Effect of aftertreatment on ship particulate and gaseous components at ship exhaust

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[1]**Kimmo Teinilä, [3]Päivi Aakko-Saksa, [1]Jukka-Pekka Jalkanen, [2]Panu Karjalainen, [1]Matthew Bloss, [1]Jaakko Laakia, [1]Sanna Saarikoski, [3]Hannu Vesala, [3]Rasmus Pettinen, [3]Päivi Koponen, [2]Niina Kuittinen, [3]Pekka, Piimäkorpi, [1]Hilkka Timonen**

[1]Finnish Meteorological Institute, Atmospheric Composition Research, Atmospheric Aerosols, FI-00560, Helsinki, Finland

[2]Tampere University of Technology, Faculty of Natural Sciences, Aerosol Physics, FI-33101, Tampere, Finland

[3]VTT Technical Research Centre of Finland Ltd., FI-02044, VTT, Finland

Abstract

Particle chemical composition, physical properties and concentrations of selected gaseous compounds were measured on-board a large RoRo passenger ship equipped with an open loop scrubber and diesel oxidation catalyst. Measurements were made using on-line measuring devices with high time resolution together with filter based samplings. The aim of the measurements were to gather information on the performance of exhaust aftertreatment.

Measurements showed that scrubber reduce effectively the SO_2 concentration from the exhaust gas and also concentration of NO_x was reduced. CO and hydrocarbon concentrations were reduced by diesel oxidant catalyst located before scrubber. Particulate matter (PM) consisted mainly sulphate, organics and black carbon (BC). During open sea cruising (65% engine load) the major particulate chemical compound measured after scrubber was sulphate (66%). However its concentration was very low (~40 mg/Sm^3 dry). Markedly lower sulphate concentrations were measured at 17% engine load which is connected to lower engine temperature and reduced conversion of SO_2 to SO_3. About one third of measured PM was organic matter and only about 4% (<5 mg/Sm^3 dry) of PM was black carbon (BC). For lower engine loads (17%) larger concentrations of black carbon were measured (~10 mg/Sm^3 dry) which can be explained by the incomplete combustion when lower engine load is used. Diesel oxidant catalyst seemed to reduce also concentrations of measured metals and polycyclic aromatic hydrocarbons (PAH) in particulate phase.

Abbreviations

AE   Aethalometer
AMS   Aerosol Mass Spectrometer
BC   Black carbon
CO_2 Carbon dioxide
CO   Carbon monoxide
CPC   Condensation Particle Counter
D_{va} Particle diameter (vacuum aerodynamic)
D_p Particle diameter (mobility)
DMA   Differential Mobility Analyzer
DOC   Diesel Oxidation Catalyst
eBC   Equivalent black carbon
EC   Elemental carbon
EEPS   Engine Exhaust Particle Sizer
ELPI   Electric Low Pressure Impactor
epToF   efficient particle Time-of-Flight
FID   Flame ionization detector
FMI   Finnish Meteorological Institute
FPS   Fine Particle Sampler
FSN   Filter Smoke Number
FTIR   Fourier transformation infrared
HFO   Heavy fuel oil
HO_2 Hydroperoxyl
IC   Ion chromatography
ICP-MS   Inductively coupled plasma mass spectrometry
i.d.   inner diameter
IMO   International Maritime Organisation
LNG   Liquefied Natural Gas
MCP   Multi-channel plate
MGO   Marine Gasoil
MS   Mass Spectrum
Nd:YAG   Neodium-doped Yttrium Aluminum Garnet
Sm^3 Flow normalized to 273.15 K and 101325 Pa
NO_X Nitrogen oxides (NO and NO_2)
O_2 Oxygen
O_3 Ozone
OH   Hydroxyl radical
OC   Organic carbon
PAH   Polyaromatic hydrocarbons
PAM   Potential Aerosol Mass chamber
PC   Pyrolytic carbon
PM   Particulate matter
PSM   Particle size magnifier
rBC   Refractory black carbon
RH   Relative humidity
Ropax   Roll in/Roll out passenger

RoRo   Roll in/Roll out
SDS   Ship Dilution System
SECA SO_x Emission Control Areas
SMPS Scanning Mobility Particle Sizer
SOA   Secondary organic aerosols
SO_2 Sulfur dioxide
SO_x Sulfur oxides
SP-AMS   Soot particle aerosol mass spectrometer
TFE   Tetrafluoroethylene
ToF   Time-of-Flight
TUT   Tampere University of Technology
US EPA   United States Environmental Protection Agency
UV   Ultraviolet
VOC   Volatile organic compounds
VTT   Technical Research Centre of Finland Ltd.

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1. Introduction

Sulphur reduction from 1.0%S to 0.1%S from Jan 1st 2015 provided the ship owners several options how to adjust to the new requirements. First option was to fleet-wide shift to low sulpur fuels, which has generally been considered as a very expensive option because of large difference in price of 0.1%S and 1.0%S fuel. Second method was the introduction of liquefied natural gas (LNG), but this mainly concerns newbuilds, because retrofitting existing vessels for LNG use has not normally been an economically viable option. The third method concerns installing exhaust abatement techniques, which reduce sulphur emissions to levels similar to low sulphur fuels as required in the EU sulphur directive (The European Parliament and The Council of the European Union, 2012). The adoption of SO_x scrubber devices instead of low sulphur fuel largely depends on the cost. If a vessel mainly operates in SO_x Emission Control Areas (SECAs) and annual fuel consumption is high, scrubber use may prove to be cheaper than operating entirely with low sulphur fuel. This balance shifts towards scrubbers if the price difference between fuel grades is high.

Globally, there were about 200 vessels using SO_x scrubber devices (FMI, spring 2016 situation), but not all of these operate in the Baltic Sea. About one third of the global scrubber installations are the cheapest open-loop type equipment and most of these are found in passenger cruise vessels. In areas where sea water salinity is too low for open loop scrubbing, for example in the Baltic Sea region, additional chemicals (NaOH, caustic soda) may be needed. Open loop scrubbers wash the ship exhaust gases using seawater spraying and release the wash water to the sea. The sulphur (along with metals and various organic compounds) in exhaust will be transferred to the sea with the wash water. In contrast, a closed system recycles the wash water, but requires constant injection of chemicals to neutralize the gaseous sulphur emissions. A third type is a hybrid between these two extremes and it allows closed loop operation of the scrubber in sensitive areas where pollutant release to the sea is not acceptable. An open loop mode can be used in other regions where wash water release is within International Maritime Organization IMO limits.

Open loop scrubbing requires significant amounts of sea water to be pumped during normal operation of the ship. Typically, a RoPax (roll on/roll off passenger) ferry between Helsinki and Stockholm needs about 300 litres/second water flow to maintain SO_x scrubbing efficiency at sufficient level. However, Germany and Belgium have forbidden the use of open loop scrubber use in their coastal waters, because of a possible conflict with the European Water Framework Directive (European Community, 2000) which limits the release of harmful substances to surface waters. For this reason, any vessel equipped with an open loop scrubber and operating close to German coastline in the Baltic Sea will need to switch to low sulphur fuel.

Openly available scientific literature reports only handful of cases of scrubber performance in realistic operating conditions. The scrubber measurement campaign within the EnviSuM project provides a performance report of a vessel equipped with an open loop scrubber and aims to fill this gap in knowledge. Currently, it is not very well known how efficiently the scrubber reduces the emissions of primary combustion particles. The inhalable small particles play a key role when human health effects of air quality are assessed and it has been used as a primary justification for the establishment of SECAs. The scrubber itself will reduce gaseous emissions of sulphur effectively, which reduces atmospheric

formation of particles after the exhaust has left the ship funnel, but its effectiveness in reducing other climate forcers, like black carbon (BC) emissions, is currently debated at the IMO. Further, European legislation requires that any abatement technique applied to reduce sulphur emissions will need to continuously perform at least at a level comparable to low sulphur fuel use.

This report describes the measurements done onboard a large RoRo passenger (RoPax) ship equipped with an open loop scrubber and a diesel oxidation catalyst (DOC). The vessel operates on a regular route between Finland and Germany and has to switch off the scrubber when approaching Germany and use low sulphur fuel instead. This vessel provided an excellent opportunity to study various situations when scrubber was in operation and when it was not used.

Particle chemical composition and physical properties together with concentration of selected gaseous compounds were measured on two sequential cruises in April 2017. Measurements were made in co-operation between Finnish Meteorological Institute (FMI), Tampere University of Technology (TUT) and VTT Technical Research Centre of Finland Ltd. (VTT). VTT measurements were financial supported by Trafi (58942).

2. Measurement set-up and calculations

Exhaust from one of the ships four main engines (Wartsila 9L46D, 514 rpm, MCR power output 10 400 kW) equipped with an open loop scrubber (ECO-DeSO$_x$, Ecospray Technologies), and a diesel oxidant catalyst (DOC, Ecospray Technologies) was measured. Both the scrubber and DOC were installed in 2016. Measurements were conducted for both the open sea cruising and harbor operation (Port A and Port B). The RoRo passenger ship used two different fuel types: Marine Gas Oil (MGO) and Heavy Fuel Oil (HFO). Fuel samples were analysed at ASG and engine oil samples at Fluidlab Oy (Appendix 1.). Sulphur content of HFO was 1.9 wt% and that of MGO was 0.02 wt%. Properties of engine oil resembled those of SAE 40 oil for HFO applications. Concentrations of engine wear metals were relatively low and oil was in good condition.

Ship operated normally and thus engine load varied during cruise. The most typical engine load range was from 60 to 70%. During short time intervals, engine load was appr. 90%, 77%, 50% and below 20%. Major part of data was achieved at high loads on-sea, but some data was achieved also at appr. 17% engine load in ports A and B. Otherwise HFO fuel was used, except MGO in port B.

Measurements were conducted from the following locations:

- C = After scrubber

- B = Before scrubber (After DOC), engine room

- A = Engine-out (Before DOC), engine room.

Many parameters were recorded including humidity, pressures and temperatures of test cells and exhaust gas (Fig. 1). Humidity in area close to point C was higher (35–44%) and temperature lower (14–21 °C) than those close to sampling points A and B (21–27% and 22–24 °C).
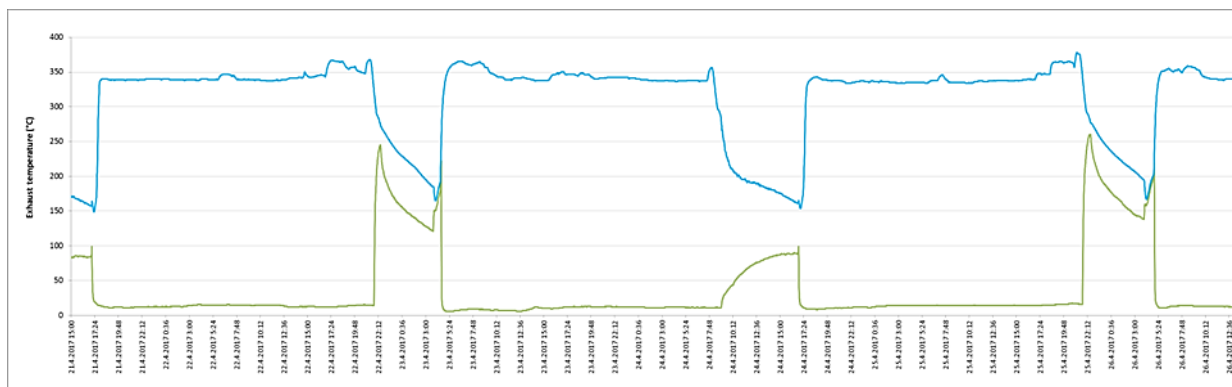
Figure 1. Exhaust temperatures before (blue) and after scrubber (green).

Engine load was available from ship data. Fuel consumption recorded by ship was a sum for two engines, and thus not useful for the calculations of the results for the measured engine. Based on the theoretical fuel consumption of 170 g/kWh, measured exhaust CO_2 concentrations and fuel composition, fuel consumption (1113 and 300 kg/h) and exhaust flows (42 400 and 24 400 kg/h) were calculated at 60–65% (power 6549 kW) and at 17% engine load (1 767 kW). These values were used in the calculations of emissions as mass per kg fuel or per kWh.

3. Instrumentation

The measurement set-up is shown in Fig 2. Real-time measurements of particle chemical and physical properties were done by FMI and TUT. The sampling for real-time particle measurements (FMI&TUT) downstream the scrubber system (C) was performed with a Fine Particle Sampler (FPS, Dekati Oy) equipped with a stack heater probe. In the FPS, the first stage dilution is performed with a perforated tube diluter whereas the second stage dilution unit is an ejector. The dilution air was set to the temperature of about 25 ˚C. Total dilution ratio was determined with trace gas (CO_2) measurements in both exhaust and diluted exhaust. The used dilution ratio was ~200-300 when fresh exhaust was measured and an additional dilution (6-10) was used when aged exhaust measurements were made using a potential aerosol mass (PAM) chamber.

Gaseous components from exhaust gas were measured continuously at all three locations with VTT Fourier transformation infrared (FTIR) devices (raw exhaust sampling). VTT also conducted black carbon measurements (raw exhaust sampling) and filter based aerosol samplings for further chemical analyses at all three sampling points. Special multiple measurement probes completely inserted to the exhaust duct were used for extracting the sample from the exhaust duct (particulate sampling i.d. 6 mm, gaseous components i.d. 4 mm). Exhaust gas temperature measurement was included in the probes. Probe before the scrubber was unheated, however, heated lines, filters and diluters were connected immediately to the probe outlet and the connections were isolated for avoiding any "cold spots" in the sampling lines. The probe used after the scrubber was heated up to 250 °C to avoid any water droplets to the sampling lines and filters (cold spots). Based on additional sampling, heating of probe did not affect the particulate matter results.

For each instruments the sampling location as well as the institute responsible of instrument operation (FMI/TUT/VTT) is shown in the detailed device list below.
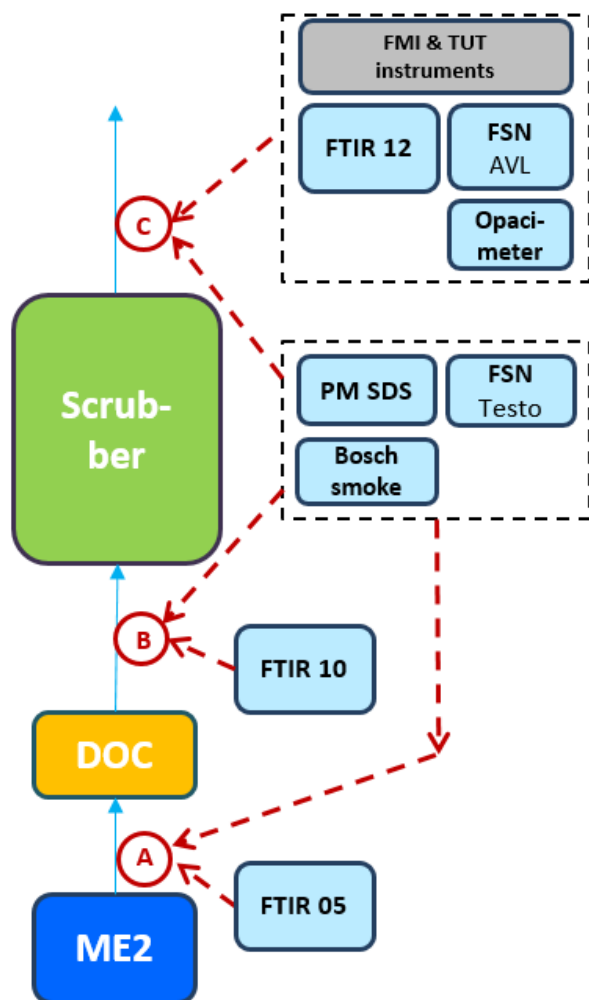

Figure 2. Set-up of the instruments.

SP-AMS (FMI, C)

Soot Particle Aerosol Mass Spectrometer (SP-AMS; Aerodyne Inc., De Carlo et al., 2006; Onasch et al., 2012) was used for real-time measurement of particle chemical composition for both inorganics, organics as well as refractory black carbon (rBC) and some metals. A narrow beam of particles formed with an aerodynamic lens is transmitted into the AMS vacuum chamber where they are vaporized with a tungsten vaporiser at 600 ˚C. In order to measure the concentration of non-refractory material e.g. organic material and inorganic species such as sulphate, nitrate, ammonium and chloride. Refractory material, rBC and refractory organics and inorganics, are vaporised with the Nd:YAG laser (1064 mm) above 600 °C. The vaporised compounds are ionised using electron impact ionisation (70 eV). Ions formed are guided to the time-of-flight (ToF) chamber and a multi-channel plate (MCP) is used as a detector. The SP-AMS was operated in both MS (Mass Spectrum) and epTOF (efficient particle time-of-flight) mode alternately.

The SP-AMS data was analysed using AMS software (SQUIRREL 1.60 and PIKA v1.20) with Igor Pro 6.37-7 (WaveMetrics, Lake Oswego, OR). The collection efficiency of the SP-AMS depends upon three parameters, aerodynamic lens losses, particles bouncing off the vaporiser before full vaporization and particle beam overlapping the laser (Onasch et al., 2012). The collection efficiency of SP-AMS was estimated based on the acidity of the sampled aerosol (Middlebrook et al., 2012). The SP-AMS data was also corrected using the measured CO_2 concentrations.

Aethalometer (FMI, C)

Concentration of BC was measured using a dual-spot aethalometer (AE33, Magee Scientific, Drinovec et al., 2015). The flow rate was set to 5 L/min and the time-resolution of measurement was 1 min. The filter tape used was a TFE-coated glass fiber filter (M8020)

SMPS (FMI, C)

Particle number size distributions for the sub-micrometer particles were measured using Scanning Mobility Particle Sizers (SMPS, Wang and Flagan, 1990). SMPS has a Differential Mobility Analyzer (DMA, Model 3071 Electrostatic Classifier, TSI Inc.) for particle size selection and a Concensation Particle Counter (CPC, Model 3775, TSI Inc.) to measure particle number size distribution in the size range 10-400 nm (mobility diameter). The nano-SMPS is similar to the SMPS but it uses different DMA (Model 3080, TSI Inc.) and CPC (Model 3776, TSI Inc.) enabling measuring of particles in the size rage 2-65 nm (mobility diameter). Number size distributions were converted to mass size distributions and total particle mass using particle density of 1 g/cm^3.

PAM chamber (FMI, C)

The potential aerosol mass (PAM, Aerodyne Inc., Kang et al, 2011) chamber was used to simulate aerosol aging in the atmosphere. The PAM chamber is a small flow through reactor with two UV lamps positioned inside to produce photons at the wavelengths 185 and 254 nm. Photolysis of O_2 and H_2O produced the oxidants O_3, OH and HO_2. A second stage dilution with additional dilution factor between 7 and 10 was used when performing measurements with PAM chamber. The flow through the PAM chamber was ~9 L min^{-1} composed of the ring flow (1.5 L min^{-1}) and central flow (7.5 L min^{-1}). The aging potential of PAM chamber varied with the used voltage (2.9-9 V) being 1-14 days. The aging in the PAM chamber was calibrated against the decay of CO which was injected into the sample line before the PAM and measured both before and after the chamber (Lambe et al., 2011).

PSM (TUT, C)

The combination of a particle size magnifier (PSM; A10; Airmodus Oy) and a CPC (model A20; Airmodus Oy), refers to as a PSM. The device measures the number concentration of particles larger than 1.3 nm. The PSM was run in step mode to select different cut sizes for the particle counter.

ELPI+ (TUT, C)

Electrical Low Pressure Impactor ELPI+ (Dekati Oy) is an improved version of the ELPI –system. ELPI+ measures particle size distribution and concentration in real-time in the aerodynamic size range of 6 nm – 10 μm with 10 Hz sampling rate. ELPI+ was especially used to determine particle mass and number concentrations, and about half of the time the device measured downstream the PAM chamber.

EEPS (TUT, C)

The Engine Exhaust Particle Sizer (EEPS, model 3090, TSI Inc.) spectrometer measures the size distribution of engine exhaust particle emissions from 5.6 to 560 nm with 10 Hz time resolution. The EEPS spectrometer displays measurements in 32 channels total (16 channels per decade). It operates over a wide particle concentration range, including down to 200 particles/cm³. It operates at close to ambient pressure to prevent evaporation of volatile and semivolatile particles. The instrument was used to monitor to particle number size distribution all the time right after the FPS dilution system.

SIDOR CO_2 analyzer (TUT, C)

A CO_2 analyzer SIDOR (Sick) was used to measure the concentration of CO_2 downstream the FPS dilution system. Based on the measured CO_2 concentrations, the dilution ratio can be determined in real time.

FTIR (VTT, A/B/C)

More than 10 gaseous compounds were measured on-line at 20 seconds intervals using three FTIR equipment (Gasmet DX-4000) purchased in 2005 (FTIR05), 2010 (FTIR10) and 2012 (FTIR12). Raw exhaust sample was drawn and conditioned to 180 °C. Compounds measured were SO_2, H_2O, CO_2, CO, NO, NO_2, CH_4, N_2O, NH_3, ethylene, formaldehyde, acetaldehyde and octane. NO_x is a sum of NO and NO_2 (calculated as NO_2). Examples of detection limits are: NO_2, CH_4 and N_2O 2 ppm, NH_3 4 ppm, formaldehyde and acetaldehyde 5 ppm. Only concentrations exceeding the detection limit of the FTIR instruments are significant. FTIR12 measured always after scrubber (location C), and its data is the most extensive. Measurements with FTIR10 and FTRI05 started late and their locations (A, B) were switched on 25.4.2017 at 13:33. On-line analysis with FTIR allowed continuous monitoring and a large amount of data was gathered. Average over 10 minutes consists of 30"data points". The standard deviation presented illustrates rather the variation of engine load than the instrumental spread.

AVL 415S Smoke Meter (VTT, C)

Filter Smoke Meter AVL 415S measures FSN, a traditional "smoke number", from raw exhaust gas. The measurement principle implemented in the AVL Filter Smoke Meter is based on light absorption. The change in optical reflectance of visible light from a loaded filter relative to clean filter is measured. Conversion of FSN (Filter Smoke Number) to the BC concentration was according to the equation provided by the manufacturer (otherwise correlations available by ISO 8178-1 (2006, eq. A. 16) could be used). FSN is a standardized method conforming to ISO 10054. In these measurements, 2 meters transfer line (70 °C) was used and temperature of cabin was 63 °C.

Testo 338 Smoke Meter (VTT, A/B/C)

Testo 338 is portable, small (270 x 92 x 127 mm, 770 g) instrument for measuring FSN soot number and Bosch number, and the BC concentrations (mg/m³) are calculated. Raw exhaust is drawn through filter, which darkens with accumulation of BC. Absorbance of light is measured. In opposite to AVL 415S Smoke meter, sample line is not heated in Testo 338 as a short line is expected to stay sufficiently hot. Prior to each measurement, reference test is run using ambient air for pressure and temperature corrections. User needs to estimate exhaust pressure by adjusting by-pass manually depending on

pressure. Instrument does not warn of the false by-pass adjustment. Two scales are switched automatically depending on the BC concentrations to adjust collection time to 20 s at high scale and to 40 s at low scale.

Bosch smoke (VTT, A/B/C)

An old Bosch smoke meter was used in the measurements. In this instrument, sample is drawn through a filter with help of a simple spring assisted system. Blackness of filter is evaluated with a separate unit to provide a reading (Bosch number). For the conversion of Bosch number to BC, equation A.16 of ISO 8178 was used.

Opacity (VTT, A/B/C)

Opacity measures reduction of light transmittance over a column path usually expressed as a percentage. Sample was drawn from exhaust duct using a pump.

PM-SDS system (VTT, A/B/C)

Commercial ISO 8178 dilution and sampling systems for particulate matter (PM) are large and heavy, for example AVL 472 Smart Sampler at VTT weights over 260 kg. It was not possible to move this system between different locations on-board a ship with limited room. At VTT, a movable Ship Dilution System (PM-SDS) was designed and built-up. This system can be moved between floors of ship without aid. In the ISO 8178 dilution and sampling, a partial flow from the raw exhaust was taken for dilution with filtered air, and then the flow was drawn through filter to collect the particulate matter to the filter substrate. Dilution ratio was 10 in PM collections. Temperature on filter face was between 42 and 52 °C. Face velocity requirement was within the requirements (35–100 cm/s). Heating of transfer line (6 m) was 250 °C. For PM measurements, three replicate tests with four filter materials were conducted in locations **C**, **B** and **A.**

PM filter materials

PM was collected using the following filter materials:

- Pallflex TX40HI20-WW, o.d. 47 mm. Filter material is borosilicate microfibers reinforced with woven glass fibre coated with cloth and bonded with polytetrafluoroethene (PTFE, Teflon). Both primary and back-up filters were used. This filter type is common in Europe for PM measurements.

- Pallflex Teflo 2, o.d. 47 mm, PTFE reinforced with polymethylpentene (PMP). Typical thickness 46 µm (516-8912, VWR), 2 µm porosity. Flow 53 l/min/cm^2 (0.7 bar). Back-up filters were not used. PTFE filters are used in USA for PM measurements.

- Whatman PM2.5 PTFE. O.d. 46.2 mm, 2 µm porosity. Back-up filters were not used. Meet EPA PM2.5 requirements (40 CFR Part 50, Appendix L). PTFE filters are used in USA for PM measurements.

- Tissuquarz 2500QAT-UP, o.d. 47 mm. A pure quartz without binder. The quarz filters were pre-cleaned at 850 °C for two hours and stabilized. The back-up filters were not used in the collections with quartz filters. Quarz filters are used for EC/OC and metal analyses.

Four different filter materials gave comparable results, particularly at PM concentrations below 100 mg/m^3. At higher PM concentrations, PTFE Whatman collected lower amount of aerosols than other filters. Quarz filter collected most aerosol and resulted in the largest spread in the results. Mass observed in the back-up filters was in most cases below 4% of PM. Material on back-up filters did not contain sulphates, and it assumedly consist of semivolatile organic compounds. Pallfelx TX40 and PTFE Whatman filters collected similarly sulphates.

Elemental and organic carbon (EC/OC)

A Sunset Laboratories Inc's analyser model 4L was used at VTT for EC/OC analysis from quarz filters. EC/OC analysis was carried out using the EUSAAR2 temperature program. EC/OC method is based on a thermal-optical analysis technique (Bauer et al. 2009). Measurement program consist of steps where temperature and gas atmosphere is adjusted while continuously measuring the laser transmission through the sample matrix. In the first phase, sample is heated in steps in Helium (He) atmosphere to remove OC. The organics may be pyrolytically converted to pyrolytic carbon (PC) in this phase, which is monitored by measuring continuously the laser signal as pyrolysis decrease transmittance of the laser. In the second phase, 2% O_2/He gas mixture is introduced and temperature is raised again. Both the PC and original EC are oxidized to CO_2, which is then converted to methane and detected by the FID. PC is compensated by detecting split time when laser transmittance is same as in the start of pyrolysis. Based on the flame ionization detector (FID) response and laser transmission data, the quantities of OC and EC in the sample are calculated. Methane is injected into the sample oven providing for the calibration of each sample analysed to a known quantity of carbon. Saccharose is used as an external standard.

Ion analyses

Anions, including sulphates, were analysed from water/isopropanol extracts of Pallflex TX40 filters by Labtium using ion chromatography (IC).

Metals

Metals were analyses from the quartz filters by Labtium. Filters were extracted in micro oven using nitric acid and hydrofluoric acid (EN 14385) and analysed by using inductively coupled plasma mass spectrometry (ICP-MS). Metals analysed were Al, B, Ba, Ca, Co, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Sr, U, V, Zn.

Polyaromatic hydrocarbons (PAHs)

Polyaromatic hydrocarbons (PAHs) were analysed by Metropolilab. In total, 24 individual PAH compounds were analysed according to ISO 16000 and EN 14662 analysis methods. Filter samples were extracted with toluene in ultrasonic bath. Detection limits of the PAH analysis at MetropoliLab are 10–30 ng per compound per sample and measurement uncertainty is 30%. Sum of 16 priority PAHs defined by the US EPA (1998) include naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, antracene, fluoranthene, pyrene, benz[a]antracene*, chrysene*, benzo[b]fluoranthene*, benzo[k]fluoranthene*, benzo[a]pyrene*, dibenz[a,h]antracene, indeno[1,2,3-cd]pyrene* and benzo[ghi]perylene. Six priority PAHs (marked with asterix) are included in the list of 7 priority PAHs defined by the US EPA (2007).

4. Results

4.1 Gaseous emission species

The CO_2 and NO_x concentrations were higher at high engine loads than at low loads, which reflects more complete combustion at high engine loads (Fig. 3). Scrubber reduced the NO_x concentrations of exhaust to some extent.
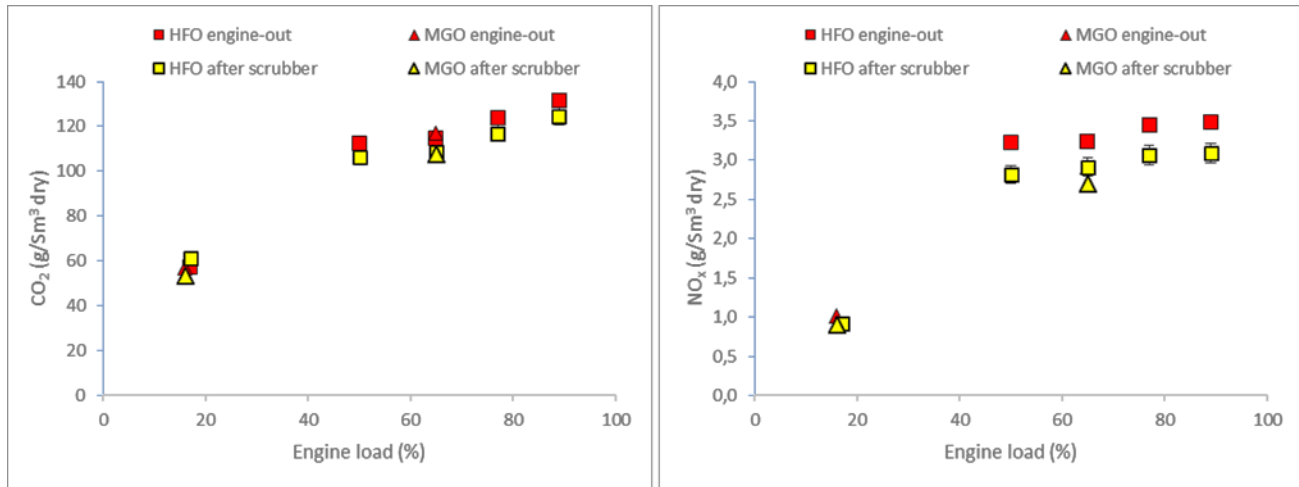

Figure 3. The CO_2 and NO_x concentrations at different engine loads

Also CO concentrations were load-dependent showing higher concentrations at low loads than at high loads (Fig 4). Indicatively, the CO and hydrocarbon concentrations were reduced in DOC that was located before scrubber, at least at high engine-out concentrations (Fig. 5).
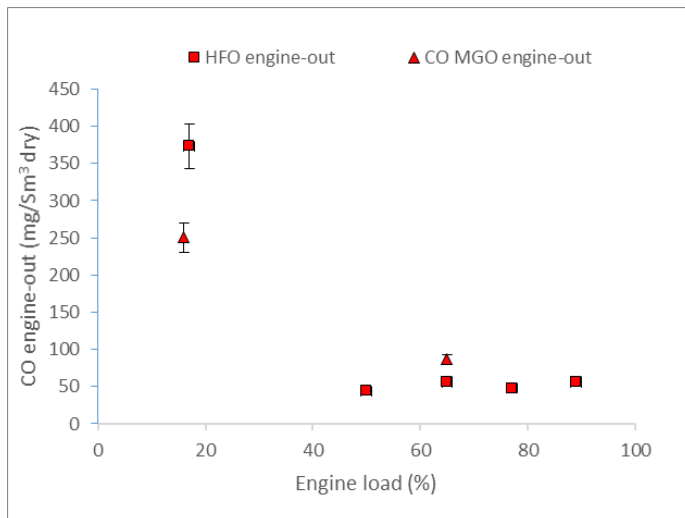

Figure 4. The CO concentrations at different engine loads before the emission control devices.
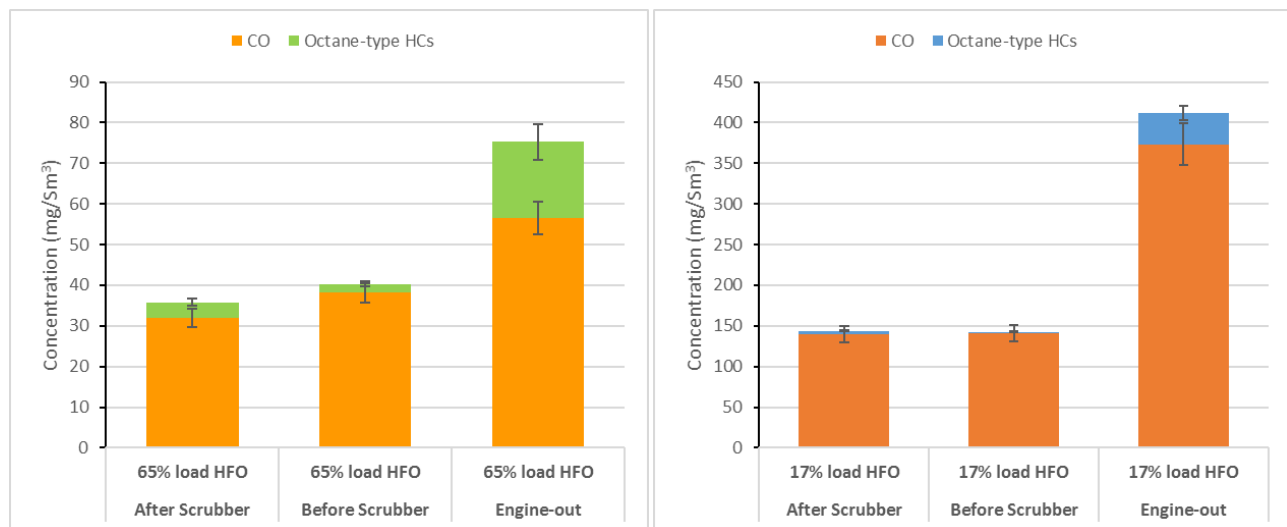
Figure 5. Concentrations of CO and octane-type hydrocarbons at different engine loads before and after the emission control devices.

Scrubber reduced effectively the SO_2 concentrations from the exhaust gas (Fig. 6). Fuel sulphur content calculated from the measured SO_2 and CO_2 concentrations was on average 2-2.5 %(m/m) before scrubber, while it was only below 0.02 %(m/m) after scrubber, which correspond to > 99% SOx removal rate.
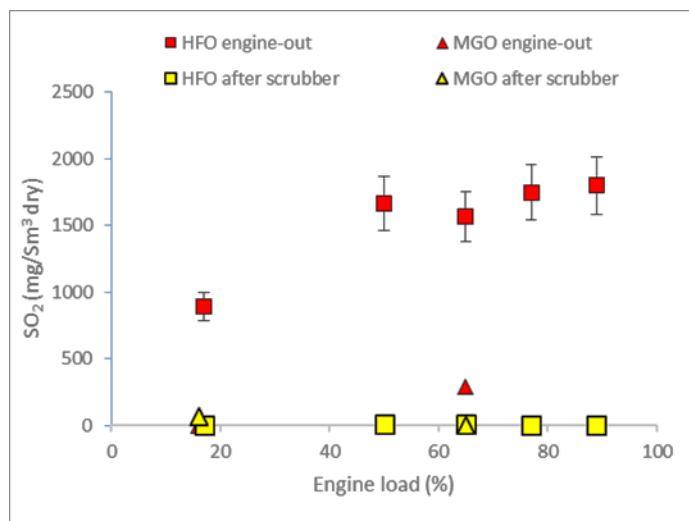

Figure 6. SO_2 concentrations at different engine loads before and after the emission control devices.

SO_2 concentrations were constantly at very low level after scrubber (Fig. 6). Only for a short time period during arrival in Port B slightly elevated SO_2 concentrations were seen when using MGO without scrubber (Fig. 7), but not during other arrivals or departures. However the amount of SO_2 during arrival in Port B was still insignificant amount of SO_2.
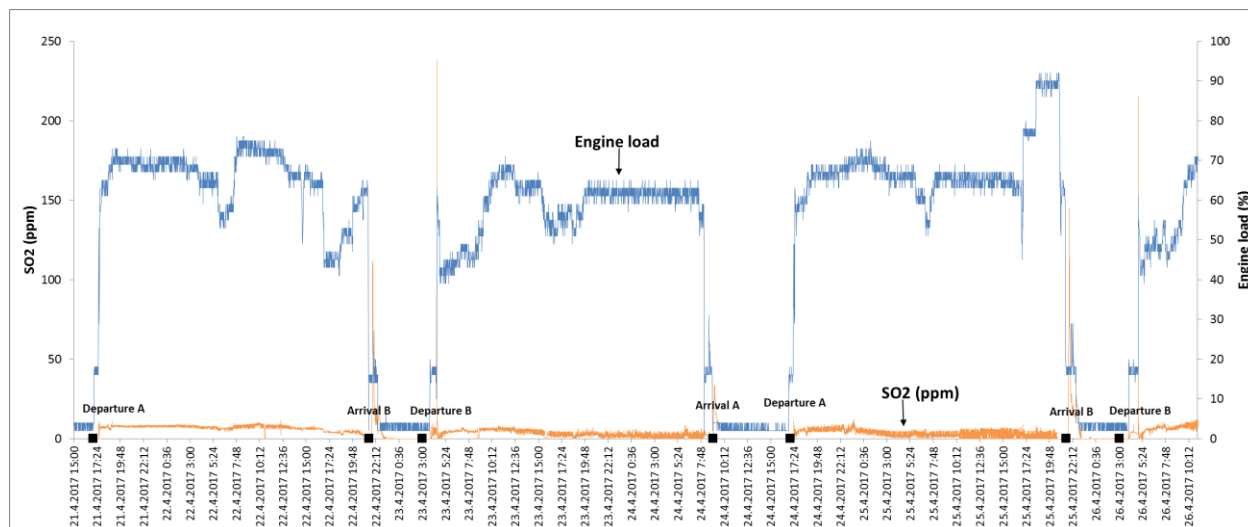
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Figure 7. SO₂ concentrations after scrubber (orange line) and engine load (blue line) during the measurement campaign.

4.2   Particulate matter

4.2.1 Black carbon

The international maritime organization (IMO) is preparing to limit BC emissions of ships. IMO has agreed on a technology-neutral definition for BC covering different properties according to Bond et al. (2013); black carbon is defined as a distinct type of carbonaceous material, formed only in flames during combustion of carbon-based fuels (Bond et al., 2013). Black carbon is aggregate of small carbon spherules that is refractory and water insoluble, absorbs strongly in visible wavelengths (Bond et al., 2013). In this report black carbon' and the abbreviation 'BC' is used to denote particulate material with the above characteristics. However, we note that BC can be confused with other names, such as EC, Soot, eBC etc. The naming is often based on measurement method; thermally measured elemental carbon is called EC, whereas optically measured is called BC. From environmental perspective, BC is problematic since it absorbs solar radiation, thus warming the atmosphere. BC in the atmosphere also affects cloud formation and cloud properties and when deposited on ice, snow or glacier BC changes the albedo of surface and accelerates the melting (e.g. Bond et al., 2013; IPCC, 2014).

BC concentrations measured with different devices at ship exhaust emissions were generally low, below 5 mg/Sm³ (Fig. 8, Fig. 9, Table 1). For example, at 65% engine load using HFO, BC was 2.9 mg/Sm³ (0.087 g/kg fuel, 0.015 g/kWh). Only at the lowest engine load (below 20%), the BC concentrations were high (up to 30 mg/Sm3 dry). Larger BC concentrations when engine was operating 17% load compared to 65% load were observed for both fuels. The explanation for higher BC concentrations is less effective combustion at lower engine loads. Concentration of total organics were quite similar for both engine loads when HFO fuel was used but lower when MGO fuel was used.

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Portable Testo instrument measured BC also before scrubber and before exhaust after treatment (engine-out). These measurements indicated that BC may be slightly reduced in scrubber, particularly when using the MGO fuel. However, Testo results were associated with high uncertainty related to the manual adjustment of by-pass flow.
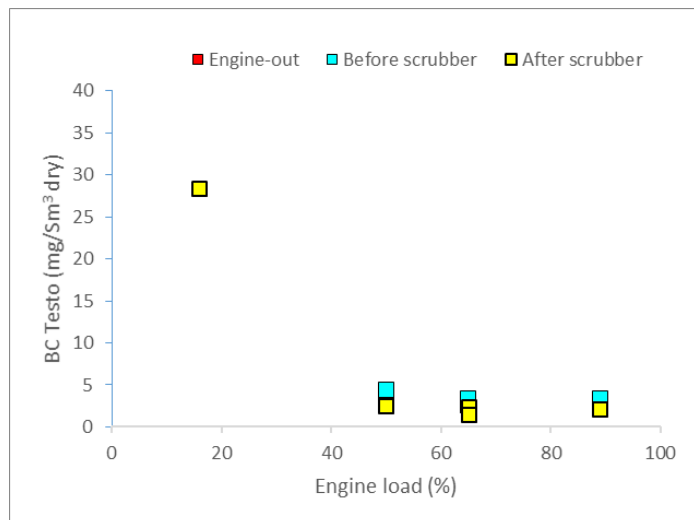

Figure 8. BC results at different engine loads before and after the emission control devices. BC measured with portable Testo.

As mentioned, the results obtained with the Testo instrument are associated with uncertainty, and thus these results were compared with those obtained with the other instruments (Fig. 8). Smoke Meter AVL 415S was has been found reliable for ship BC measurements, and EC is also often discussed with the BC results (Aakko-Saksa 2016; Aakko-Saksa et al. 2017; Timonen et al., 2017). AVL 415S was located always after scrubber, while portable Testo was measuring also engine-out and before scrubber (after DOC).

Comparability of portable Testo 338 with AVL 415S was surprisingly good, although installing probe quickly between reference and sample measurement was challenging for Testo. Manual adjustment of by-pass flow may lead to overestimated dilution of sample. When considering use of Testo 338 in wider perspective, there are many risks related to its use, such as user-dependent bias in the results and durability aspects. EC results were expectedly at the same level or lower than the BC results, although in one case EC was unrealistically high.

4.2.2 Particle chemical composition

The average chemical composition of PM after scrubber from real time chemical composition measurements were calculated for 65% (open sea) and 17% (ports A and B) engine loads (Fig. 9). Averaging of continuous measurement data were done for situations when the engine load stayed stable. The major measured chemical components were organics, sulphate and black carbon (BC). Concentrations of nitrate, ammonium and chloride were also measured and their concentrations were

above detection limit. However their contribution to total particle mass was below 0.1%, so only the concentrations of organics, sulphate and black carbon are shown below.
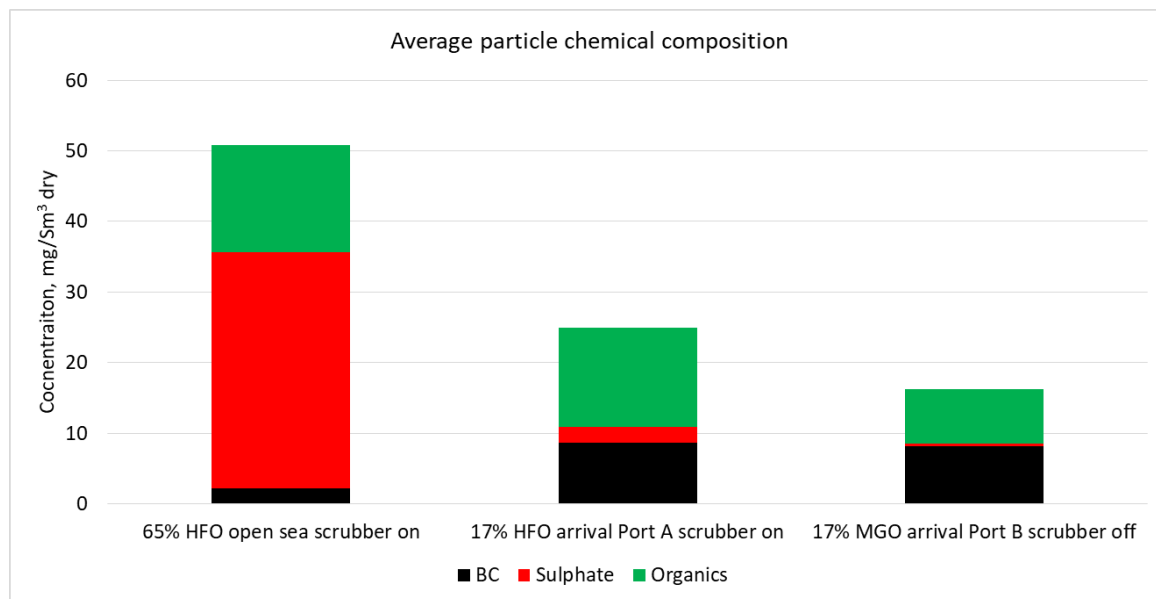

Figure 9. Chemical composition of particulate matter from exhaust measured after DOC and scrubber on open sea and at Ports A and B. At Port B the scrubber was not operated and MGO fuel was used. Concentration of sulphate and organics were measured using the SP-AMS and concentration of BC using an aethalometer.

For open sea cruising (65% engine load, scrubber on) the major chemical components in particulate phase were sulphate (66%) and organics (30%) (Table 1). The sulphate concentrations measured from sampled filters showed slightly lower concentrations which is due to the differences in sampling, dilution and measurement principles. Also the measurements of sulphate with SP-AMS and filter samplings were not made at the same time. In general the sulphate concentration measured with SP-AMS was very low, only ~40 mg/Sm^3 dry (~1 g/kg fuel). The contribution of BC at open sea cruising after scrubber was low (4%). At port A, where HFO is also used and the scrubber was operating, the main components of PM were organics (56%, 15.6 mg/Sm^3 dry, 883 mg/kg fuel) and BC (35%, 9.6 mg/Sm^3 dry, 546 mg/kg fuel). Sulfate concentrations measured at port A, were markedly smaller (contribution 9%, 2.5 mg/Sm^3 dry, 143 mg/kg fuel) than at open sea. When MGO was used as a fuel, the main components of PM were BC (50%, 9.1 mg/Sm^3 dry, 516 mg/kg fuel) and organic compounds (48%, 8.6 mg/Sm^3 dry, 490 mg/kg fuel).

Figure 10 shows the change in engine load, exhaust gas temperature and particle chemical composition when the ship was arriving to Port A. A clear decrease is seen in sulphate concentrations, whereas the organic concentration stays fairly stable and BC concentration increases. The decrease in sulphate concentration was clearly related to the lowered exhaust temperature which was again connected to the lowered engine load. Earlier studies have shown that conversion of SO$_2$ to SO$_3$ is less effective at lower temperatures (Aakko-Saksa et al., 2017) which may explain observed lower sulphate concentrations.

Table 1. Chemical composition measured after scrubber for 65% engine load.

| After scrubber Dry, STP 273,15 °C& 101,323 kPa	On-sea ~65% load HFO	On-sea ~65% load HFO	On-sea ~65% load HFO	Number of replicate tests
	mg/Sm^3 dry	mg/kWh	mg/kg fuel	
BC (FSN-based, AVL 415S)	2.9	14.3	84.1	n=29
BC (AE33)	2.5	11.1	65	
PM	48.2	235.0	1382.9	n=9
EC	1.8	8.7	51.4	n=3
OC	5.6	27.2	159.8	n=3
SO4 (filter sampling)	18.2	88.6	521.1	n=2
SO4 (SP-AMS)	37.2	167.6	986	
Organics (SP-AMS)	16.8	75.7	445.2	
Metals	bd	bd	bd	n=2
PAH7	0.0	0.0	0.1	n=2
Rest (mainly oxygen)	20.4	99.3	584.6	n=2
	g/Sm3 dry	g/kWh	g/kg fuel	
Carbon dioxide CO2	108.4	528.6	3110.3	n>30
Carbon monoxide CO	0.03	0.2	0.9	n>30
NOx	2.9	14.2	83.5	n>30
Sulfur dioxide SO2	0.015	0.071	0.419	n>30
Octane-type	0.004	0.019	0.110	n>30
Methane CH4	bd	bd	bd	n>30
Ethylene C2H4	bd	bd	bd	n>30
Formaldehyde HCOH	bd	bd	bd	n>30
Acetaldehyde CH3CHO	bd	bd	bd	n>30
Ammonia NH3	bd	bd	bd	n>30
Nitrous oxide N2O	bd	bd	bd	n>30

bd = below detection limit
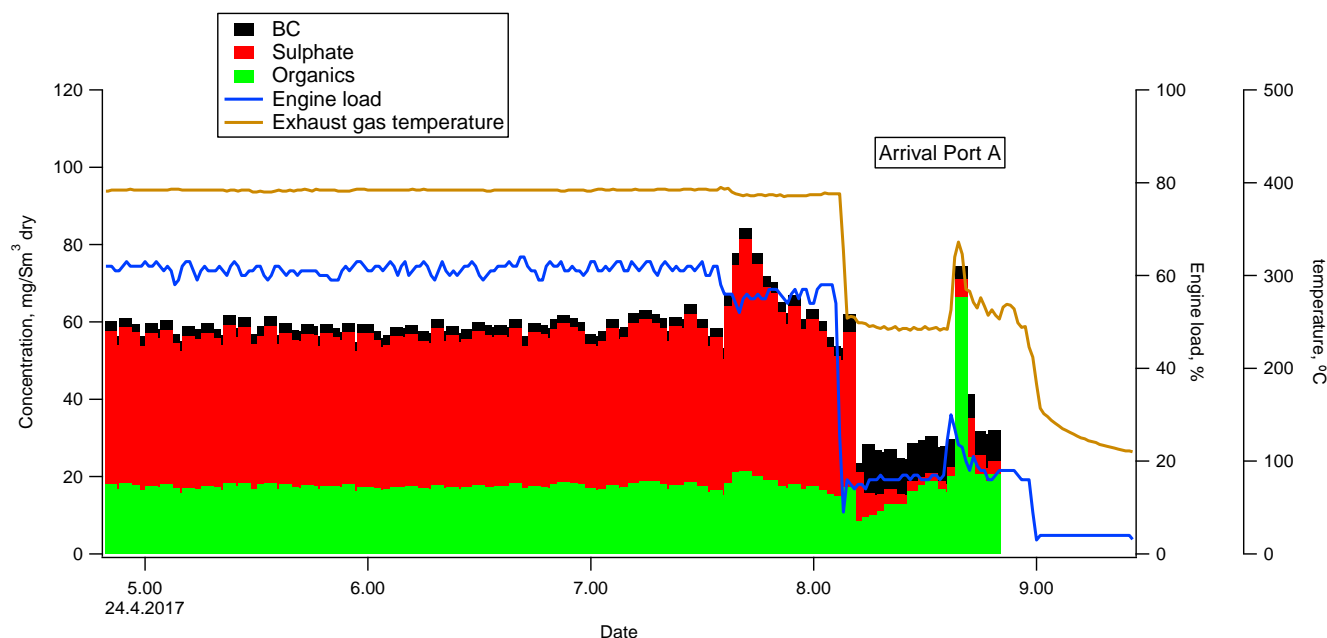
Figure 10. Chemical composition, engine load and exhaust temperature from real-time measurements. On open ocean and Port A HFO fuel is used with scrubber operating.

Besides real-time measurements, particulate matter samples to filter substrates were collected for detailed composition analysis. We note that PM sampling conditions favor condensation of semivolatile constituents of aerosol, and therefore are not directly comparable with the results discussed above. However, PM concentration after scrubber using HFO at 65% load (48 mg/Sm^3, 1.4 g/kg fuel, 0.24 g/kWh) was relatively close to the PM concentration shown in Figure 11 (~50 mg/ Sm^3). The PM sampling was conducted before and after the emission control devices, and thus their performance of emission control devices can be evaluated. PM consisted mainly of sulphates (sulphuric acid, metal sulphates), elemental and organic carbon, and oxygen associated with water and metal oxides while concentrations of metals and PAHs were low (Fig. 12). Other anions than sulphates were not present substantially.

Engine-out PM concentrations were higher when using HFO than MGO due to the differences in the fuel sulfur induced sulphates in PM. For MGO, PM was low even at engine-out exhaust. DOC reduced concentrations of sulphates, metals and associated oxygen, and also OC of PM, and further reductions of these constituents were achieved using scrubber.
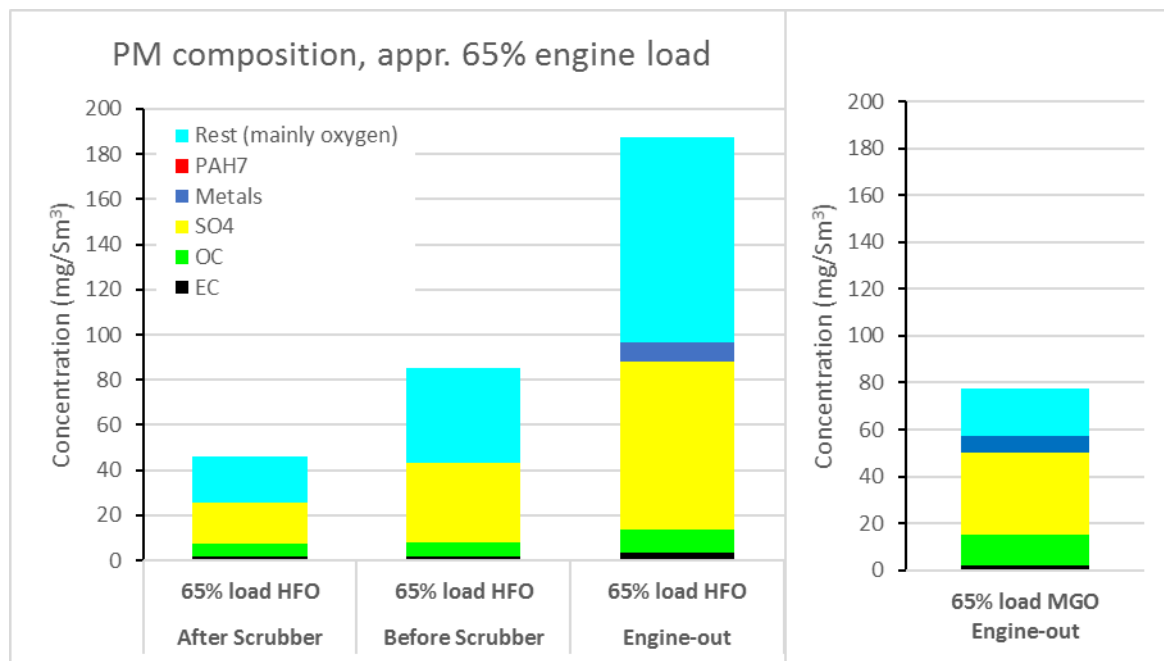
20

Figure 11. The PM concentrations and their compositions.

Concentration of 7 priority PAHs in PM are shown in Figure 12. Amount of polyaromatic hydrocarbons in PM was low. DOC reduced these PAH concentrations, while the effect of scrubber was smaller.
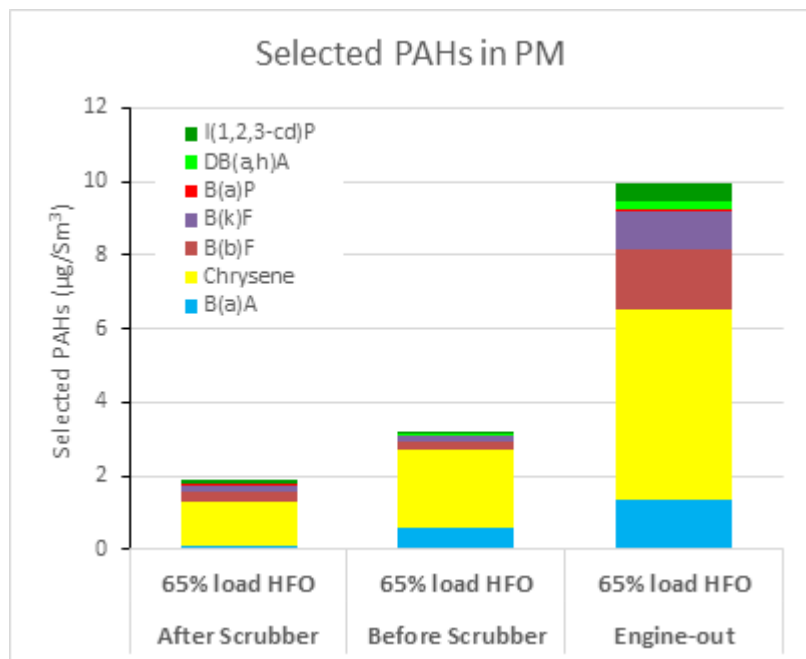

Figure 12. Seven priority PAHs in PM.

In engine-out PM, metals were present when using HFO, particularly vanadium, nickel, sodium, iron and calcium (Fig. 13). When using MGO, aluminum in PM was observed probably due to engine wear. DOC seemed to reduce the metal concentrations to below detection limit.
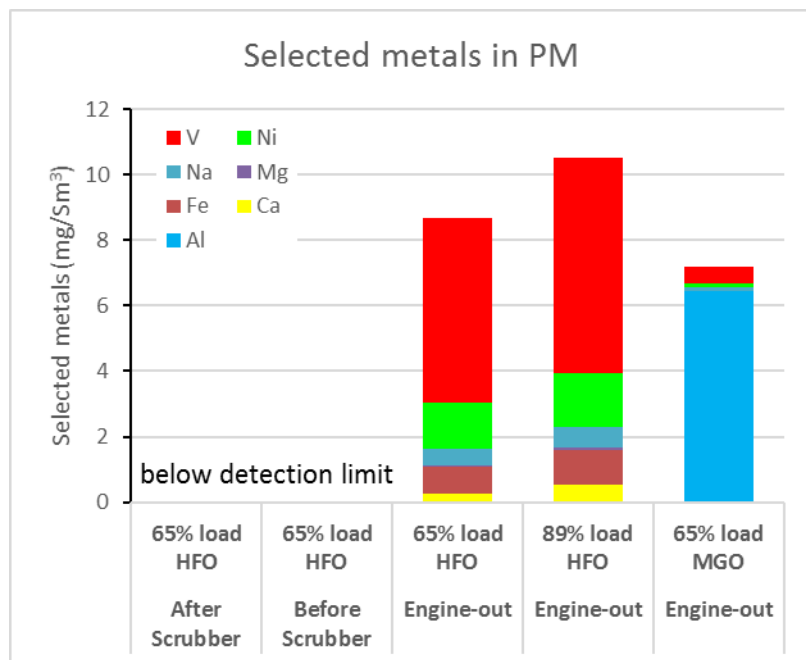

Figure 13. Concentrations of selected metals in PM

4.2.3 Aerosol aging

Aging of exhaust (after DOC and scrubber) emissions in the atmosphere was simulated using a PAM chamber. The aging time of exhaust was approximately two weeks when UV lamp voltage is set to 9 V and around two days for the 2.9 V. When voltage was set to zero, there were no oxidants formed in the PAM chamber so for 0 V the sample was similar to fresh exhaust. The concentration of chemical components for fresh exhaust (0 V) was slightly lower compared to those measured without PAM chamber. The reason is that there were some losses of particles and precursor gases inside the PAM chamber. Concentrations of major particulate components (sulphate, organics and BC, Fig 14) showed very similar concentrations with different UV lamp voltages. This indicates that markedly no secondary aerosol mass formation was taking place in the PAM chamber. This is expected since DOC and scrubber removed efficienly gaseous SO_2 and volatile organic compounds (VOC) which are precursors for secondary organic aerosol (SOA) and sulphate aerosol.
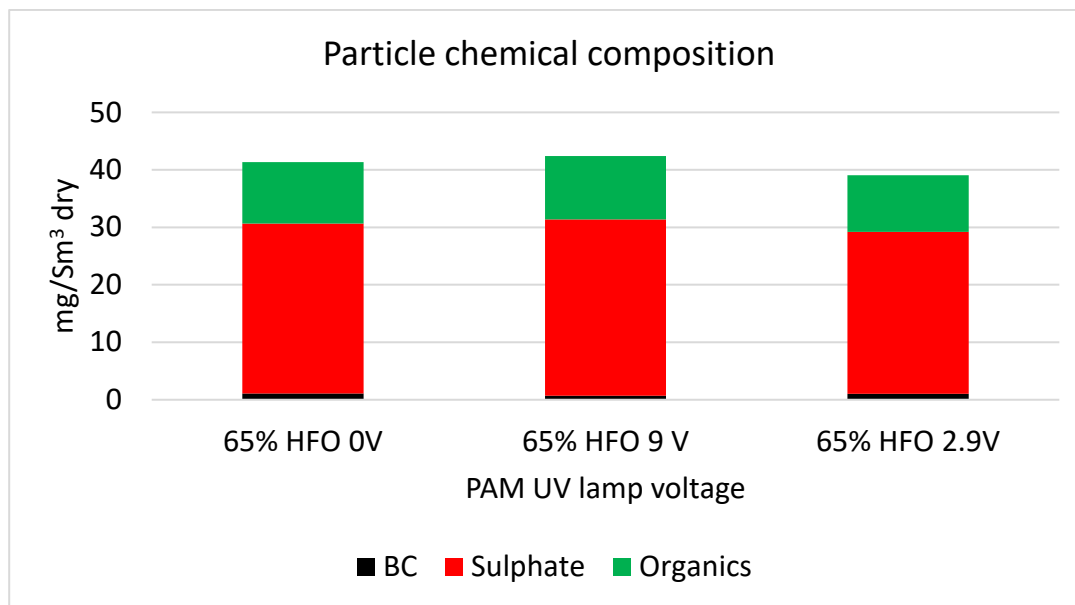
Figure 14. Averaged particle chemical composition during open sea cruise (HFO fuel, scrubber on) for aged (2.9 and 9 V) and fresh (0 V) aerosol. Particle losses inside PAM chamber is estimated to be between 10 and 25 % (Karjalainen et al., 2016).

4.2.4 Particle size distributions

Figure. 15 shows the measured particle mass size distributions (averaged ~6 hour time) during open sea cruise measured after DOC and scrubber. The unsymmetrical shape of the distribution indicates that there is another mode centering at few tens of nanometers. The dominating mode is centered in the mass size distribution at 120 nm (mobility diameter, D_p). SP-AMS measurements showed a mode that consisted sulphate, organics and black carbon (Fig 16). The measured size distributions of this compounds were centered at 240 nm (vacuum aerodynamic diameter, D_{va}). The SP-AMS measures particle vacuum aerodynamic diameter which depends on particle density (and shape). The ratio of these two diameters (D_p and D_{va}) was near 2 indicating that the density of measured particles were near 2 g/cm^3 assuming that the particles were spherical in shape.
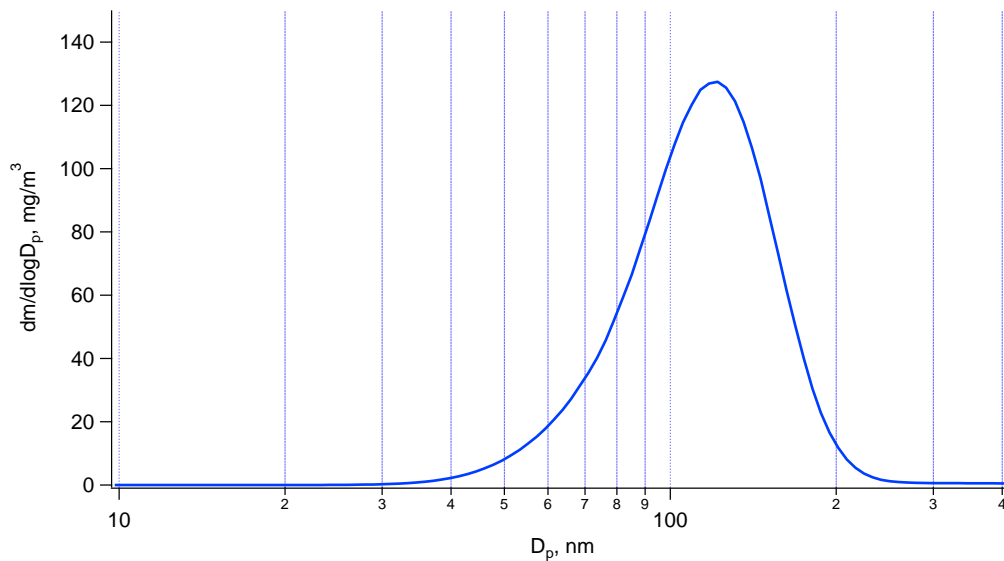
Figure 15. Averaged particle mass size distributions during open sea cruise (HFO fuel, scrubber on, 65% engine load).
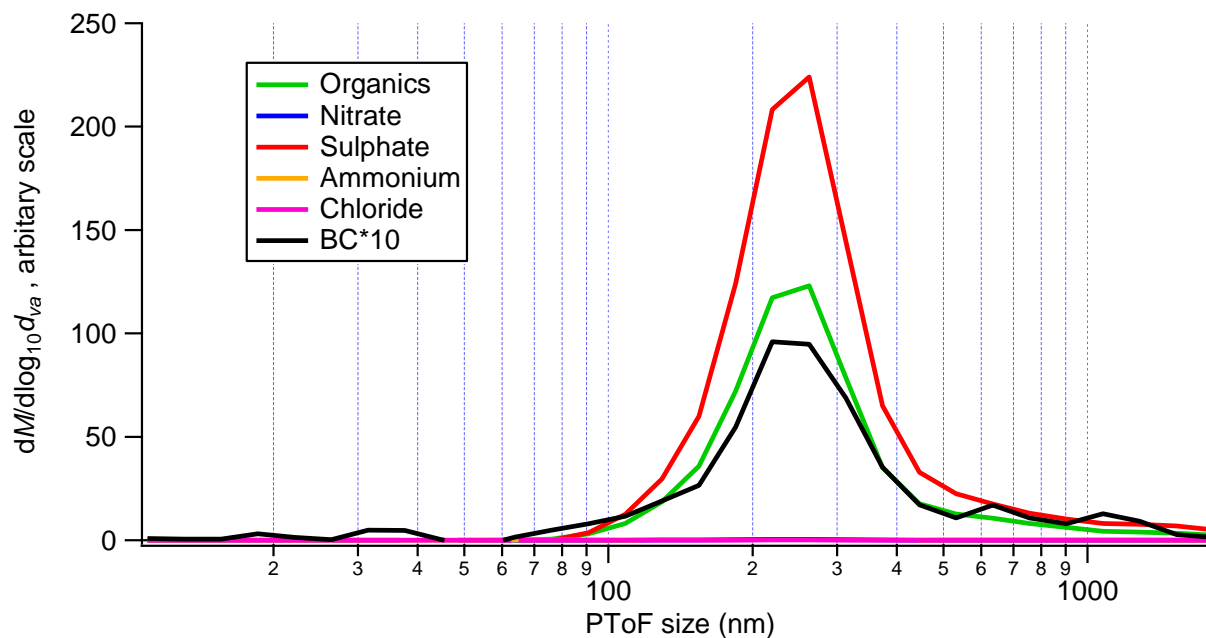

Figure 16. Mass size distributions of measured chemical components corresponding same time and conditions as in Fig. 15. Notice that the y scale is in arbitrary units and that the concentration of BC is multiplied by 10.

5. Conclusions

Particle chemical and physical properties together with gaseous compounds were measured on board a large RoRo passenger ship equipped with open loop scrubber and diesel oxidant catalyst (DOC). The objective of this study was to gather information on scrubber performance in realistic conditions. Exhaust from one of the ships four main engines were measured. Measurements were made before and after scrubber and also before DOC.

Measurements showed that scrubber effectively reduced the SO_2 concentrations from the exhaust gas. Calculated fuel sulphur content was on average 2-2.5 % (m/m) before scrubber, but below 0.02 % (m/m) after scrubber, which corresponds to > 99% SO2 reduction rate. Scrubber also reduced the NO_x concentrations of exhaust to some extent. CO and hydrocarbon concentrations on the other hand were reduced already in DOC that was located before scrubber.

Conducted measurements show that PM in ship exhaust emissions consisted of sulphates, elemental and organic carbon, metals, and associated oxygen (water, oxides). Engine-out PM was higher for HFO than for MGO. DOC seemed to reduce particulate sulphate, metals and associated oxygen, and also OC of PM, and scrubber seemed to further reduce their concentrations. Especially the DOC seemed to reduce the metal concentrations to below detection limit.

Real time measurement of particle chemical composition with the SP-AMS gave similar results compared to filter based measurements. Concentration of sulphate after scrubber was low for 65% engine load. For 17% engine load the sulphate concentration was even lower. Black carbon on the other hand showed increased concentrations when engine load was lowered. This is related to the more effective combustion when higher engine loads are used.

Measurements showed that when aftertreatment of engine exhaust (DOC+scrubber) was operating, the concentrations of SO_2 and sulphate were on a very low level. Also the concentration of black carbon was low, especially when the engine was operating on 65% load. Differences in the BC concentrations before and after emission control devices were within the standard deviation, although a slight decrease over scrubber was indicated. The measured concentrations corresponded to those measured previously in ship engine laboratory tests using low sulfur fuel (0.1%S) with engine loads of 75% and 25% (Aakko-Saksa et al., 2017). Exhaust aftertreatment (DOC+scrubber) effectively removed gaseous components like SO_2 and hydrocarbons, which via oxidation can form secondary PM in the atmosphere. It seems that aftertreatment of ship exhaust also reduce secondary PM formation in the atmosphere. Measurements using PAM chamber, which simulates the formation of secondary PM in the atmosphere, also confirms this result.

References

Aakko-Saksa P., Murtonen. T., Vesala. H., Nyssönen, S., Puustinen, H., Lehtoranta, K., Timonen, H., Teinilä, K., Hillamo, R., Karjalainen, P., Kuittinen, N., Simonen, P., Rönkkö, T., Keskinen, J., Saukko, E., Tutuianu, M., Fischerleitner, R., Pirjola, L., Brunila, O.-P. & E.H., (2016). Black Carbon Measurements Using Different Marine Fuels. *28th CIMAC World Congress on Combustion Engines, At Helsinki, Finland, Volume: CIMAC, Paper no. 068.*

Aakko-Saksa, P., Murtonen, T., Vesala, H., Koponen, P., Timonen, H., Teinilä, K., Aurela, M., et al., (2017). Black Carbon Emissions from a Ship Engine in Laboratory (SEA-EFFECTS BC WP1).

Bauer, J. J., Yu, X.-Y., Cary, R., Laulainen, N., and Berkowitz, C., (2009). Characterization of the Sunset Semi-Continuous Carbon Aerosol Analyzer. *Journal of the Air & Waste Management Association* 59 (7): 826–33. doi:10.3155/1047-3289.59.7.826.

Bond T.C., Doherty, S.J., Fahey, D.W., Forster, P.M., Berntsen, T., DeAngelo, B.J., Flanner, M.G., Ghan, S., Kärcher, B., Koch, D., Kinne, S., Kondo, Y., Quinn, P.K., Sarofim, M.C., Schultz, M.G., Schulz, M., Venkataraman, C., Zhang, H., Zhang, S., Bellouin, N., Guttikunda, S.K., Hopke, P.K., Jacobson, M.Z., Kaiser, J.W., Klimont, Z., Lohmann, U., Schwarz, J.P., Shindell, D., Storelvmo, T., Warren, S.G., Zender, C.S., (2013). Bounding the role of black carbon in the climate system: A scientific assessment. *J. Geophys.Res.*, 118, 5380-5552, doi:10.1002/jgrd.50171.

DeCarlo, P.F., Kimmel, J.R., Trimborn, A., Northway, M.J., Jayne, J.T., Aiken, A.C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K.S., Worsnop, D.R., Jiminez, J.L., (2006). Field-Deployable, High-Resolution, Time-of-Flight Aerosol Mass Spectrometer. *Anal. Chem.*, 78 (24), 8281-8289.

Drinovec, L., Močnik, G., Zotter, P., Prévôt, A., Ruckstuhl, C., Coz, E., Rupakheti, M., Sciare, J., Müller, T., Wiedensohler, A., (2015). The" dual-spot" Aethalometer: an improved measurement of aerosol black carbon with real-time loading compensation. *Atmospheric Measurement Techniques 8*, (5), 1965-1979.

European Community: Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy, Off. J. Eur. Parliam., L327(September 1996), 1–82, doi:10.1039/ap9842100196, 2000.

Kang, E., Toohey, D.W., and Brune, W.H., (2011). Dependence of SOA oxidation on organic aerosol mass concentration and OH exposure: experimental PAM chamber studies. *Atmos. Chem. Phys.*, 11, 1837-1852, doi:10.5194/acp-11-1837-2011.

Karjalainen, P., Timonen, H., Saukko, E., Kuuluvainen, H., Saarikoski, S., Aakko-Saksa, P., Murtonen, T., Bloss, M., Dal Maso, M., Simonen, P., Ahlberg, E., Svenningsson, B., Brune, W.H., Hillamo, R., Keskinen, J., Rönkkö, T., (2016). Time-resolved characterization of primary particle emissions and secondary particle formation from a modern gasoline passenger car. *Atmos. Chem. Phys.*, 16, 8559-8570, doi:10.5194/acp-16-8559-2016.

Lambe, A.T., Ahren, A.T., Williams, L.-R., Slowik, J.G., Wong, J.P.S., Abbatt, J.P.D., Brune, W.H., Ng, N.L., Wright, J.P., Croasdale, D.R., Worsnop, D.R., Davidovits, P., and Onasch, T.B., (2011). Characterization of aerosol photooxidation flow ractors: heterogeneous oxidation, secondary organic aerosol formation and cloud condensations nuclei activity measurements. *Atmos. Meas. Tech.*, 4, 445-461, doi:10.5194/atm-4-445-2011.

Middlebrook, A.M., Bahreini, R., Jiminez, J.L., and Canagaratna, M.R., (2011), Evaluation of composition-dependent collection efficiencies for the Aerodyne Aerosol Mass Spectrometer using field data. *Aerosol Sci. Tech.*, 46(3) 258-271, doi:10.1080/02786826.2011.620041.

Onasch, T.B., Trimborn, A., Fortner, E. D., Jayne, J.T., Kok, G.L., Williams, R.L., Davidovits, P., Worsnop, D.R., (2012). Soot prticle aerosol mass spectrometer: Development, validation and initial application. *Aerosol Sci. Tech.* 46 (7), 0278-6826 doi: 10.1080/02786826.2012.663948.

The European Parliament and The Council of the European Union: DIRECTIVE 2012/33/EU regards the sulphur content of marine fuels THE, Off. J. Eur. Union, 1–13, 2012.

Timonen, H., Aakko-Saksa, P., Kuittinen, N., Karjalainen, P., Murtonen, Lehtoranta, K., Vesala, H., elt al., (2017). Black Carbon measurement validation onborad (SEA-EFFECTS BC WP2).

Wang, S.C and Flagan, R.C., (1990), Scanning electrical mobility spectrometer. *Aerosol. Sci.Tech.*, 13(2), 230-240, doi:10.1080/02786829008959441.

APPENDIX 1

Fuel properties analysed by ASG.

			ASG analyses	
			HFO	MGO
			22.4.2017	25.4.2017
Density (15 °C)		kg/m3	984,6	849
Kin. Viscosity (40 °C)		mm2/s	625,6	3,484
Kin. Viscosity (50 °C)		mm2/s	297	-
Calorific value, lower		J/g	40453	42792
CCAI		-	848	-
Cetane index		-	-	51,4
Sulfur content		%(m/m)	1,86	0,0206
Carbon		%(m/m)	86,6	86,5
Hydrogen		%(m/m)	10,7	13,5
Oxygen		%(m/m)	2,1	<0,5
Nitrogen		%(m/m)	0,54	0,011
Ash content (775 °C)		%(m/m)	0,165	<0,005
Water content		%(V/V)	0,2	0,0063
Carbon residue		%(m/m)	16,2	<0,10
Asphaltens		%(m/m)	7,3	0,41
Monoaromatics		%(m/m)		26,8
Diaromatics		%(m/m)		3,8
Triaromatics		%(m/m)		0,4
PAH		%(m/m)		4,2
Total aromatics		%(m/m)		31
FAME		%(V/V)		0,1
Flash point		°C	109	74
Pour point		°C		
10%(V/V)	recovery	°C		218,3
50%(V/V)	recovery	°C		292,3
90%(V/V)	recovery	°C		345,2
Copper	(Cu)	mg/kg	<0,5	<0,5
Aluminium	(Al)	mg/kg	<0,5	<0,5
Sodium	(Na)			<0,5
Potassium	(K)	mg/kg	<0,5	<0,5
Chromium	(Cr)	mg/kg	<0,5	<0,5
Manganese	(Mn)	mg/kg	<0,5	<0,5
Nickel	(Ni)	mg/kg	21,1	<0,5
Iron	(Fe)	mg/kg	12,9	<0,5
Molybdenum	(Mo)	mg/kg	<0,5	<0,5
Barium	(Ba)	mg/kg	0,7	<0,5
Boron	(B)	mg/kg	<0,5	<0,5
Calcium	(Ca)	mg/kg	2	<0,5
Magnesium	(Mg)	mg/kg	<0,5	<0,5
Lead	(Pb)	mg/kg	1,7	<0,5
Vanadium	(V)	mg/kg	110	<0,5
Tin	(Sn)	mg/kg	<0,5	<0,5
Zinc	(Zn)	mg/kg	0,7	<0,5
Silicon	(Si)	mg/kg	1,2	<0,5
Titanium	(Ti)	mg/kg	<0,5	<0,5
Phosphorous	(P)	mg/kg	0,7	<0,5
Cobalt	(Co)	mg/kg	<0,5	<0,5
Silver	(Ag)	mg/kg	<0,5	

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