting information of more than 570 000 ships. The site can also be used to watch live locations, current status, and destination of ships.

5.2 Defining and extracting ship plumes from data

There weren't any previous measurements of background CO_2 and soot particle concentrations available. Therefore, the background CO_2 and background absorption coefficient (black carbon) had to be extracted from the total CO_2 and total absorption coefficient. This was done through a percentile-based method used by Kivekäs et al. (2014) but with some adjustments. The 40th percentile values were taken from a sliding window. The window has a different width depending on the amount of data points per minute. CO_2 (with its data measured in seconds) have a sliding window width of 500 consecutive measurement points (8.3 minutes) (Figure 10). Black carbon from the MAAP (with its data measured in minutes) has a sliding window width of 150 consecutive measurement points (150 minutes). The percentile and different window widths was chosen by testing different values. A higher or a lower percentile would not result in a proper calculation of the background concentration, in which case the value would be tilted to either the lower or higher end of the background noise. The window width was chosen in order to establish a background value unaffected by several consecutive plumes, yet not too many points to affect the mean average of smaller fluctuations in background levels.
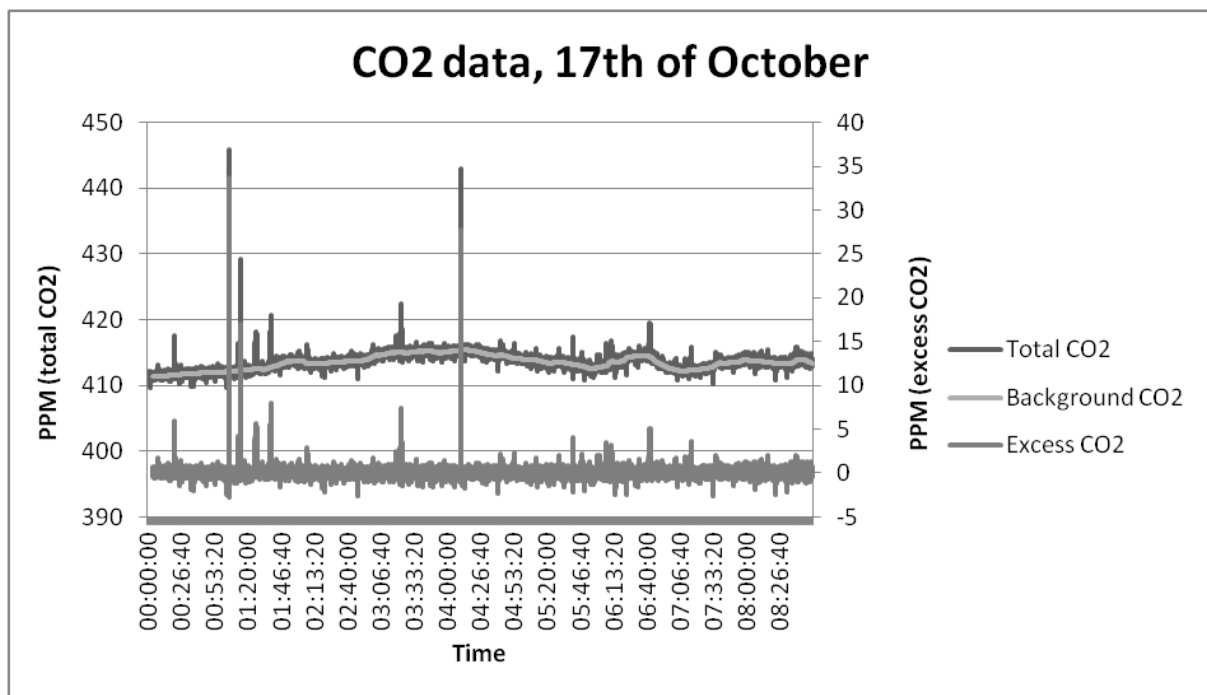

Figure 10: Using CO_2 data from October the 17th, this is an example of the calculated background data and the resulting excess data. The left axis is the total ppm of CO_2, while the right axis is the excess ppm of CO_2 (ship plumes only).

The excess CO_2 and excess absorption coefficient is defined as the difference between the measured total and the calculated background data, an example of which can be seen in Figure 10. The excess data ends up being both the ship plumes and the noise, which means that there are values below zero in the excess data. This also means that emission peaks with little or undetectable levels of black carbon will be no different from background noise. Depending on what data points is included in a

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black carbon "peak", this will cause some boats to have a negative emission factor value when in fact it should be at or just above the value zero. Vice versa, it will also cause some boats to have a slightly positive emission factor value, when it should be at or just above zero. This is left unchanged so as to avoid subjective bias in the calculations and mean values. However, when ships are analysed and presented on a comparative individual scale the negative values were set to just above zero.

The passage of a ship was identified as a rise in CO_2 readings of $\geq$ 2 ppm, forming a peak. This was to ensure that peaks weren't caused by other factors in the data. Peaks that were too close to each other in time were deemed unusable, since it became impossible to separate two ships from each other. This affected the black carbon peaks especially, since their peaks are longer in time due to the function of the MAAP.

For each plume the following was calculated: the start and end time of the plume, plume duration, and the area of the peak using the trapezoidal rule. The plume area was then used to calculate emission factors.

5.3 Calculating Emission Factors

Emission factors for absorption at 637 nm was calculated using equation (3) used by Lack et al. (2009). The conversion factor $\int fuel - optical$ (1.62 m^2 ppmv Mm kg^{-1}) convert concentration of the parameter in air (absorption coefficient for black carbon) to concentration per unit fuel burnt (Lack et al., 2009).

$$EF_{Optical}\ (m^2\ kg^{-1}) = \frac{Optical\ parameter\ (Mm^{-1})}{CO2\ (ppmV)} \times \int fuel - optical \qquad (3)$$

Emission factor for black carbon was calculated using equation (4) used by Müller et al. (2011).

$$EF_{Black\ carbon}(g\ kg) = (EF_{Optical}\ (m^2\ kg^{-1}))/Q_{BC}/1.05 \qquad (4)$$

5.4 Limitations

There were two additional instruments that would have added to the result in this study, the PASS-3 and SP-AMS.

The result from PASS-3 were not very usable, it was mostly noise. While there were hints of peaks correlating with CO_2 peaks, there were also peaks at places where no CO_2 or soot peaks occurred. This is very unfortunate, since without PASS-3, we are not able to calculate the Ångström absorption exponent, which in essence would show if the particles consist of pure soot, or if there are also other compounds, like brown carbon that are able to absorb the solar radiation.

The SP-AMS was also available at the same time as the MAAP, but analysis of this data would require a separate diploma work. SP-AMS data would possibly have added to the results on soot particle emissions.

Five days of data was not enough to get enough statistics on individual ship identifications. Out of the 228 plumes, only 45 ships were identified. Out of these 45 individual ships, there were 13 different ship types.

6 Results and discussion

In this chapter, results and relevant discussion will be presented.

Table 2: Summary of averaged Emission Factors from this study in comparison to other studies.

Reference	Absorption, 637 nm (m2/kg)	Black carbon (g/kg)
This study (2015)	3,9 ± 9,7	0,57 ± 1,40
Lack et al. (2009)	6.6 ± 5.7	0.85 ± 0.76
Petzold et al. (2008)		0,17 ± 0,04
Sinha et al. (2003)		0,18 ± 0,02

The result from this study is presented in Table 2. The emission factor for absorption is also presented since it is used to calculate the emission factor for black carbon. The resulting mean emission factor for the shipping fleet connected with Gothenburg is 0,57 gram black carbon per kilogram burnt fuel (with an uncertainty of ± 1,40 g/kg).

There is no previous study done with the same instruments and methods as this one, but one other study uses the same methods of calculations (Lack et al, 2009). The result from this study (2015) can therefore not be directly compared with the others, but the differences can at least be somewhat discussed. The calculated emission factors in this study (2015) are within the same area as the other three studies. The two recent studies out of the four (2009 and 2015) have large standard deviations, resulting in an overlap between the four studies. The different methods, calculations, and instruments used in the studies make it difficult to reach a proper conclusion.

As seen in Table 2, the result of this study is not very different from the others. The reduction in sulphur fuel content in Gothenburg does not result in a clear reduction of emitted black carbon, compared to the year 2006. At this low level of sulphur fuel content, it seems like engine load has the biggest impact on emitted black carbon. According to Lack and Corbett (2012), the emissions of black carbon increase when the ship engine load decrease.
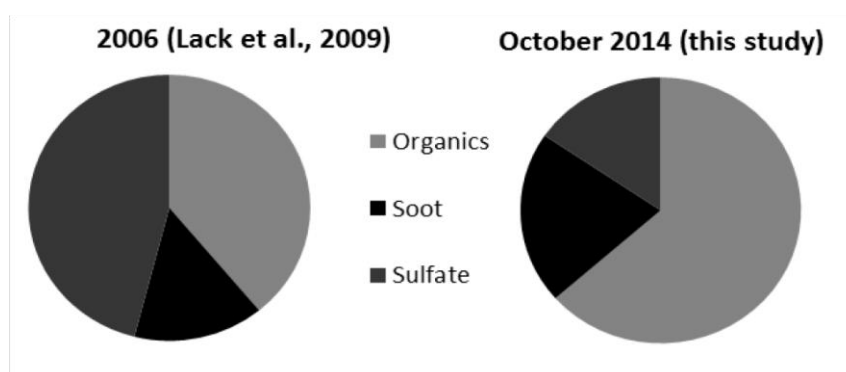

Figure 11: The distribution of particles in 2006 and 2014. To the left, the result from Lack et al. (2009). To the right, preliminary result from the measurement campaign in Gothenburg. The preliminary result is from the instrument SP-AMS, which was not used in this study.

The figure above is a preliminary analysis of the data from the SP-AMS, which was not used in this study (more info regarding the instrument in section 4.2.3). In this figure it can be observed that the sulphate particles have been greatly reduced with the reduction of sulphur fuel content. The amount of black carbon particles (soot), however, have not been significantly reduced.

It is therefore suggested that the measurements for this study is replicated after the new regulation of 0.1 % sulphur fuel content in January 2015. In order to replicate the procedure as good as possible the project should have the same preconditions as this one had, using the same instrument (MAAP), the same measurement location, same time of year, etc. The result from this study could then be compared to the future one, and hopefully give more insight as to how this new sulphur regulation affect the emissions.

Another option is to do the same measurements but on ships travelling outside the SECA areas instead, with a higher sulphur fuel content of 3.5 %. Seeing as these results might be on too low sulphur fuel content, the same measurement method on higher sulphur fuel content could be more comparable. Additionally, the method of measuring from a coastal field station is very practical since measurements can be done on an unlimited amount of ships, compared to measurements done on planes and ships.

Yet another option is to research the ships individually, checking fuel sulphur content, engine type, ship type, engine load, etc. This could be done over several days in November. With this research you could observe how the emission factors vary with the previous factors.

Finally, it should be stated that this study do not include a complete characterization of black carbon emissions and light absorption. Other equipments are needed for even further researching. Other equipments could have given information such as: Ångströms coefficient, microscopic images on the actual black carbon particles, characterization of the particles size and density, chemical characterization of black carbon particles and the compounds condensed upon them, how condensed compounds affect the light absorption, a characterization of the actual surface of the particles would be of interest, and how the structure of a black carbon particle change over time.
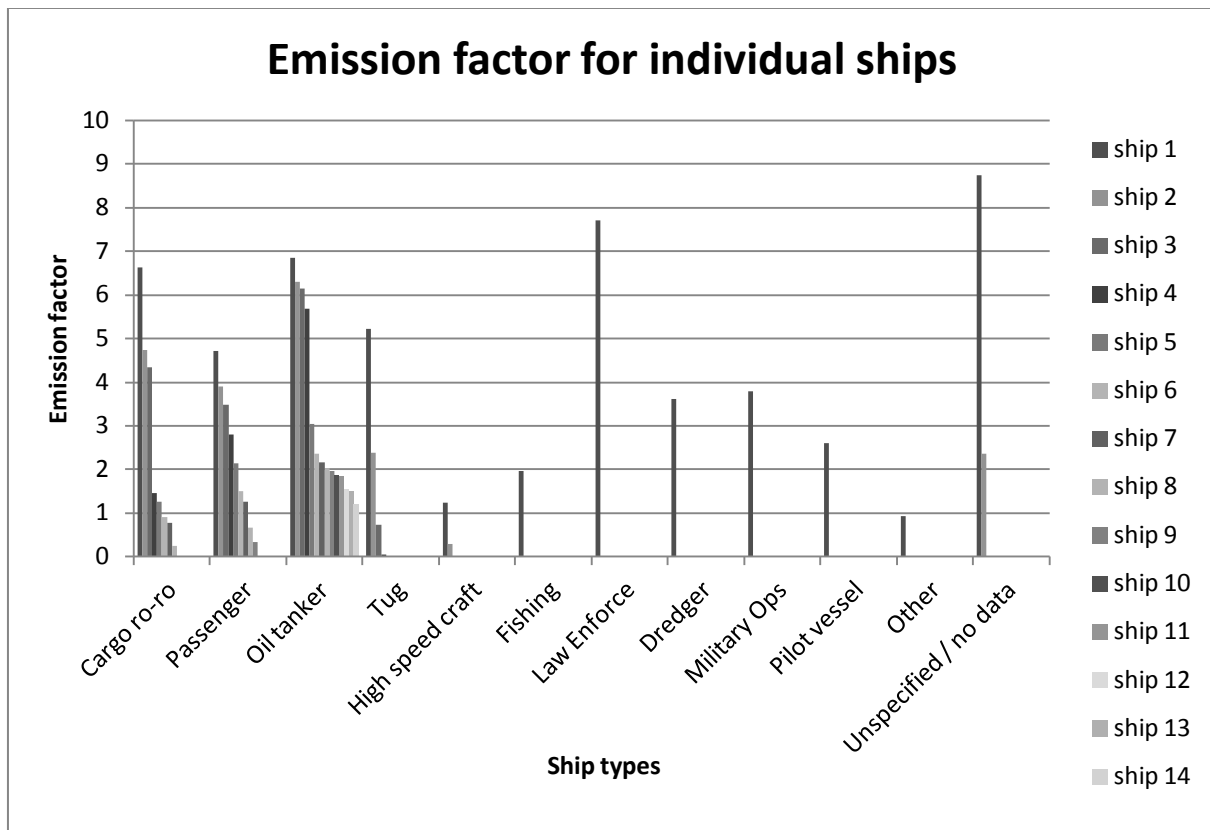
Figure 12: The emission factor *light absorption coefficient* (LAC) for individual ships. It is the amount light absorbing material emitted per kilogram fuel. All negative emission factors have been changed to 0,05 m^2/kg. This is because ships cannot have a negative emission factor, and also to make those small values visible in the graph.

The resulting difference in emission factor between individual ships is presented in Figure 11. It seems that some oil tankers have very high emissions of light absorbing material, higher than most other ship types (Figure 11). However, more than half of the oil tankers also seem to have lower values between 1-2. The emissions of passenger ships are clustered, with every individual ship having a different emission factor value ranging from about 0,4 to 4,7. The distribution of emissions from cargo ro-ro ships is similar to that of oil tankers. A few cargo ro-ro ships seem to have very low emissions between 0-1. The tugboats have a few ships with very different emissions.

It is difficult to assume anything definite about the other ship types, as they only have one or two identified ships.

It is crucial to investigate the reason behind the difference in emissions between ships. In order to do this, information from each individual ship is needed regarding engine load, engine type, fuel quality, etc. This information was not procured during the course of this study, and could therefore not be analysed.

7 Conclusion

The reached conclusions will be presented in this chapter.

- The calculated emission factor for black carbon is 0,57 gram black carbon per kilogram burnt fuel (with an uncertainty of ± 1,40 g/kg). However, it is not certain how a reduction in sulphur fuel content will affect the emissions of black carbon. At this low level of sulphur fuel content, black carbon seems to be more affected by other factors (like engine load) than sulphur, according to Lack and Corbett (2012).

- It is important to continue the research on how sulphur fuel content affects emissions of black carbon. A study that follow up on this one, using the same instruments and methods, should give results that can be compared with this one. The comparison can give an indication of how the SECA reduction of sulphur fuel content from 1 % to 0.1 % affect emissions of black carbon. Alternatively, compare the inside of SECA areas (0.1 %) to the outside (3.5 %).

- A further characterization of black carbon particles is necessary for a better understanding on the subject. The addition of data from other instruments such as the PASS-3 and the SP-AMS would have contributed to this.

- Individual ships consisted mainly of oil tankers, cargo ro-ro's, passenger ships, and a few tugboats. All ship types have some individuals with high emissions of light absorbing material, and some with lower emissions. It is difficult to draw a conclusion from most ship types. Oil tankers had one third of individuals with very high emissions, although more than half was on the lower end. Cargo ro-ro's also had one third with higher emissions, and more than half with lower emissions. The lower emitting individuals of cargo ro-ro's were the lowest among all identified ships.

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