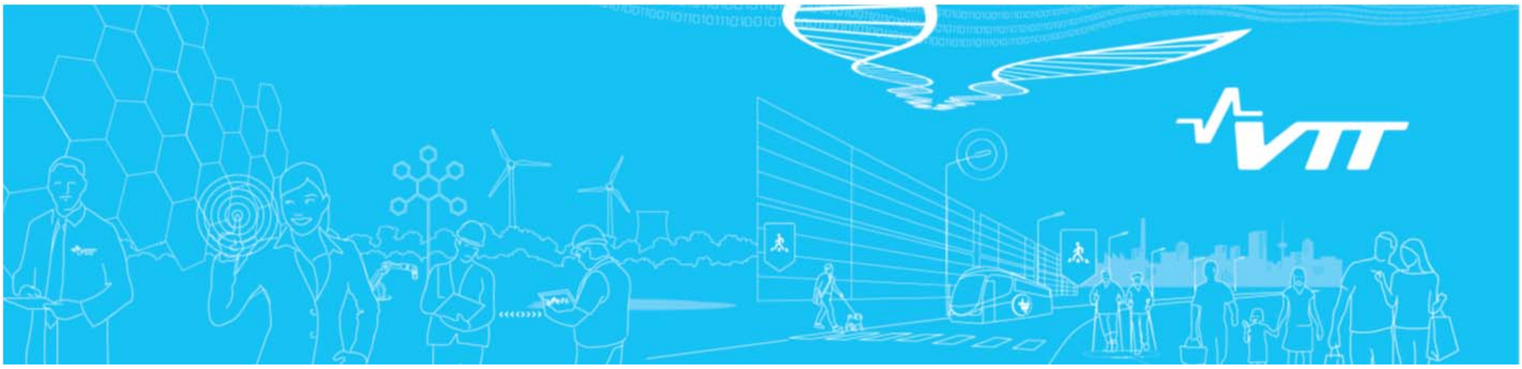
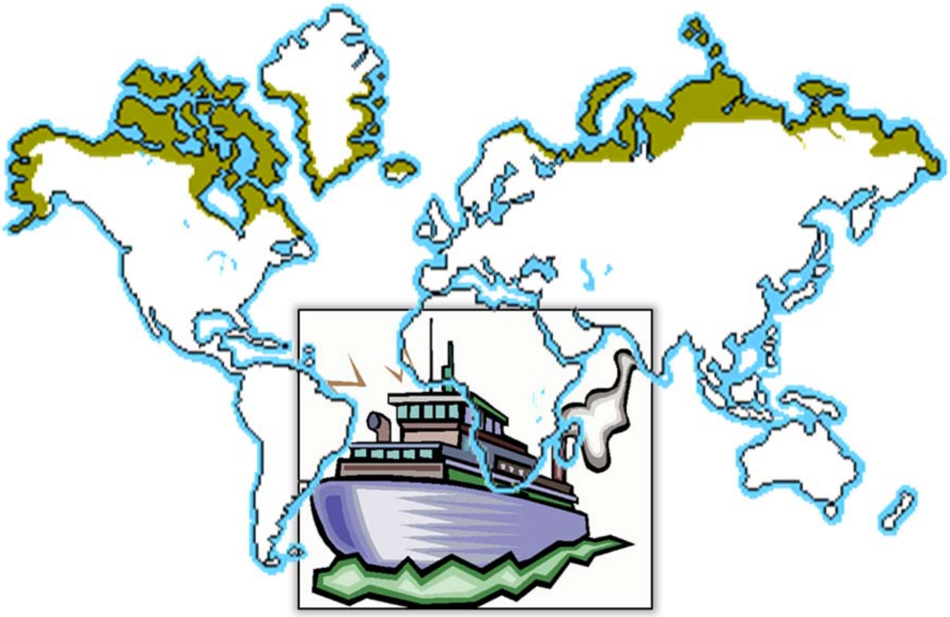


RESEARCH REPORT

VTT-R-04493-17



Black carbon measurement validation onboard (SEA-EFFECTS BC WP2)

Authors: Hilkka Timonen[2], Päivi Aakko-Saksa[1], Niina Kuittinen[3], Panu Karjalainen[3], Timo Murtonen[1], Kati Lehtoranta[1], Hannu Vesala[1], Matthew Bloss[2], Sanna Saarikoski[2], Päivi Koponen[1], Pekka Piimäkorpi[1], Topi Rönkkö[3]

[1]VTT, [2]FMI, [3]TUT

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Project name Shipping Emissions in the Arctic – Black Carbon	**Project number/Short name** SEA-EFFECTS BC
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Summary

In-depth measurements of gaseous and particulate emissions were conducted onboard an ocean vessel by researchers from VTT Technical Research Centre of Finland Ltd, Finnish Meteorological Institute and Tampere University of Technology. Altogether more than 20 different instruments were used in these onboard measurements. A variety of instruments, MAAP (Multi-angle absorption photometer), Aethalometer, FSN (Filter smoke number), AVL MSS (Micro Soot Sensor) were used to measure black carbon (BC) concentrations. In addition, in-depth characterization of gaseous emissions as well as particulate emissions (concentration, composition, size distribution) and their properties (e.g. volatility, secondary aerosol formation potential) of a ship equipped with a modern after treatment system (catalyst + scrubber) was achieved by using state-of-the-art online measurement devices (e.g. SP-AMS, ELPI, SMPS, PSM, CPC, FTIR, Horiba PG-250A, Pegasor PPS –sensor, Nephelometer, Thermodenuder, PAM -chamber) and filter collections (AVL Smart Sampler). Fuels during measurements were HFO (0.7% Sulphur) and MGO (<0.1% Sulphur). The aim of this measurement campaign was to 1) evaluate suitability of BC instruments for onboard measurements and 2) to conduct in-depth characterization of gaseous and particulate emissions of a modern low emission ship. A special focus was on BC emissions as the international maritime organisation (IMO) limit is anticipated for BC emitted by ships. Measurements were successful and large amount of data about the ship emissions was collected. The particulate and gaseous emissions of ship were very low, as expected for a modern ship. The goal is to publish results in the scientific journals and as conference publications. In addition information for authorities and IMO about the suitability of BC measurement methods for onboard BC measurements will be provided.

Confidentiality	Public

Espoo 28.9.2017

Written by	**Reviewed and accepted by**
Hilkka Timonen (FMI) Docent	Jukka Lehtomäki Research team leader

VTT's contact address

P.O.Box 1000, FI-02044 VTT

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Preface

The measurements and results described in this report are a part of TEKES funded SEA-EFFECTS BC –project (2015-2017). The SEA-EFFECTS BC project aimed at more reliable BC evaluation for ships as well as towards finding suitable monitoring techniques for BC. Various BC measurement techniques were tested in exhaust measurements in laboratory and onboard a ship. Additionally, new business opportunities and potential related to BC measurements were studied. This project produced large amounts of new information which will be very relevant in the near future as marine industry prepares to comply with new emission limitations. Furthermore, the measured detailed composition and optical properties of ship PM can be used in future to estimate their influence to arctic environment, climate change and health.

Research organizations participating to SEA-EFFECTS BC were VTT Technical Research Centre of Finland Ltd. (VTT), Finnish Meteorological Institute (FMI), Tampere University of Technology (TUT) and University of Turku (UTU). Financial support from Tekes (40356/14), Trafi (172834/2016) and from industrial partners, Wärtsilä, Pegasor, Spectral Engines, Gasmet, VG-Shipping, HaminaKotka Satama Oy, Oiltanking Finland Oy, Kine Robotics, and the in-kind support from AVL List GmbH.

Co-operation between participating research institutes and companies is gratefully acknowledged. Also, without support from the companies, it would have not been possible to arrange and conduct the laboratory and onboard measurements needed in this project. Additionally, personnel who has contributed to measurements and publication of results, reports and scientific publications is sincerely thanked. Without your hard work and dedication it would not have been possible to accomplish this project.

Espoo 28.9.2017

Authors

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Appendix 1-3.

1 Abbreviations

AE	Aethalometer
BC	Black carbon
CO_2	Carbon dioxide
CO	Carbon monoxide
CPC	Condensation Particle Counter
CS	Catalytic stripper
D_p	Particle diameter
DR	Dilution ratio
eBC	Equivalent black carbon
EC	Elemental carbon
ELPI	Electric Low Pressure Impactor
FID	Flame ionization detector
FSN	Filter Smoke Number
FTIR	Fourier transformation infrared
HC	Hydrocarbons
HCLD	Heated Chemiluminescence
ICP-MS	Inductively coupled plasma mass spectrometry
IMO	International Maritime Organisation
IR	Infrared
LII	Laser Induced Incandescence
Lpm	Liters per minute
MAAP	Multiangle Absorption Photometry
MSS	Micro Soot Sensor
NDIR	Nondispersive Infrared
Sm^3	Flow normalized to 273.15 K and 101325 Pa
NO_X	Nitrogen oxides (NO and NO_2)
OC	Organic carbon
o.d.	Outer diameter
PAH	Polyaromatic hydrocarbons
PAM	Potential Aerosol Mass chamber
PAS	Photoacoustic Spectroscopy
PM	Particulate matter
PN	Particle number
PPS-M	Pegasor Particle Sensor
PTD	Porous tube diluter
rBC	Refractory black carbon
RH	Relative humidity
SCR	Selective Catalytic Reduction
SMPS	Scanning Mobility Particle Sizer
SOA	Secondary organic aerosols
SP-AMS	Soot particle aerosol mass spectrometer
SPC AVL	SmartSampler, ISO 8178 compliant partial flow PM sampling system
TD	Thermodenuder
UPS	Uninterruptible power source
UV	Ultraviolet

Introduction

The international maritime organization (IMO) is preparing to limit BC emissions of ships. In general, ship emissions are anticipated to increase particularly in the Arctic areas with the expected rise in commercial shipping if preventive actions are not implemented (Winther et al., 2014). Share of shipping in the global black carbon (BC) emissions is less than 2%, however, in the north of 70° latitude BC mostly originate from shipping (AMAP, 2011). In 2012, the largest share of Arctic ships' BC emissions originated from fishing ships (45%) followed by passenger ships (20%), tankers (9%), general cargo (8%) and container ships (5%) (Winther et al., 2014).

Special emission control areas are defined to reduce environmental and health effects of airborne emissions from ships. The sulphur content of shipping fuels is required to be below 0.1%, or alternatively scrubber has to be used, in the SO_X emission control area (SECA) of Baltic Sea, North Sea and English Channel starting from 1.1.2015. Furthermore, marine fuel sulphur content will be reduced globally to 0.5% from today's 3.5% in 2020. Also NO_X emissions from shipping are regulated. Tier III regulations will be applied for new builds in 2016 in NECA (NO_X emission control areas) areas of North America and the United States Caribbean Sea. Methane emissions are getting more attention with increasing use of LNG. Other emissions of importance may be regulated from medium to long term, such as short-lived climatic forcers (BC, methane, ozone, HFCs), N_2O, ammonia, particles, formaldehyde, and noise. These emissions are known to have adverse impacts on climate, environment and health.

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). The environmental influences of BC are expected to be significant especially in vulnerable arctic areas (Bond et al., 2013; Hienola et al., 2017). Recent studies have shown that in addition to local BC sources, long-range transported BC has influence in sub-arctic regions (Hienola et al., 2017).

Several different approaches to measure black carbon concentration exists. These can be coarsely divided to instruments developed for emission measurements (e.g. FSN, MSS) and instruments mainly developed for the ambient BC measurements (e.g. MAAP, Aethalometer). Instruments that are developed for emission measurements are required to tolerate higher BC concentrations and difficult conditions (e.g. high temperature). Instruments that are developed for ambient measurements need high dilution in order to be applicable for emission measurements (Aakko-Saksa et al., 2016) and they don't typically tolerate high temperature. Also must be noted that application of research instruments that are hard to move, delicate and sensitive to ambient conditions can be challenging in ship conditions.

Currently IMO is evaluating needs for local and global control of BC. Work is launched to establish definition and methodology for BC, as no generally approved BC methods exist. 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. Additionally, IMO has defined four candidate methods for the BC measurements: Photoacoustic Spectroscopy (PAS), Multi-angle

Absorption Photometry (MAAP), Laser Induced Incandescence (LII) and Filter Smoke Number (FSN).

After the IMO statements regarding relevance and analytical needs for BC in the Arctic much activity has risen in the related research and business field globally. There are different technological options (e.g. by using scrubbers, MGO or LNG as a fuel) to meet current and anticipated emissions requirements. Capability of these technological options to reduce emissions vary. LNG is a low-emission fuel having also negligible BC emissions, whereas MGO does not reduce NO_X or BC emissions, by default (Sippula et al., 2014). Capability of scrubbers or methanol to reduce to BC emissions has not been evidenced.The influence of SOx scrubbing, offered as a viable alternative to the low sulphur fuels, to particulate matter and BC emissions is currently poorly known.

In this WP2 emissions from a ship equipped with scrubber was used as a platform for validation of black carbon measurement methods (MAAP, Aethalometer, FSN, and PAS) used in WP1. In addition, in depth characterization of gaseous emissions as well as particulate emissions (concentration, composition, size distribution) and their properties (e.g. volatility, secondary aerosol formation potential) of a ship equipped with a modern after treatment system (scrubber + catalyst) was achieved by using state-of-the-art measurement devices. Sampling locations before and after scrubber enabled quantification of scrubber’s influence to particulate emissions including BC concentrations. Data from WP1 was taken into account when measurements and instrumentations were planned.

2 Materials and methods

2.1 Measurement setup

Emission measurements were conducted from three points in the vessels exhaust lines for ME 1 (main engine 1) and ME2 (main engine 2);

- Before SCR (Selective Catalytic Reduction) after treatment for ME2
- Before scrubber (measurement days 6-9) for ME1 and ME2.
- After the scrubber (measurement days 1-4) for ME1 and ME2.

Measurement locations are shown in schematic figure 2.1 and pictures of measurement locations are shown in figure 2.2. Locations of VTT and AVL instrumentation are shown in figure 2.1 and FMI and TUT instrumentation shown in figures 2.3 and 2.4.

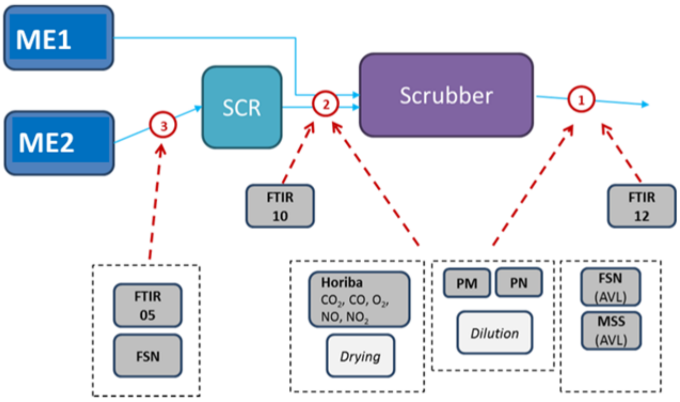


Figure 2.1. Locations of the VTT and AVL instruments. FSN measurements after the ME2 engine was conducted with non-heated transfer line, while the transfer lines of the other FSN measurements (before and after the scrubber) were heated.

Figure 2.2. Left: Instruments at the engine out of ME2. Middle and right: Instruments before scrubber. For VTT's measurements, heated lines were used. For FMI and TUT measurements, a 10 mm Cu-tubing was used to transfer the diluted sample to upper level (after scrubber) for instruments that were not moved to lower level.

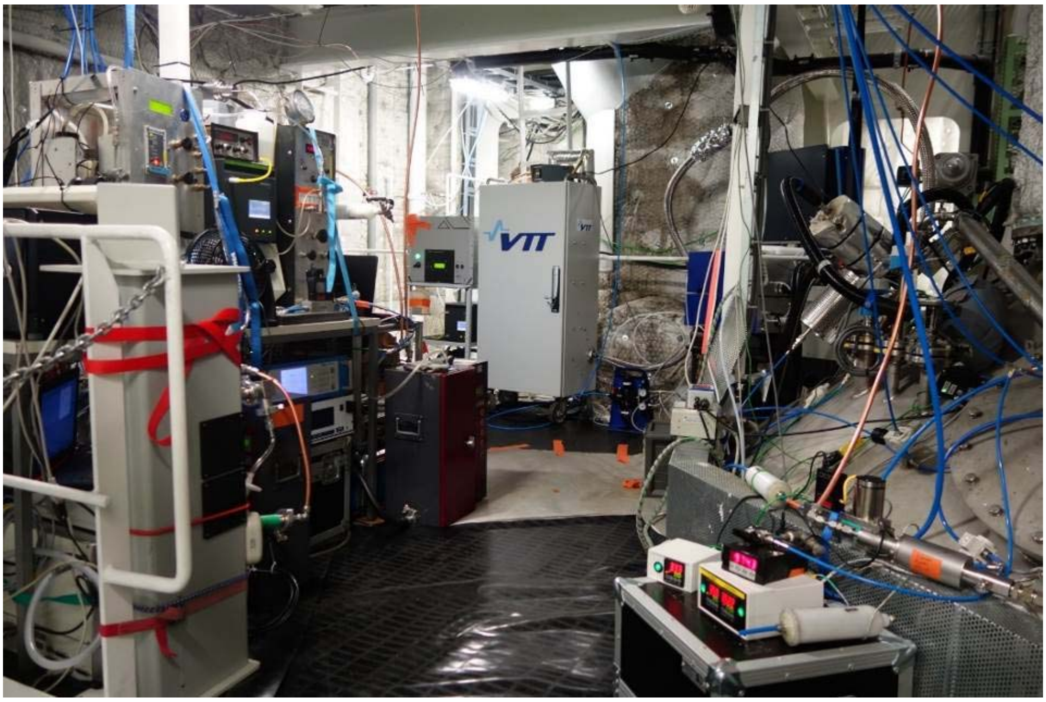


Figure 2.3. Measurement setup after the scrubber.

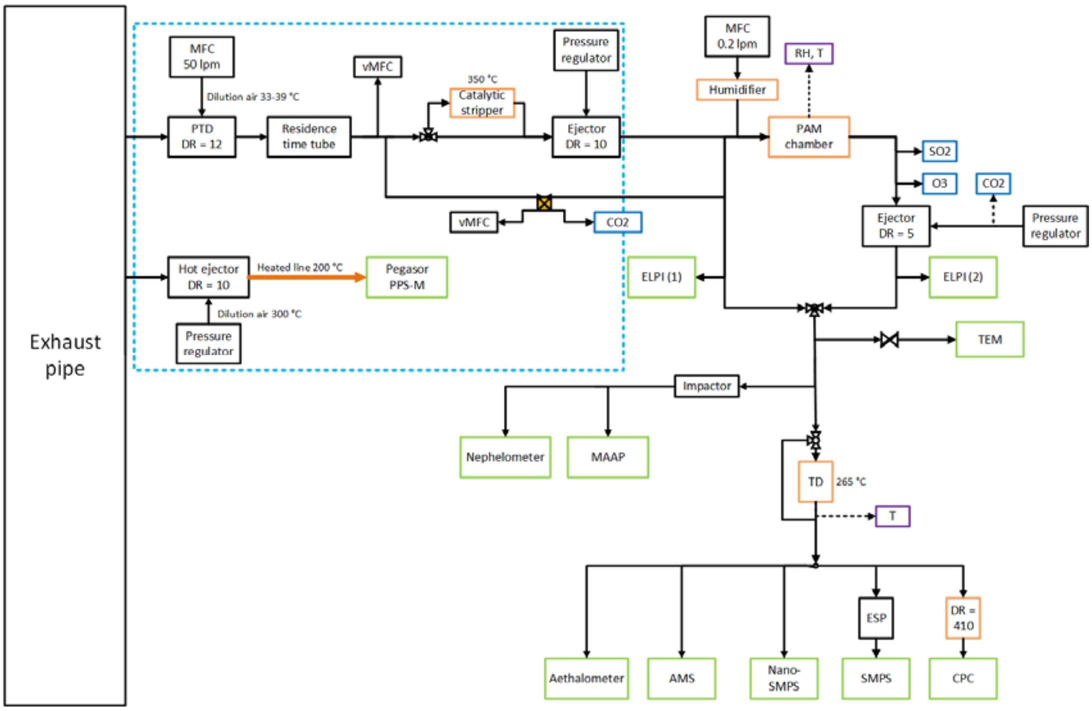


Figure 2.4. Measurement setup for the FMI and TUT instruments used at the onboard measurements. The instruments inside blue dashed box were moved before the scrubber.

2.2 Measurement probes

Special measurement probes were used for extracting the sample from the exhaust duct. The probes before and after the scrubber were a combination of six separate measurements probes having inner diameter of 6 mm for particulate sampling (5 probes) and 4 mm for gaseous components (one probe). Exhaust gas temperature measurement was included in the both probes. The probe before the scrubber was unheated and the probe was completely inserted to the exhaust duct. Heated lines, heated 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 measurement probe used after the scrubber was heated up to 250 °C. This was done to avoid any water droplets to the sampling lines and filters. The length of both measurements probes were ca. 70 cm (Figure 2.5).

Figure 2.5. Left: Measurement probes. On the right hand side a heated measurement probe for installation after the scrubber. On the left the measurement probe for installation before the scrubber. Right: Probe installation after the scrubber.

2.3 Dilution

In order to dilute the sample for the instruments several different dilution setups were used. The TUT porous tube diluter (PTD) sampling system mimics exhaust dilution and nanoparticle formation processes in the atmosphere regarding particle formation by nucleation (Rönkkö et al., 2006; Keskinen and Rönkkö, 2010). FMI and TUT instruments were downstream the PTD dilution system. VTT samplers used their own dilution setups.

The TUT PTD setup for delayed primary aerosol measurements consisted of two diluters that resulted a nominal dilution ratio (DR) of over 100. DRs were verified on-line by using gas analysers at different locations for raw and diluted exhaust gas. Temperature, pressure, humidity and dilution air impurities were also monitored. The primary dilution was executed with a porous tube diluter (PTD) where the dilution ratio was set to be approximately 12, dilution air being at high temperature of 33-39 °C (close to ambient temperature) even though the desired value would be about 30 °C. The secondary dilution was executed with an ejector diluter (ED, Dekati diluter) with a nominal dilution ratio of 8. The third diluter, an ED located downstream the PAM chamber, was used during secondary aerosol and reference primary aerosol measurements.

Dilution ratios (TUT)

- Primary PTD: 168±43 (Average ± st.dev)
- Secondary ED : 1050±171 (Average ± st.dev)
- ED before PPS-M: 10

Diluters (TUT)

- 1st dilution PTD

  - Dilution air temperature 33-39°C in the PTD
- 2nd dilution Cold ejector
- 3rd dilution for secondary emissions: humidifier + cold ejector
- Pegasor PPS: hot ejector
  - Dilution air temperature 300°C, line and sensor in 200°C

VTT

- AVL Smart Sampler DR=10
- Dilution tunnel according to ISO 8178
- AVL MSS^{plus} own dilution unit with DR=10

Figures 2.6 and 2.7 show used dilution ratios (average) for primary and secondary measurement points.

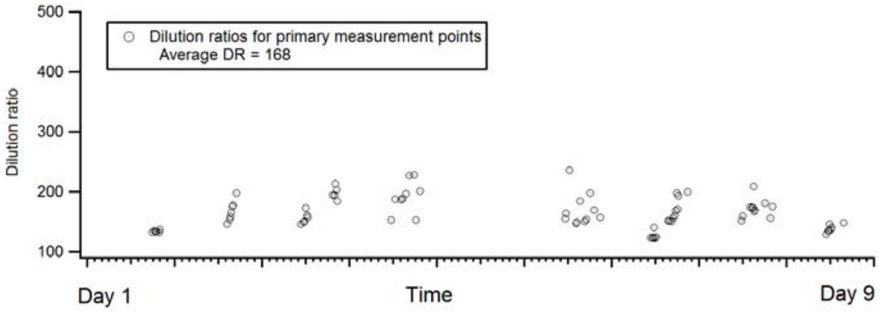


Figure 2.6. Dilution ratios calculated for primary measurement points during the campaign. On average the used dilution ratio was 168 ± 43 (average ± st.dev) for primary emission measurement points.

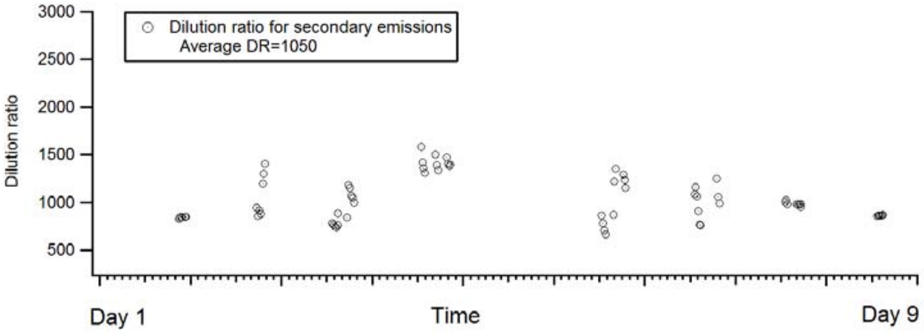


Figure 2.7. Dilution ratios calculated for secondary emission measurement points during the campaign. On average the used dilution ratio was 1050 ± 171 (average ± st.dev) for secondary emissions.

2.4 Instruments

A comprehensive set of instruments measuring black carbon (FSN, MSS, MAAP, Aethalometer, SP-AMS), gaseous emissions and particulate matter properties (concentration, size distribution, optical properties, secondary aerosol formation potential) were used to characterize the gaseous and particulate emissions of front engine pair (ME1 and ME2) during the measurement campaign. Used instruments are collected to table 1 and detailed description of each instrument is given in 2.4.1 - 2.4.5. Most of the instruments were online instruments with a good time resolution, typically between 1s-1min. In addition, filter samples were collected for in-depth chemical analysis.

Table 1. Used instruments, measured compounds and the providing institute.*

	Instrument	**Measured compound/s**	**Institute**
1	AVL 415SE and AVL 415S (2 x FSN)*	BC (optical)	VTT*
2	AVL MSS^{plus}	BC (photo acoustic)	VTT*
3	Horiba PG-250A analyser	NOx, CO, CO_2, O_2	VTT
4	Gasmet DX-4000 (3 x FTIR)	Multiple gaseous compounds	VTT
5	AVL Smart Sampler	Particle mass, OC/EC, Chemical composition of PM	VTT
6	SP-AMS (Aerodyne Research Inc)	Chemical composition of PM	FMI
7	PAM (Aerodyne Research Inc)	Secondary PM	FMI
8	Aethalometer AE33 (Magee Scientific)	BC (optical)	FMI
9	MAAP 5012 (Thermo Scientific)	BC (optical)	FMI
10	Nephelometer 3565 (TSI)	PM Scattering	FMI
11	Pegasor PPS	PM concentration	TUT
12	SMPS (TSI)	PM size distribution	TUT
13	Nano-SMPS (TSI)	PM size distribution	TUT
14	ELPI (2, Dekati)	PM size distribution	TUT
15	CPC A20 (Airmodus)	Particle number concentration	TUT
16	Gas analysers (Sick MAIHAK SIDOR, AF22 Module, Ozone Monitor Model 205)	CO_2, SO_2, O_3	TUT

*From AVL, Wärtsilä

2.4.1 BC instruments

Filter Smoke Number – Two different versions of Filter Smoke Meters were used: AVL 415SE (heated, owned by AVL GmbH) and AVL 415S (non-heated, owned by Wärtsilä) were operated onboard by VTT. FSN is a traditional method used to measure “smoke number” in the exhaust gas without the need for exhaust dilution. The FSN 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 to the BC concentration was according to the equation provided by the manufacturer and correlations are available also by ISO 8178-1 (2006, eq. A. 16). FSN is a standardized method conforming to ISO 10054.

AVL Micro Soot Sensor MSS^{plus} (owned by AVL were operated by VTT) – The measurement principle of the MSS is based on the photo acoustic spectroscopy (PAS) method, a modulated laser beam causes a sound pressure wave detected by a microphone. Diluted exhaust gas is directed through a measuring chamber and thermally animated by a modulated laser beam. The 808 nm light is absorbed by the particles. Modulated heating produces periodic pressure pulsation, which is detected by a microphone as an acoustic wave. The signal is amplified in a preamplifier and filtered in a “Lock-In”- amplifier. The MSS consists of a sensor unit and a conditioning unit for dilution, and provides a continuous on-line measurement of BC concentration.

Multiangle Absorption Photometer – MAAP 5012 manufactured by Thermo Scientific was used in these measurements. The MAAP measures the relative change in optical transmission as particles are collected on a filter combined with measurement of reflectance of scattered light with multiple detectors simultaneously (Petzold and Schönlinner, 2004). Reflection and scattering of light in multiple directions is due to particle size and shape. Long wavelength 670 nm is used. BC concentration calculation is based on a known mass absorption (6.6m2/g) of BC at a certain wavelength. MAAP detects transmitted and backscattered light at two angles reducing instrumental artefacts and thus providing a more accurate measurement of BC than aethalometers. MAAP provides continuous on-line measurement, but requires high dilution ratio for diesel exhaust.

Aethalometers (AE) – Aethalometers are based on the change in absorption of transmitted light due to collection of aerosol deposit on reinforced quartz fibre tape, which advances automatically when loading threshold is reached. A new aethalometer model, MAGEE AE33, described by Drinovec et al. (2015) was used in these tests. In this instrument, BC concentration is calculated based on absorption at 880 nm. AE33 uses seven wavelengths: 370 (UV), 470 (blue), 520 (green), 590 (yellow), 660 (red), 880 (IR-1) and 950 nm (IR-2). AE33 has also a DUALSPOT™ technology, in which aerosol is collected on two spots in parallel using different loading rates and both spots are simultaneously analysed to avoid "spot loading effects". Aethalometers can provide continuous on-line BC measurements, but require high dilution ratio for diesel exhaust.

Soot Particle Aerosol Mass Spectrometer – SP-AMS is a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) with added laser (intracavity Nd:YAG, 1064 nm) vaporizer (AMS described in detail by DeCarlo et al., 2006 and SP-AMS by Onasch et al., 2013). Dual vaporizer system enables the real-time measurements of PM mass and size-resolved chemical composition of submicron non-refractory particulate matter, refractory BC and some metals and elements. In the HR-ToF-AMS an aerodynamic lens is used to form a narrow beam of particles that is transmitted into the detection chamber, where the non-refractory species are flash-vaporized upon impact on a hot surface (600ºC) under high vacuum. Only non-refractory species are vaporized at this temperature. Crustal material, sea salt, metals and BC cannot be vaporized and thus are not detected using this technique. In the SP-AMS, particles are vaporized either by normal tungsten vaporizer in (600°C) to analyse inorganic ion and OC concentrations and with SP laser (intracavity Nd:YAG, 1064 nm) in order to analyse light absorbing refractory species such as BC and metals. The vaporized compounds are ionized using electron impact ionization (70 eV). Ions formed are guided to the time-of flight chamber. A multi-channel plate (MCP) is used as a detector. The time resolution of AMS measurements was 60 seconds (30 seconds for composition and 30 s for size distribution). SP-AMS provides on-line analysis of refractory BC (rBC), composition of PM (organics, sulphates, nitrates, etc.), and chemically resolved particle size distribution. However, high dilution ratio is needed for diesel exhaust. In addition, particles smaller than 30 nm are not detected due to limitations of aerodynamic lens. Also must be noted that SP-AMS is a research instrument and thus not ideal to onboard measurements due to its large size, high price and sensitivity to conditions.

2.4.2 Gaseous emissions and test parameters

CO, CO_2, NOx and O_2 were measured with the Horiba analysers; NOx by Heated Chemiluminescence (HCLD, Horiba); CO, CO_2 by Nondispersive Infrared (NDIR, Horiba). O_2: Paramagnetic cell (Horiba). The concentrations were recorded in 15 second time intervals and averaged over the each PM measurement time interval.

FTIR - More than 10 gaseous compounds were measured on-line at 20 seconds intervals using three Fourier transformation infrared (FTIR) equipment (Gasmet DX-4000) purchased in 2005, 2010 and 2012. Sample temperature was 180 °C. The compounds measured with FTIR include sulphur dioxide (SO_2). Correlation between Horiba and FTIR results is shown in Chapter 3.3.1. Only concentrations exceeding the detection limit of the FTIR instruments were taken into account when calculating the results.

The SO_2 and NH_3 concentrations from the ME2 engine after SCR are underestimated due to formation of ammonia sulphate on the FTIR pre-filter. Filter was cleaned several times during the measurement campaign. Theoretical SO_2 concentration was also calculated based on fuel consumption and exhaust flow.

Parameters - In addition to the regulated gaseous emissions, many parameters were recorded at one second time intervals and averaged over 10/15 minutes. These parameters included exhaust gas temperatures before SCR, before scrubber and after scrubber, engine power and urea feed, amongst others.

2.4.3 Filter collection (mass and composition)

ISO 8178 partial flow dilution was used to collect PM (AVL Smart Sampler). 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. No cyclone or hat for removing large particles was used. Dilution ratio was 10 in PM collections with AVL Smart Sampler (ISO 8178 limit: DR not less than 4). Temperature on filter face was between 42 and 52 °C. Face velocity requirement is 35–100 cm/s. Transfer line heating was set to 250 °C.

ISO 8178 PM samples were collected with Pallflex TX40HI20-WW filters (o.d. 47 mm) using both primary and back-up filters. Filter material is borosilicate microfibers reinforced with woven glass fibre coated with cloth and bonded with PTFE. These filters were used for the following analyses:

- PM results, which are used also in the calculations of the PM composition (mass per mg PM) to concentrations and mass emissions
- Anion analysis (sulphates, nitrates etc.)
- PAH analyses

Other used filter was Pallflex Tissuquarz 2500QAT-UP quartz filter (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. The quartz filters were used for sampling for the following analyses:

- EC/OC analyses
- Metal analyses
- Carbon, hydrogen, nitrogen, sulphur and oxygen (CHNSO)

The loaded filters were stored in a portable refrigerator. Close to 300 filters were used for PM collections, including the back-up and reference filters. Different PM loadings were designed for the TX40 and Tissuquarz filters depending on the target analyses. PM mass on the back-up filters was in most cases below 5% of the total PM mass. Only for samples after SCR, higher share of PM mass on the back-up filters compared with the total PM was observed (Figure 2.8).

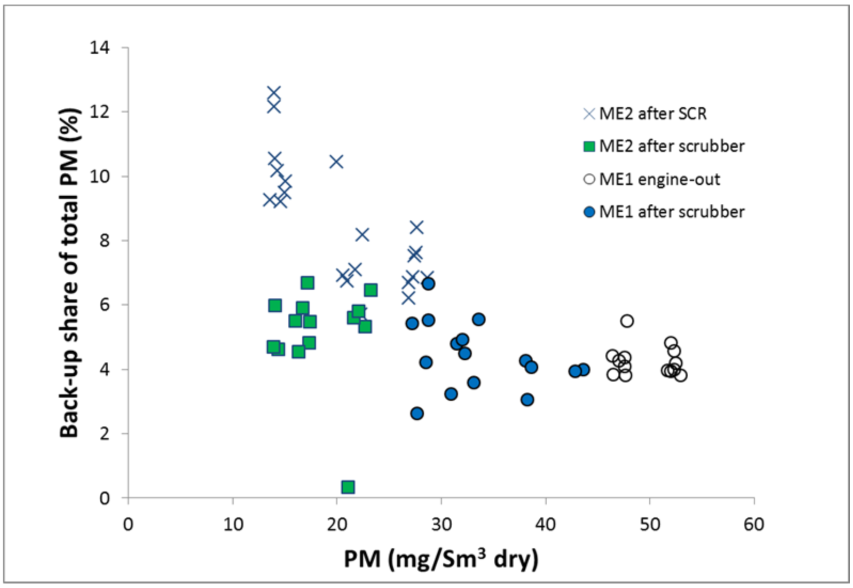


Figure 2.8. Share of PM mass on the back-up filter of total PM mass.

Elemental and organic carbon (EC/OC) – A Sunset Laboratories Inc's analyser model 4L was used at VTT for EC/OC analysis. 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 EC in this phase, which is monitored by measuring continuously the transmission of a laser. Any charring of the OC results in a decrease in transmittance of the laser. In the second phase, 2% O_2/He gas mixture is introduced and temperature is raised again. Both the original EC and that produced by the pyrolysis are oxidized to CO_2, which is then converted to methane and detected by the FID. The organic compounds pyrolytically converted to EC are compensated by continuous measurement of the transmission of a laser. Based on the 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. The EUSAAR2 is deemed to minimize pyrolysis by using lower but sufficient temperature at He mode, and prolonged temperature steps.

Anions, including sulphates were analysed by capillary electrophoresis from water/isopropanol extracts. Water bound in sulphuric acid can be calculated according to SAE J1936 assuming relative humidity of 50%. However, WP1 showed that ship PM sulphates, particularly when using HFO as fuel, are not only sulphuric acid, and thus factors of SAE J1936 are not valid. Consequently, water bound in sulphates is a part of "rest" portion of PM (contains also e.g. oxygen bound in metals).

Metal analyses of particulate matter collected with ISO 8178 procedure on the quartz filters were carried out 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).

C, H, N, S and O analyses were done at VTT using FLASH 2000 series analyser. The sample was weighted in tin/silver capsules, placed inside the Thermo Scientific MAS 200R auto-sampler at a pre-set time, and then dropped into an oxidation/reduction reactor kept at a temperature of 900-1000 °C. The exact amount of oxygen required for optimum combustion of the sample is delivered into the combustion reactor at a precise time. The reaction of oxygen with the tin capsule at elevated temperature generates an exothermic reaction which raises the temperature to 1800 °C for a few seconds. At this high temperature, both organic and inorganic substances are converted into elemental gases which, after further reduction, are separated in a chromatographic column and finally detected by a highly sensitive thermal conductivity detector (TCD). Determination of oxygen is done via pyrolysis in the same analyser. Results were calculated using Certified Elemental Microanalysis standards using K factor (CHNS/CHNS-O Standards Kit: Cystine, Sulphanilamide, Methione and BBOT: Catalogue Code. Thermo: 33840010).

Polyaromatic hydrocarbons (PAH) 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 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).

Particle samples for TEM analysis were collected during the campaign on Cu grids coated with holey carbon film. Samples were analysed using the Transmission Electron Microscopy (TEM) for imaging and the Energy-dispersive X-ray spectroscopy (EDS) for elemental analysis. TEM samples were analysed from following operating points:

- After scrubber: ME2 at 40% load
- Before scrubber: ME2 at 40% load HFO/MGO and ME1 at 75% load

Samples were collected after the catalytic stripper that was heated to 350 °C. So the analysed particles should not include components that evaporate under that temperature.

2.4.3 Particle number concentration and size distribution

Several different particle sizing instruments were used in the measurements (CPC, Long-SMPS, Nano-SMPS, 2xELPI).

SMPS – The particle size distributions were measured with a scanning mobility particle sizer with a long DMA (SMPS) (Wang and Flagan, 1990), and a scanning mobility particle sizer with a nano DMA (Nano-SMPS) (Chen et al., 1998). In these experiments with the specific flow selections, the Nano-SMPS and the Long-SMPS had measurement ranges of 3−60 nm and 10−400 nm, respectively.

ELPI – an electrical low pressure impactor (ELPI) (Keskinen et al., 1992) was used to measure PM size distribution from 7n to 10µm. The ELPI was equipped with an extra stage (17 nm < Da < 28 nm) (Yli-Ojanperä et al., 2010) and a filter stage (7 nm < Da < 17 nm) (Marjamäki et al., 2002), both increasing the nanoparticle size resolution of the instrument. In these experiments, two ELPIs were used, one to measure primary particles and the other to measure secondary particles.

CPC – The particle number concentrations were measured with a condensation particle counter (CPC), model A20 by Airmodus. This CPC has the lowest size detection limit of about 7 nm. The CPC uses butanol vapour to grow particles to larger sizes to enable optical single particle detection.

Pegasor Particle Sensor – In these experiments a prototype version of the Pegasor Particle Sensor was applied. The commercial sensor, PPS-M measurement principle is based on the measurement of electrical charge carried by particles (Rostedt et al., 2014). The PPS-M comprises an ejector where the motive fluid flow is generated by pure, particle free gas. The ionized air is used to charge the particles in the sensor. Particle charging is relative to the particle size. Ions that are not attached to the particles are removed from the gas flow by an ion trap, which is basically an electrostatic precipitator with a small electrical field. When the free ions are removed, the electrical current is carried only by the flow of charged particles. The electrical current escaping from the sensor with the charged particles can be measured and this gives a direct, fast, real-time measurement of the particle number or mass concentration. The non-collective feature ensures long maintenance and cleaning interval and thus providing service-free operation with no consumables. Time response is fast and dynamic range wide. However, on-site calibration is needed at installation site, and sensitivity is limited for large particles (Dp>1).

2.4.4 Volatility and secondary aerosol formation potential characterization

Thermodenuder (TD) – The effect of sample treatment on measured BC concentration and PM composition was studied by using a thermodenuder in front of aethalometers, MAAP, SP-AMS, Scanning Mobility Particle Sizers (Nano-SMPS and Long-SMPS) and Condensation Particle Counter (CPC) according to a pre-defined program. Thermal treatment of the exhaust aerosol removes semi volatile compounds from particles and leaves more solid (or non-volatile) part of particles to be measured, which, in principle, could improve accuracy of BC determination from different exhaust matrices. The TD removes semi volatile material by adsorption of gaseous compounds. In the TD, the aerosol is first heated to 265 °C, and then the evaporated material is adsorbed by activated carbon.

A thermodenuder was used to study influence of coating material (e.g. organic or sulphur) to black carbon results. In addition, thermodenuder gives information about the volatility of particles. For the TD measured solid particle losses were 24.5%.

Potential Aerosol Mass chamber – (PAM; Aerodyne Research Inc., US) chamber is a small flow through oxidation flow reactor (OFR) developed to simulate secondary aerosol formation in the atmosphere (Kang et al., 2007; Kang et al., 2011; Lambe et al., 2011; Lambe et al., 2015). The PAM is constructed from aluminium and measures 46 cm’s in length and 22 cm’s width, with a volume of 13.3 litres. The small surface area to volume ratio of the PAM is designed to limit particle wall losses (Kang et al., 2011; Lambe et al., 2011). Two ozone producing UV lamps (BHK Ink, US) provided photons at two intensities 185 nm and 254 nm. The oxidants OH and HO_2 are produced directly in the chamber through photolysis of H_2O and O_3 is produced through photolysis of O_2. The flow through the PAM chamber was maintained at ~10L/min providing an average residence time of 80s. Temperature and humidity were measured directly from the PAM chamber with average values of 16°C and 37% respectively. Lamp voltage was varied between three intensities to cover a range of atmospheric aging from zero to seven days corresponding to OH exposures between 8.3E+11 to 3.68 E+11. Losses in the PAM chamber were estimated as 30%. The PAM chamber was installed between the ageing chamber and secondary dilution units of sampling system.

Volatility and secondary aerosol formation results are not included this report. This includes only the basic results (PM mass and number concentrations, size distributions and gaseous emissions).

2.5 Measurement line materials and lengths

The instruments were positioned as close as the sampling location (engine out, before and after scrubber) as possible. However, due to the used dilution system, the residence time chamber and physical limitations, for some instruments long sampling lines were needed. The SP-AMS had longest line (25m) since it had to be located outside the scrubber room due to its limited ability to tolerate elevated temperatures (up to 40°C in scrubber room). Inert sampling line materials (Cu, Stainless steel, Tygon) were favoured. Table 2 includes the sampling line lengths for each instrument when measurements were conducted after scrubber. For measurements before scrubber, the length of the connecting tube (4.5m) for FMI and TUT instruments have to be added to line lengths shown in Table 2.

Table 2. Line lengths for each instrument when the measurements were conducted after the scrubber

FMI instruments	Length (m) (line material)
SP-AMS	25 (6mm Cu-tubing)
Aethalometer	11.4 (10 mm Cu-tubing +10mm tygon)
MAAP	12.7 (10 mm Cu-tubing + 10mm tygon)
Nephelometer	12.7 (10mm Cu-tubing+ 10mm tygon)
PAM	6.7 (Cu-tubing)
TUT instruments	
A20 CPC	10.6 (Cu-tubing 10mm + tygon)
Nano-SMPS	11.8 (Cu-tubing 10mm + tygon)
Long SMPS	11.8 (Cu-tubing 10mm + tygon)
Pegasor PPS	1.5 (Sensor's own heated sampling line 10mm)
ELPI1	7.3 (Cu-tubing 10mm + tygon)
ELPI2	9.6 (Cu-tubing 10mm + tygon)
Gas analysers (SO_2, CO_2)	5 (Cu-tubing 10mm + tygon)
VTT instruments	
FTIR engine out	7m, 6mm inside diameter heated line+2x1m 4mm inside diameter
FTIR before scrubber	10+1m inside diameter 4mm, heated
FTIR after scrubber	5+1 m, inside diameter 4mm, heated
FSN engine out	1.2m
FSN before/after scrubber	3m heated
MSS	2.2 m heated
Horiba PG-250A analyser	2x2m, 4mm inside diameter
Smart sampler	4 mm, 8mm inside diameter, heated, 250°C surface temp.
CPC+DEED	0.5m after scrubber/ 3.8m before scrubber, 4mm inside diameter

2.6 Measurement plan

Table 3. shows the measurement plan that was followed during the measurement campaign. Plan included measurements for both front engines, ME1 and ME2, using low (40%) and high (75%) loads. Most of the emission measurements were done using HFO fuel, however MGO emissions were measured when ship was in harbour (Day 8).

Finnish time (UTC +2) is used in this report, which was also time of the measurement instruments during the campaign.

Table 3. Measurements conducted at fixed loads during the cruise. Blue days are on sea and white days in harbour.

Date	**Harbour / sea**	Start **(meas. time)**	End **(meas. time)**	**Engine / engines**	**Target engine load, %**	**Fuel**	**Note**
Day 1	on sea	13:40	20:53	ME1	75	HFO	measurements
Day 2	in harbour	15:00	20:16	ME2	40	HFO	measurements
Day 2	leave from harbour	22:00		multiple	-	HFO	-
Day 3	on sea	9:45	15:40	ME1	40	HFO	measurements
Day 3	on sea	18:27	20:55	ME2	75	HFO	measurements
Day 4	in harbour	12:01	15:51	ME2	40	HFO	measurements
Day 4	in harbour	15:52	17:35	ME2	40	HFO	measurements
Day 4	in harbour	18:05	20:30	ME2	40	HFO	measurements
Day 4	leave from harbour	22:00		ME2	40	HFO	measurements
Day5	in harbour	7:00	18:30		-	-	instruments moved to bef scrubber
Day 6	in harbour	12:40	14:09	ME2	40	HFO	measurements
Day 6	in harbour	14:44	16:16	ME2	40	HFO	measurements
Day 6	in harbour	17:06	18:41	ME2	40	HFO	measurements
Day 6	leave from harbour	20:00				HFO	measurements
Day 7	on sea	10:00	14:50	ME1	40	HFO	measurements
Day 7	on sea	17:17	19:46	ME2	75	HFO	measurements
Day 8	in harbour	8:57		ME2	40	HFO/MGO	fuel change
Day 8	in harbour	12:22	13:33	ME2	40	MGO	measurements
Day 8	in harbour	15:09	17:44	ME2	40	MGO	measurements
Day 8	in harbour	18:15		ME2	40	MGO/HFO	fuel change
Day 8	leave from harbour	22:00				HFO	measurements
Day 9	on sea	10:00	16:35	ME1	75	HFO	measurements

In addition to the measurement points at fixed loads, the ship emissions were measured in following times:

Measurements conducted outside the measurement program

- Day 7. 21.00-22.30
- Day 8. 20.03-22.33
- Day 9. 8.40-9.39
- Day 6. 19.14 - 20.48, Start-up of ME1 engine and leaving from port
- Day 7. 15.30-15.50, Start-up of ME2 engine, stopping ME1 engine

2.7 Fuel and lubricant oil

The HFO fuel contained 0.65 % (m/m) sulphur and 0.24 % (m/m) nitrogen, while the MGO fuel contained only 0.078 % (m/m) sulphur (Table 4). Asphaltene content of HFO was 0.36 % (m/m). HFO contained also e.g. vanadium, nickel, iron and sodium in concentrations between 10 and 20 mg/kg. Concentrations of aluminium, calcium and silicon were also noticeable though below 10 mg/kg. MGO fuel did not contain ash or metals above detection limits. ASG GmbH provided originally a high ash result of 0.275 %(m/m) for HFO. This was corrected to <0.005 % (m/m) in the repeated analysis. Mixing of the HFO sample by ASG GmbH may not have been sufficient to obtain homogenous samples for ash analyses.

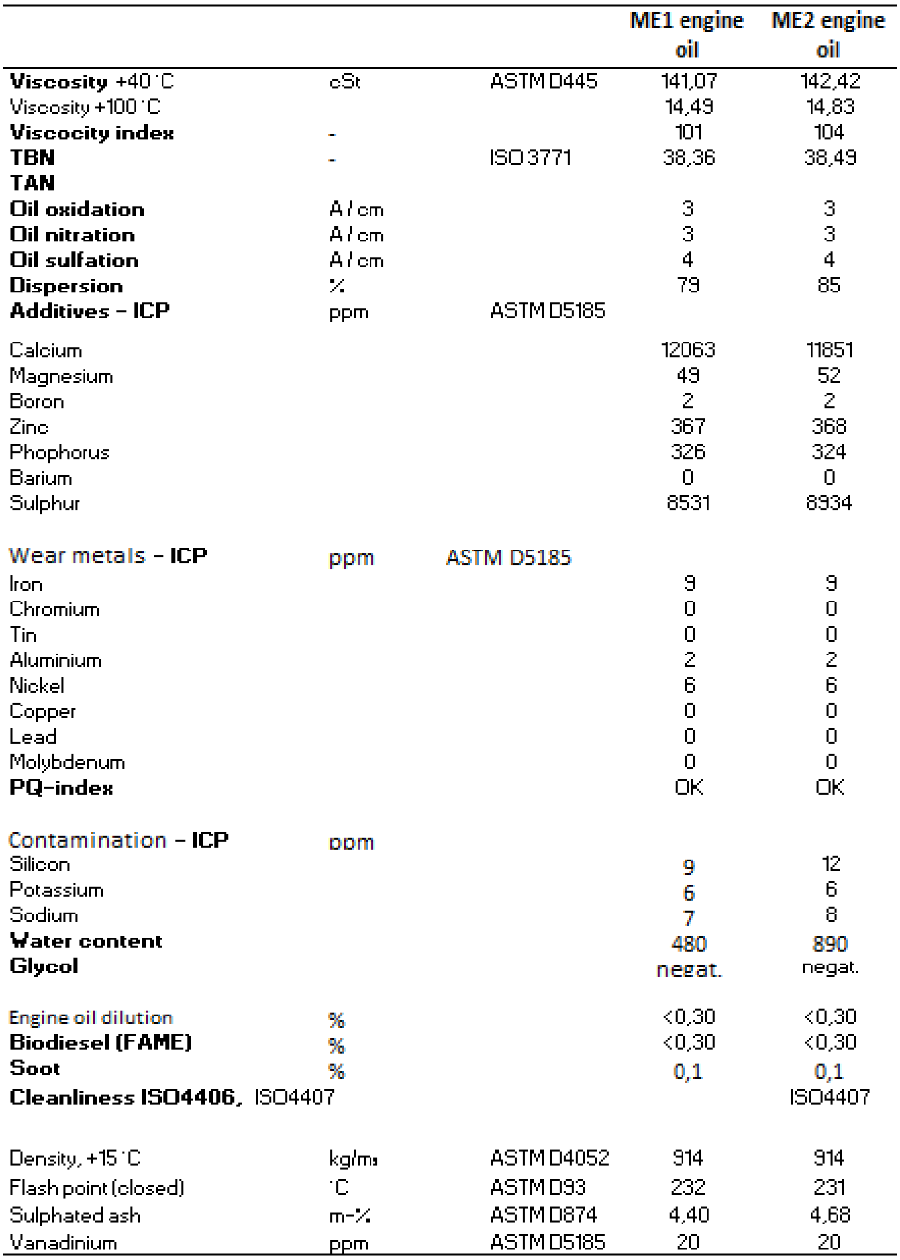
Engine oil was in good condition (Table 5). Nickel and vanadium present in engine oil originate from HFO and they are not an indication of engine wear. Engine oil dilution was low, water, soot concentrations and filterability were normal.

Table 4. Fuel properties analyzed by ASG GmbH.

Parameter	Unit	HFO	MGO
Kin. viscosity (40 °C)	mm^2/s	886,3	3,871
Kin. Viscosity (50 °C)	mm^2/s	362,8	
Density (15 °C)	kg/m^3	967,9	873,1
Calorific value, upper	J/g	43336	44809
Sulphur content	mg/kg	6520	780
Ash content (775 °C)	% (m/m)	<0,005 *	<0,001
Water content	Vol.-%	0,2	
Water content	mg/kg		31
Carbon content	% (m/m)	87,7	87,9
Hydrogen content	% (m/m)	11,5	12,8
Nitrogen content	mg/kg	2490	
Oxygen content	% (m/m)	0,6	<0,5
Cetane index			44,3
CCAI	-	828	
Carbon residue	% (m/m)	9,57	<0,10
Flash point	°C	146,0	81,0
Aromatic hydrocarbons	mol-%	-	39,7
Monoaromatics	% (m/m)		26,7
Diaromatics	% (m/m)		11,2
Triaromatics	% (m/m)		1,8
PAH content	% (m/m)		13,0
Asphaltene content	% (m/m)	0,36	0,03
Fatty acid methylester content	% (V/V)		0,1
10 % (V/V) recovery	°C		235,0
50 % (V/V) recovery	°C		295,0
90 % (V/V) recovery	°C		358,0
Silver (Ag)	mg/kg	<0,5	<0,5
Copper (Cu)	mg/kg	<0,5	<0,5
Aluminium (Al)	mg/kg	5,7	<0,5
Cadmium (Cd)	mg/kg	<0,5	<0,5
Sodium (Na)	mg/kg	15,8	<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	12,4	<0,5
Iron (Fe)	mg/kg	12,5	<0,5
Molybdenum (Mo)	mg/kg	<0,5	<0,5
Barium (Ba)	mg/kg	2,0	<0,5
Boron (B)	mg/kg	<0,5	<0,5
Calcium (Ca)	mg/kg	4,8	<0,5
Magnesium (Mg)	mg/kg	0,8	<0,5
Lead (Pb)	mg/kg	<0,5	<0,5
Vanadium (V)	mg/kg	17,2	<0,5
Tin (Sn)	mg/kg	<0,5	<0,5
Zinc (Zn)	mg/kg	0,9	<0,5
Silicon (Si)	mg/kg	6,0	<0,5
Titanium (Ti)	mg/kg	<0,5	<0,5
Phosphorous (P)	mg/kg	0,8	<0,5
Cobalt (Co)	mg/kg	0,8	<0,5
Lithium (Li)	mg/kg	<0,5	<0,5

*) Correction from ASG on 19.12.2016.

Table5. Engine oil properties.



			ME1 engine oil	ME2 engine oil
Viscosity +40 °C	cSt	ASTM D445	141,07	142,42
Viscosity +100 °C			14,49	14,83
Viscocity index	-		101	104
TBN	-	ISO 3771	38,36	38,49
TAN				
Oil oxidation	A / cm		3	3
Oil nitration	A / cm		3	3
Oil sulfation	A / cm		4	4
Dispersion	%		79	85
Additives – ICP	ppm	ASTM D5185		
Calcium			12063	11851
Magnesium			49	52
Boron			2	2
Zinc			367	368
Phophorus			326	324
Barium			0	0
Sulphur			8531	8934
Wear metals – **ICP**	ppm	ASTM D5185		
Iron			9	9
Chromium			0	0
Tin			0	0
Aluminium			2	2
Nickel			6	6
Copper			0	0
Lead			0	0
Molybdenum			0	0
PQ-index			OK	OK
Contamination – **ICP**	ppm			
Silicon			9	12
Potassium			6	6
Sodium			7	8
Water content			480	890
Glycol			negat.	negat.
Engine oil dilution	%		<0,30	<0,30
Biodiesel (FAME)	%		<0,30	<0,30
Soot	%		0,1	0,1
Cleanliness ISO4406, ISO4407				ISO4407
Density, +15 °C	kg/m$_3$	ASTM D4052	914	914
Flash point (closed)	°C	ASTM D93	232	231
Sulphated ash	m-%	ASTM D874	4,40	4,68
Vanadinium	ppm	ASTM D5185	20	20

2.8. Ship

Measurements were conducted at the onboard of a modern cruise vessel with a SCR catalyst and a scrubber.

3 Results

During the campaign BC emissions of the ship were measured with several instruments from the exhaust lines and in addition properties of PM and gaseous emissions were studied in detail. The main focus of this project was to characterize the BC emissions of a modern vessel and to find a suitable instrument for onboard measurement of BC. The other measurements are helping us to understand why the results from different BC measurement techniques differ. This report includes only the main results (PM mass and number concentration, BC, size distributions, main gaseous emissions).

3.1 Important lessons from WP1

The measurement campaign onboard a ship was planned based on WP1 results and previous onboard campaigns. WP1 measurements were conducted in the VTT engine laboratory with a Wärtsilä Vasa 4R32 LN engine. The WP1 results indicated that dilution has important role in BC results. Especially for instruments that are designed for atmospheric measurements (e.g. MAAP), high dilution ratios (DR 100-600 at sample flow 6 of lpm) are needed when exhaust emissions are measured. Uncertainty in dilution ratio is directly reflected to uncertainty in BC results. Also, WP1 indicated that in order to quantify accurately the DR accurate real time CO_2 measurements are important not only for raw and diluted exhaust, but also for dilution air and ultra-pure dilution air is recommended for the BC measurements when high DRs are applied. Overall, dilution system has to be planned carefully in order to obtain representative results. For the secondary PM measurements two ELPIs were installed in parallel so that one measured primary emissions prior the PAM chamber and another secondary emissions after the PAM chamber. This measurement setup enables real time characterization of secondary aerosol formation potential.

For some instruments, the instrument measurement range is limited, which was evidenced for MAAP in WP1. For the MAAP dilution range needs to be adjusted so that the BC concentration during measurements always remains below 30 µg m^{-3} in order to avoid exceedance of reliable measurement range.

More detailed information about the WP results can be found from Aakko-Saksa et al., 2017.

3.2 Important things to notice prior campaign

Prior to campaign it is important to discuss with the technical personnel from the ship in order to resolve availability of needed resources from the ship including e.g.

- Locations where the instruments are connected and exhaust sample is taken needs to be checked prior to the campaign. In this project two pre-visits to ship were done by measurement personnel in order to check the measurement places where instruments will be located and points where instruments will be connected. This is important in order to have suitable connectors and line materials available when the instrumentation will be installed.

-Ambient conditions (e.g. temperature, noise, space) in the space where the instruments are installed need to be resolved in advance. The needs of measurement personnel (suitable clothes, water, protective gear, ear protection, googles etc.) needs to be also taken into account.

-The instrumentation has to be as easy to install as possible since it had to be quickly installed and removed. Also, reliability of system was considered to be important in onboard measurements.

- Availability of electricity and its technical (120 or 240V, 50 or 60 Hz, fuses, needed power) parameters need to be resolved well in advance. Also, UPS was used for sensitive instruments (SP-AMS) in this campaign.

-Pressurized air is typically needed for dilution and for instruments. For this campaign pressurized air was obtained from the ship.

-Moving the large instruments to passenger ship can be challenging. In this campaign a large crane was used to move the instruments directly to the deck of the ship. All instruments were packed in wooden boxes to minimize the influences of weather and to facilitate a fast moving of instruments to the ship. Especially convenient were the boxes with wheels allowing easy moving. It is important to avoid disturbance for the customers and ship personnel as much as possible.

-Customs declaration issues need to be clarified. In this campaign a list of instrument description and prices was sent in advance to the ship yard/customs in order to speed up the customs procedure. Also, ship security checked the instruments (e.g. explosive tests) prior to moving them to the ship.

-Regulations related to using pressurized gas botthels in ship (IMO papers) needs to be taken into account in advance. Also a permission from the ship has to be obtained to bring gas bottles to onboard.

-Overall 6-12 months has to be reserved for negotiations and practical arrangements prior to the measurement campaign. In this campaign discussion with the shipping company started 14 months prior the campaign.

Also, must be noted that it is important to have competent measurement crew at onboard since conditions are challenging. It is important to monitor that instruments are working and that obtained results are as expected since often the measurements cannot be repeated. In addition measurement personnel needs to be able to do at least small repairs and calibrations for instruments if need arises. Co-operation with the ship personnel is utmost important in order to adjust the measurement points and to know the current engine parameters. After the campaign it would be very important to obtain the ship data (used engines, engine loads, fuel consumptions etc. as a function of time) in order to properly calculate the results

3.3 Gaseous emissions

Gaseous parameters, CO, CO_2, SO_2, NOx, NH_3 were measured with FTIR and HORIBA instruments in engine out and either before (days 6-9) or after scrubber (days 1-4).

3.3.1 CO and CO_2

Complete combustion of hydrocarbons with oxygen in engine forms CO_2, whereas CO forms in incomplete combustion. The CO_2 concentrations were slightly lower after scrubber than before scrubber with ME2 engine, while the respective difference for ME1 engine did not seem to be significant (Figure 3.1). CO concentrations stayed quite constant over the measurement period for each engine and load (Figure 3.2). Engine-out CO concentrations were relatively low for both ME1 and ME2 engines. The CO concentrations increased substantially for ME2 engine in the SCR catalyst. Increase in CO over SCR is a well-known as the SCR catalysts oxidizes hydrocarbons to CO_2, but partly also to CO. Post-oxidation catalysts can be used to reduce CO emissions (Gekas et al., 2002).

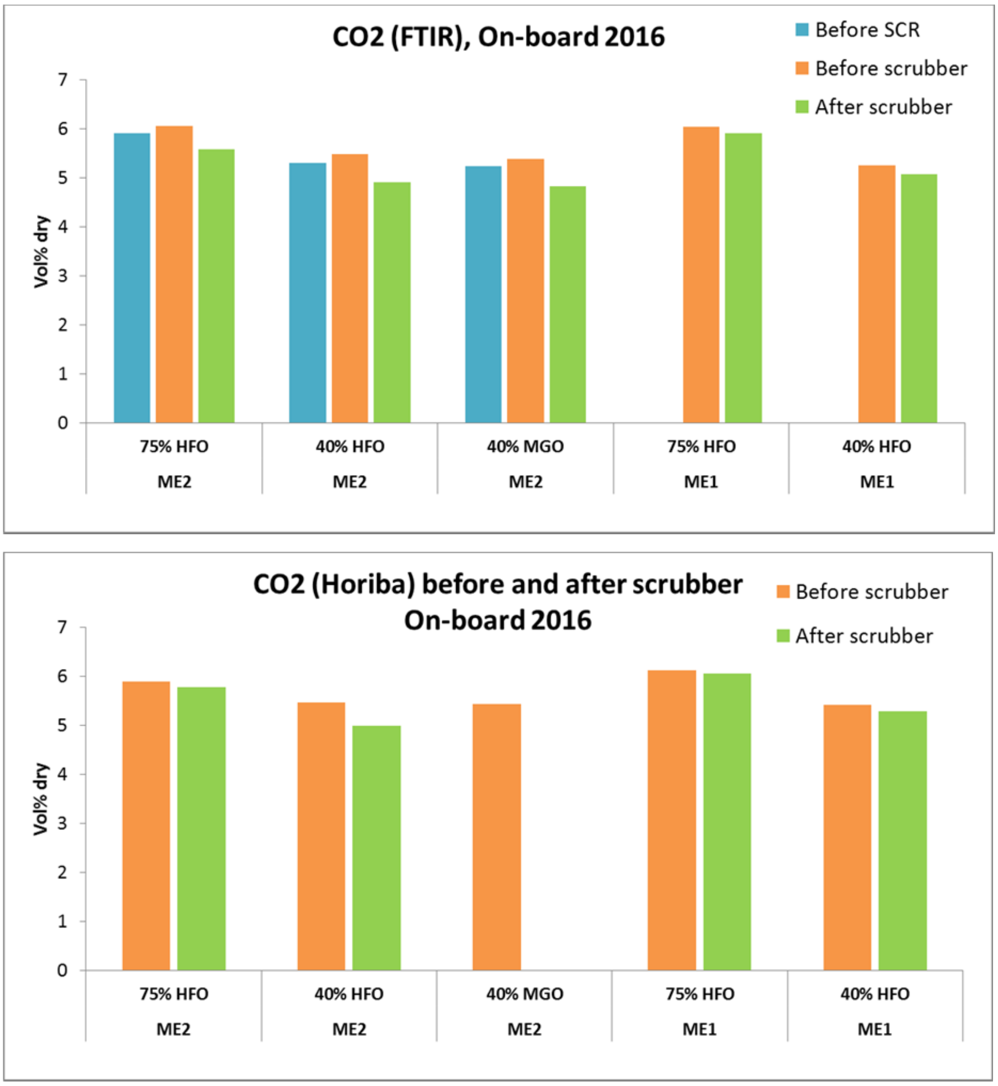


Figure 3.1. CO_2 concentrations measured with the FTIR (above) and Horiba (below) before and after the scrubber.

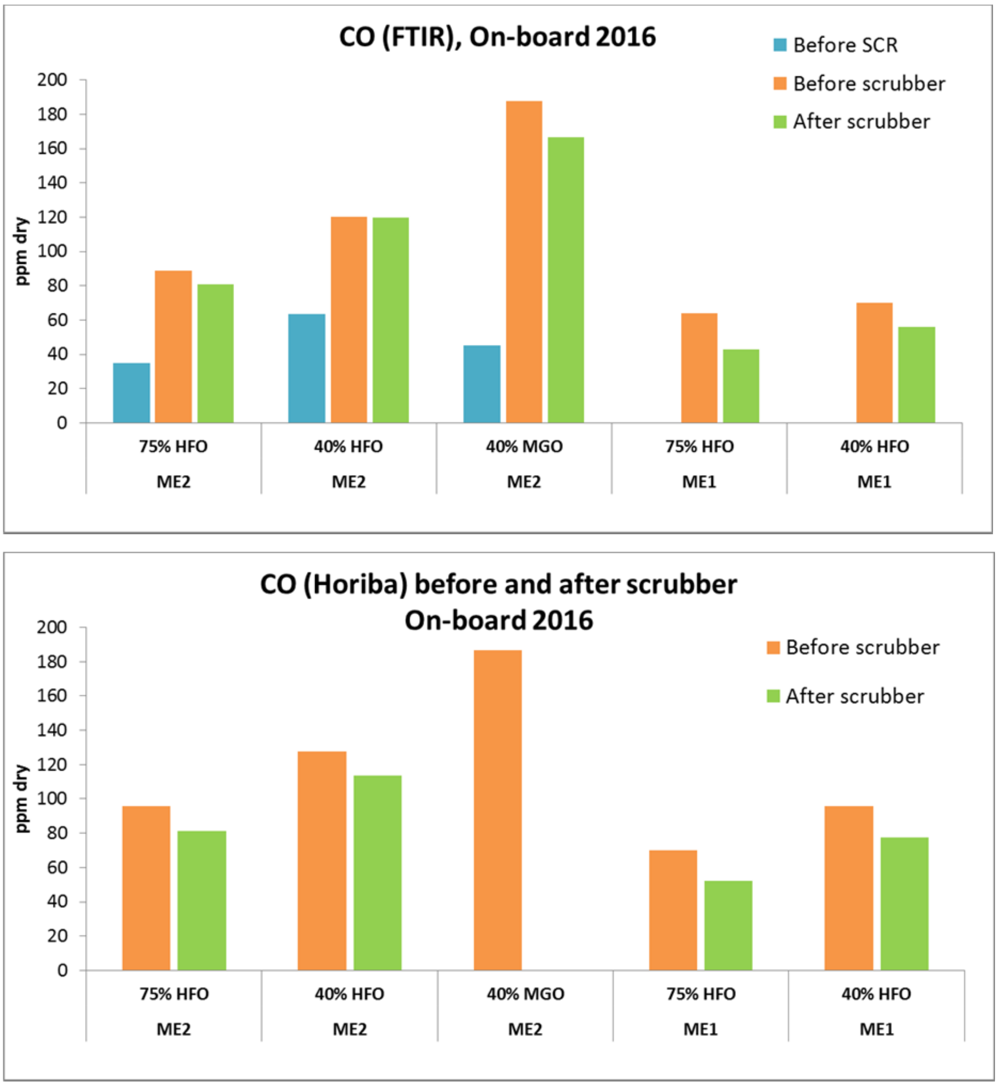


Figure 3.2. CO concentrations measured with the FTIR (above) and Horiba (below) before and after the scrubber.

3.3.2 NO_X

In this study, for the ME1, average engine-out NO_X concentrations were 1083 ppm and 1645 ppm at 75% and 40% engine loads, and for ME2 engine 929 ppm and 1301 ppm, respectively (Figure 3.3). SCR decreased the average NO_x concentrations from the ME2 engine to 111 ppm at 75% engine load and 425 ppm at 40% engine load. NO_x emissions were observed to decrease over the scrubber by 5.8-10.6% probably due to their transfer into water. Kajolinna et al. (2013) found also NO_X reduction over the scrubber.

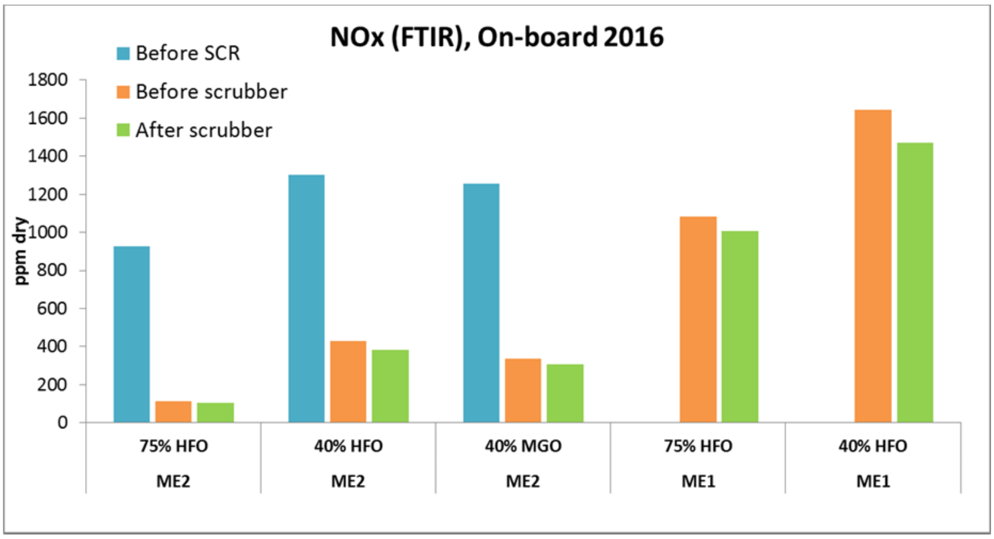


Figure 3.3. Measured NO_X concentrations (FTIR).

3.3.3 O_2

Oxygen content of the exhaust gas was lower for both engines at 75% load than at 40% load (Figure 3.4). In most cases, only slight differences were observed in the oxygen content of the exhaust gas between measurements before and after the scrubber.

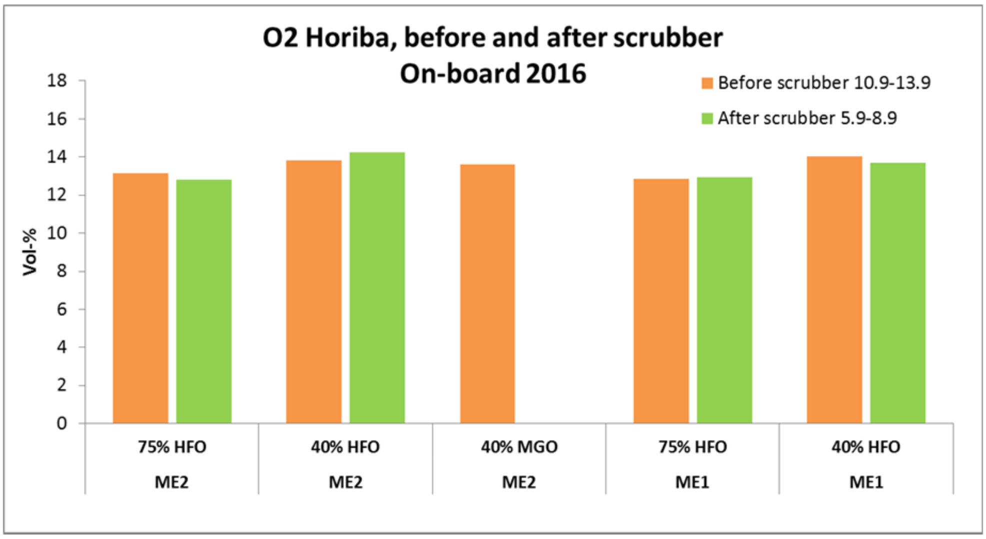


Figure 3.4. Oxygen content of the exhaust.

3.4 PM concentration

The PM concentrations after the scrubber were below 40 mg/Sm^3 for the ME1 engine and below 25 mg/Sm^3 for the ME2 engine. PM reduction over the scrubber was 17-45% depending on the used engine and fuel (Figure 3.5).

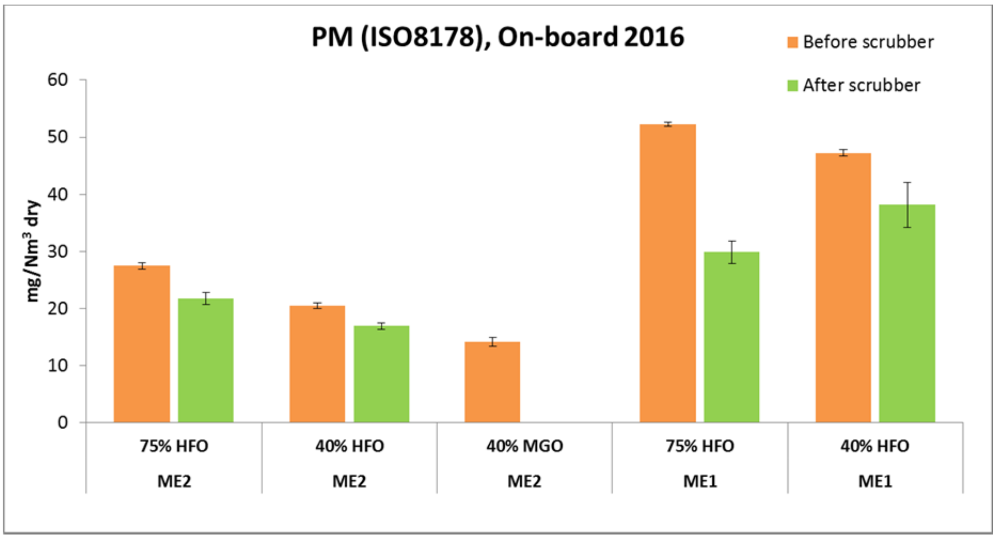


Figure 3.5 PM concentration (ISO 8178) measured onboard for the ME1, ME2 engines using HFO and engine loads 40% and 75%. For MGO measurements were only conducted before the scrubber and only for ME2 engine.

3.5 PM composition

Figures 3.6 and 3.7 represent the composition of PM measured before and after the scrubber from the filter substrates. The SO_4 concentrations in PM were low in all cases, though possibly slightly elevated over the scrubber. Major part of PM was organic carbon, while black carbon concentrations were below 5 mg/Sm^3. “Rest” in Figure 3.6 and Figure 3.7 contains water, oxygen and others, e.g. heteroatoms attached to organic carbon.

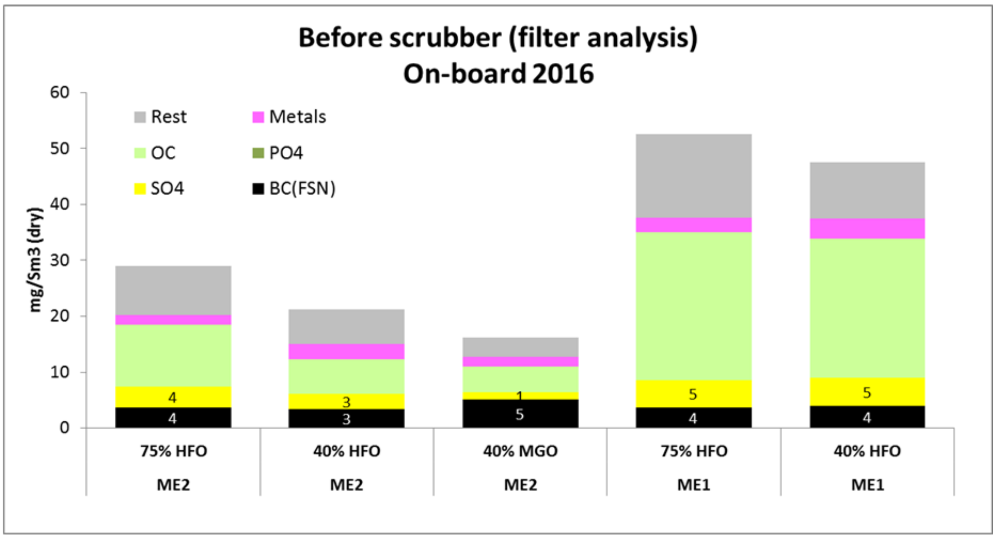


Figure 3.6. PM composition before the scrubber for all measurement points.

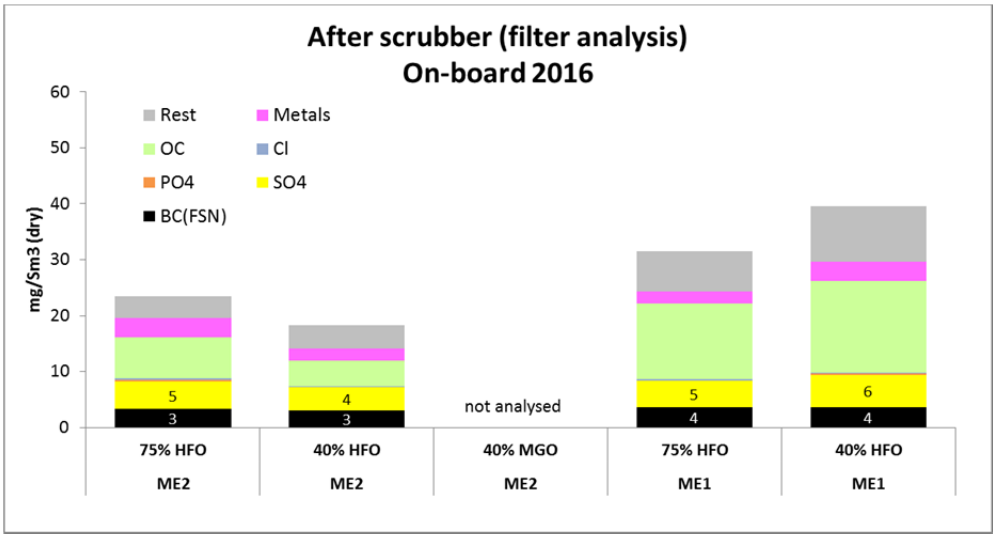


Figure 3.7. PM composition after the scrubber for all measurement points.

Organic compounds and other detailed chemical composition of submicron particulate matter (30-800 nm) was measured with the SP-AMS in real-time. Figures 3.8 and 3.9 shows the average composition of PM for each measurement point. For the ME1 engine, PM contained mostly hydrocarbons, nitrogen containing organic compounds and oxygenated compounds. Particularly low concentrations were observed for the MGO fuel.

In these figures the organic fraction is divided to its main constituents; hydrocarbons, oxidised hydrocarbons and organic compounds containing nitrogen. Following names are used in figures:

- CH=hydrocarbon CxHy
- CHO=fragment with composition CxHyO,
- CHOgt1= CxHyOz, where z is greater than 1,
- CHN=organic compound containing CxHyN,
- CHO1N= organic compound containing CxHyON,
- CHOgt1N= organic compound containing CxHyOzN where z is greater than 1.

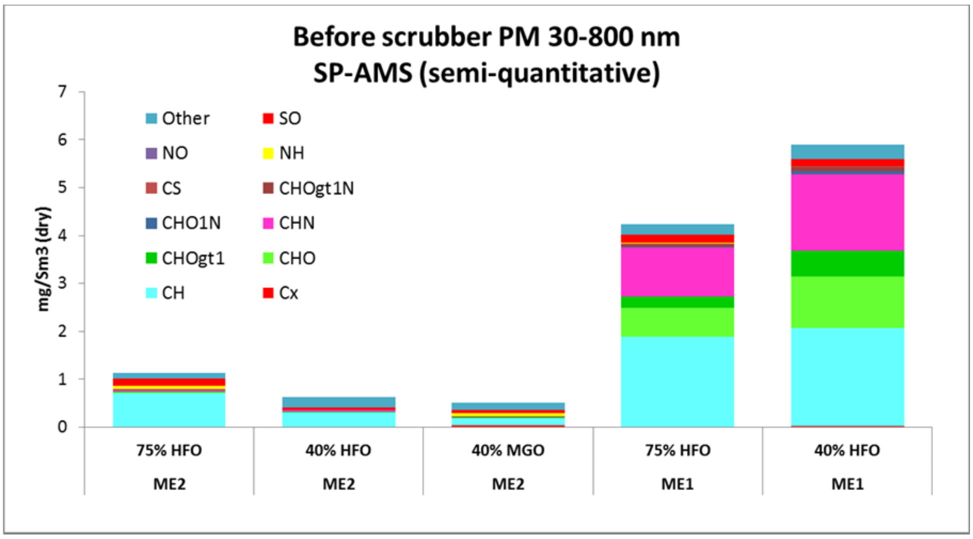


Figure 3.8. Average chemical composition of PM before the scrubber measured with the SP-AMS

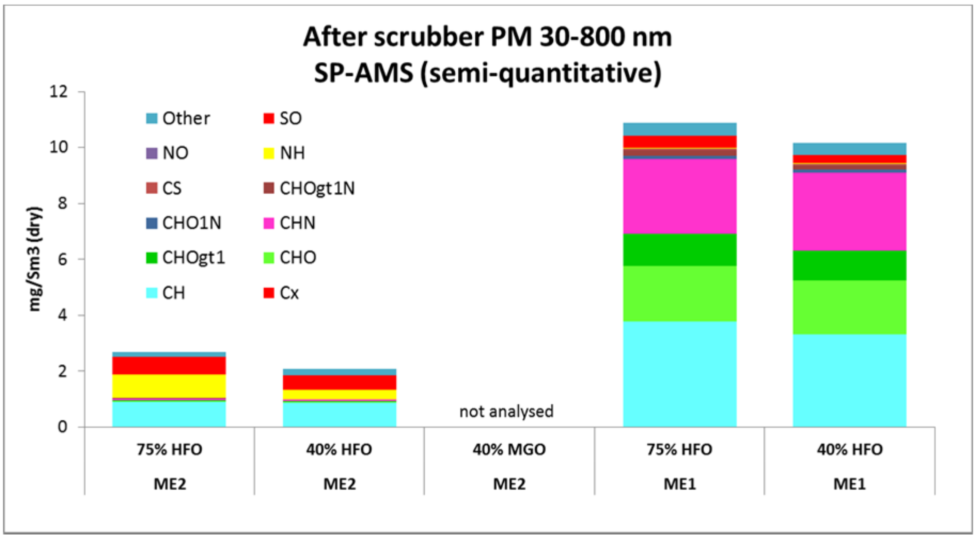


Figure 3.9. Average chemical composition of PM after the scrubber measured with the SP-AMS

<u>Metals</u>

Aluminium, vanadium, calcium, iron, potassium, sodium, nickel and thorium were present in the PM samples (Figure 3.10). Figure 3.11 represents the concentrations of individual metals observed before and after the scrubber.

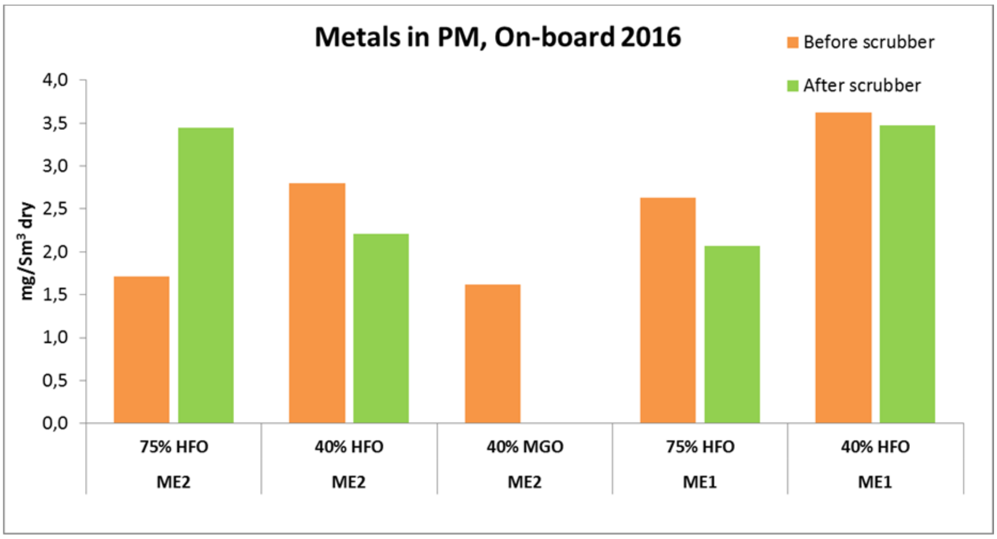


Figure 3.10. Sum of analysed metal and non-metal concentrations

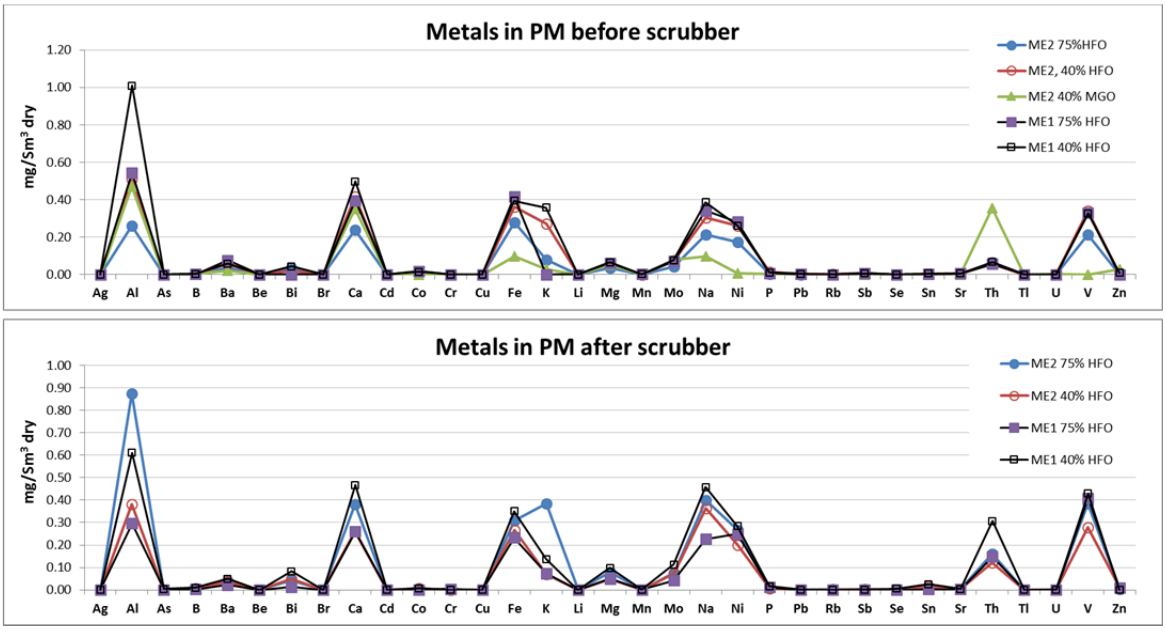


Figure 3.11. Observed elements before (top) and after the scrubber.

<u>Polyaromatic hydrocarbons (PAHs)</u>

Sum of the concentrations of six priority PAHs (benz[a]antracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and indeno[1,2,3-cd]pyrene) in PM washigher for the ME1 than for the ME2 engine, and higher before than after scrubber (Figure 3.12). This in an indication of capability of scrubber to reduce PAH emissions.

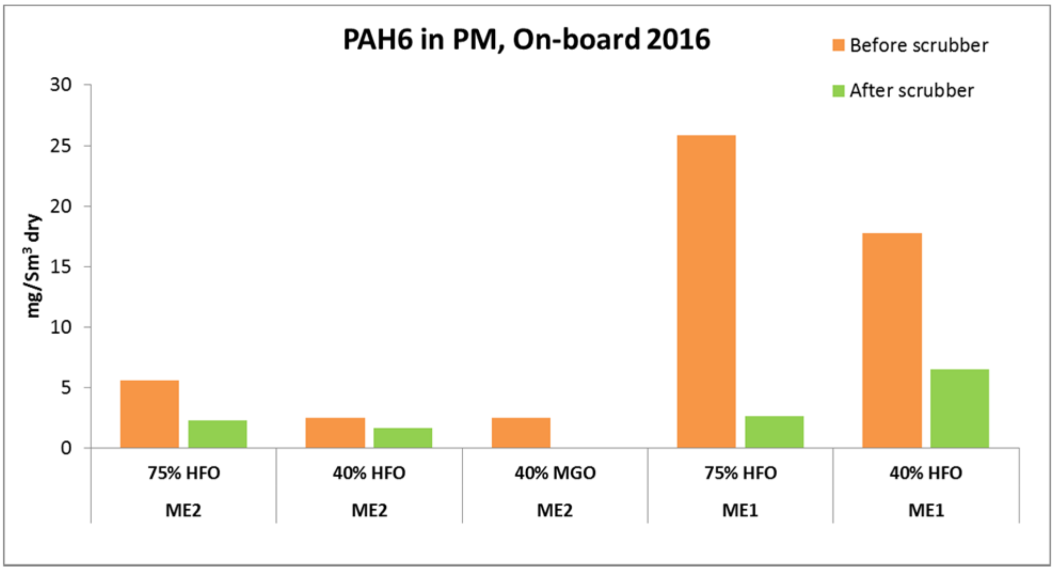


Figure 3.12 Sum of the concentrations of six priority PAHs (benz[a]antracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and indeno[1,2,3-cd]pyrene) in PM.*

Figure 3.13 represents the elements (wt%) concentrations in PM.

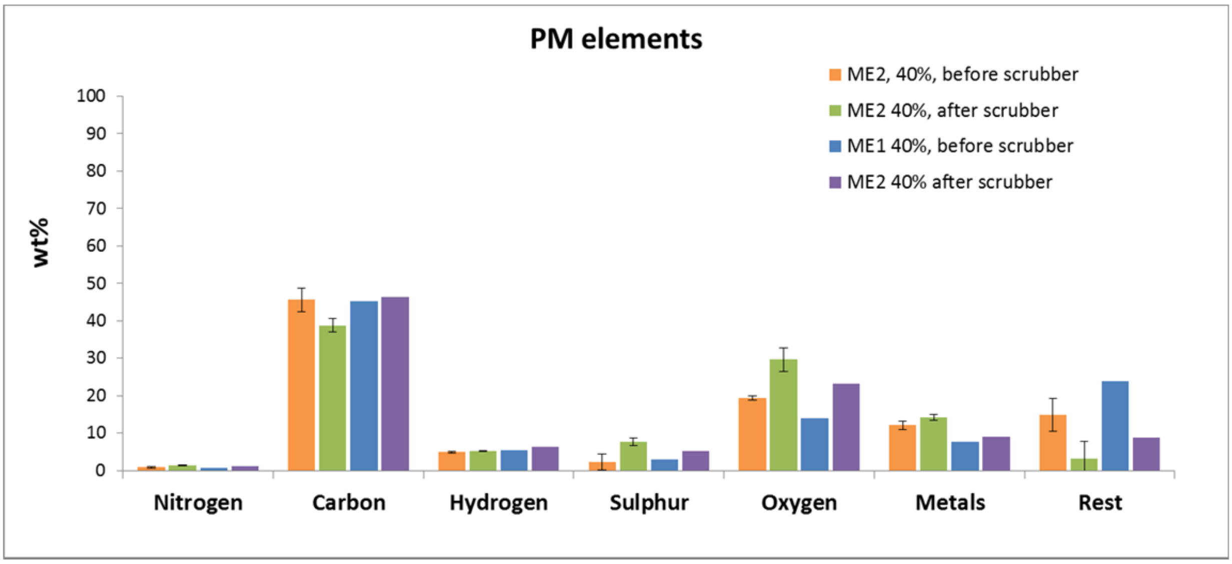
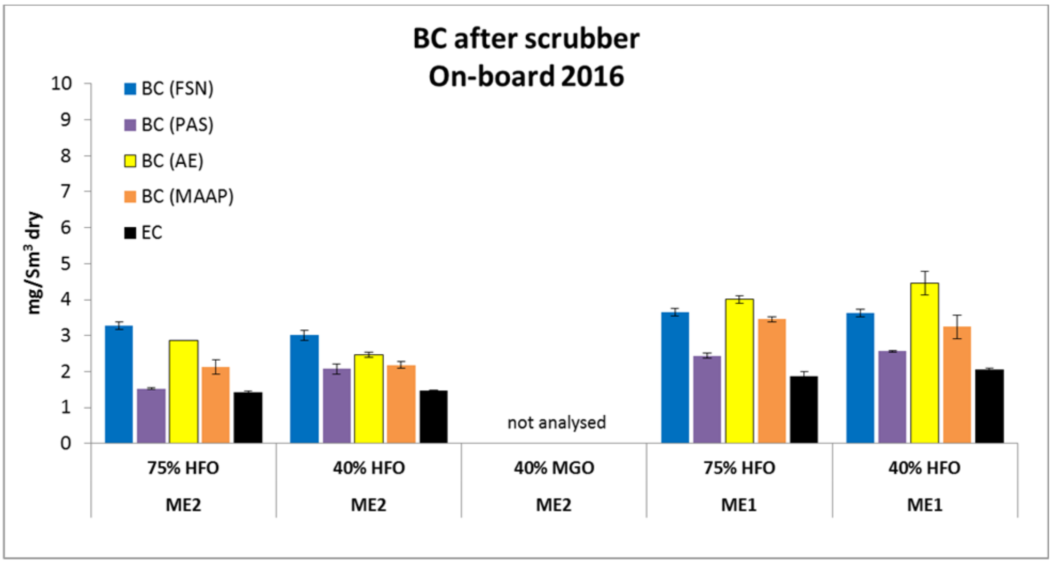


Figure 3.13. Elements (wt%) in PM.

3.6 BC

Black carbon concentrations were measured with multiple instruments (MAAP, AE33, 2xFSN, MSS) during the measurement campaign. Black carbon concentrations were low for both engines (Figure 3.14). Differences between the engine-out BC concentrations and the BC concentrations after the SCR for the ME2 and after the scrubber for both engines were small (Figure 3.15). These differences in the BC concentrations were deemed to be insignificant, particularly as the transfer line of the FSN instrument used for the engine-out BC measurements for ME2 engine was not heated, while the transfer line other the FSN instrument used before scrubber (engine-out for ME1) and after scrubber was heated.



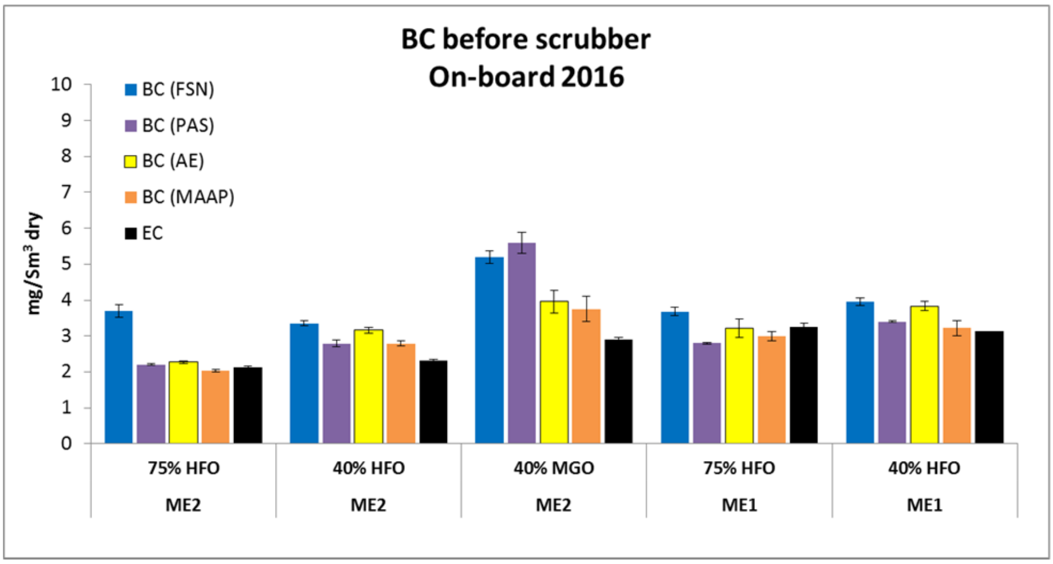


Figure 3.14. Black carbon concentrations measured before and after the scrubber.

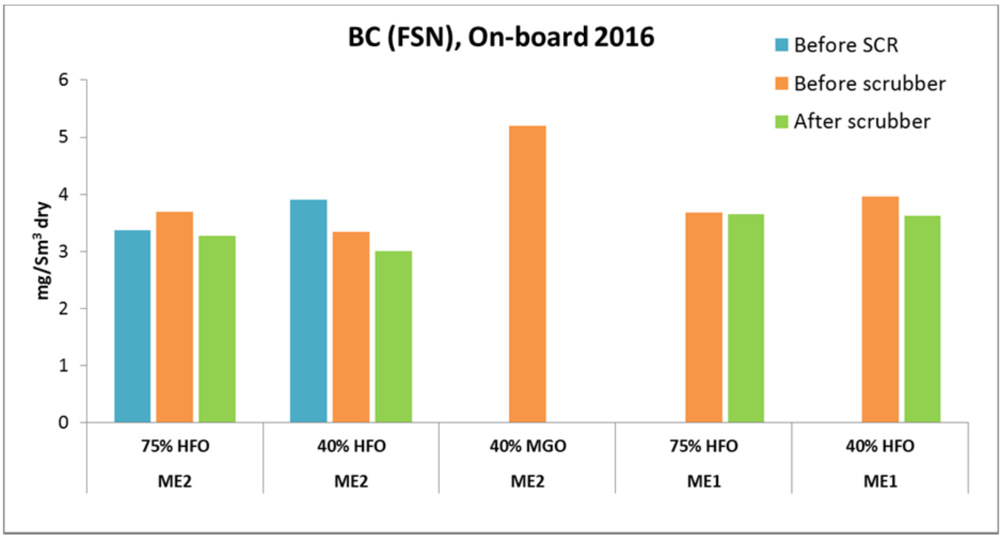


Figure 3.15 BC concentrations measured before SCR, before and after scrubber for ME1 and ME2 engines.

Black carbon concentrations were very low at all loads used, as Figure 3.16 includes many load changes and including also very low loads (20%). Even during engine adjustments and on measurement day 8 with MGO fuel, observed BC concentration constantly remained well below 7 mg m^3. This is really low BC concentration when compared with the BC concentrations from an old marine engine at low engine load of 25% in the WP1 laboratory measurements (up to 35 mg m^{-3}).

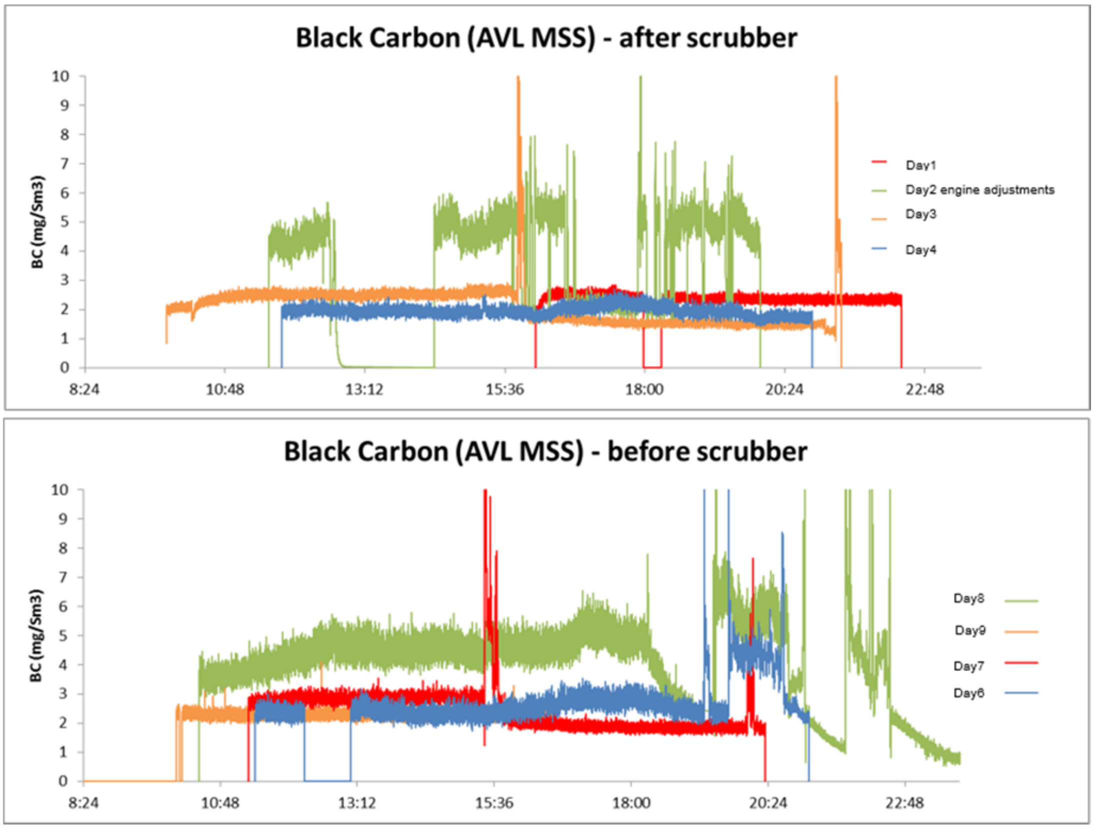


Figure 3.16. Time series of black carbon concentrations measured during real cruising conditions with large variations in load.

Figure 3.17 represents the EC and BC concentrations measured by individual instruments versus BC average (calculated from FSN, PAS, MAAP concentrations).

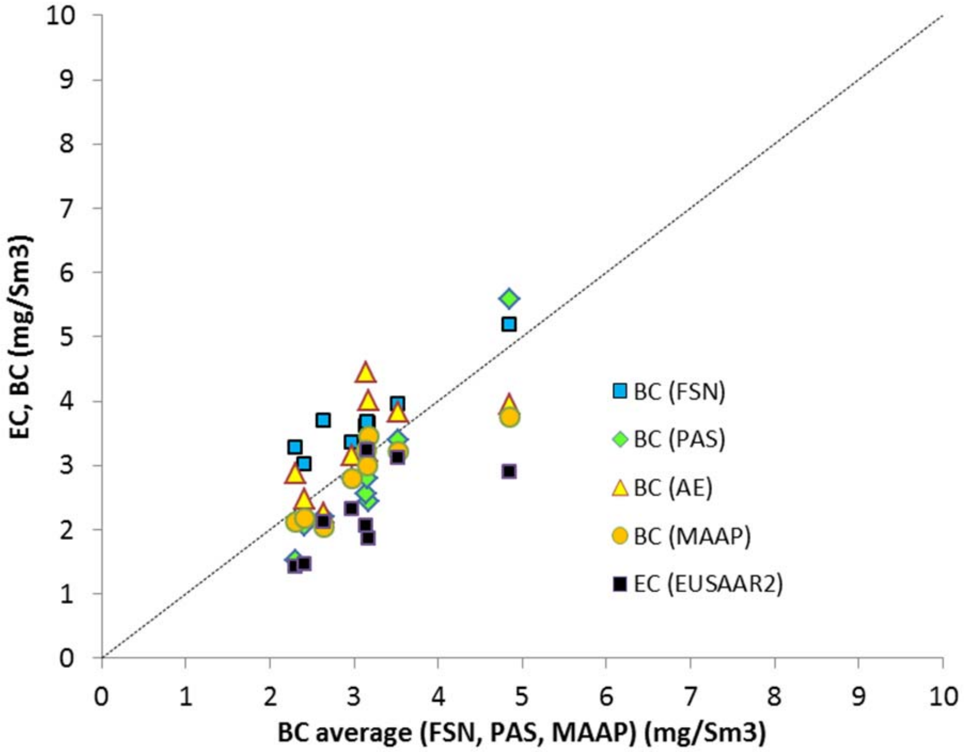


Figure 3.17 EC and BC concentrations measured by individual instruments versus average BC (calculated as a sum of FSN, PAS, MAAP results) concentration.

3.7 Particle number concentrations

Particle number concentrations were measured using a condensation particle counter (Airmodus A20) with a lower cut point at 7nm particle size. The CPC was positioned after PTD dilution setup and an additional bridge diluter was used to assure that concentrations were in the measurement range of the device. Particle number concentrations before scrubber were generally lower at higher engine load and when ME1 engine was used. Switching from HFO to MGO also reduced the particle number.

After scrubber, particle number concentrations were lower for the ME2 engine that is applying SCR, however, CPC data is missing for the ME1 40% HFO case (Figure 3.18). Overall, scrubber reduced the particle number concentrations by up to 90%.

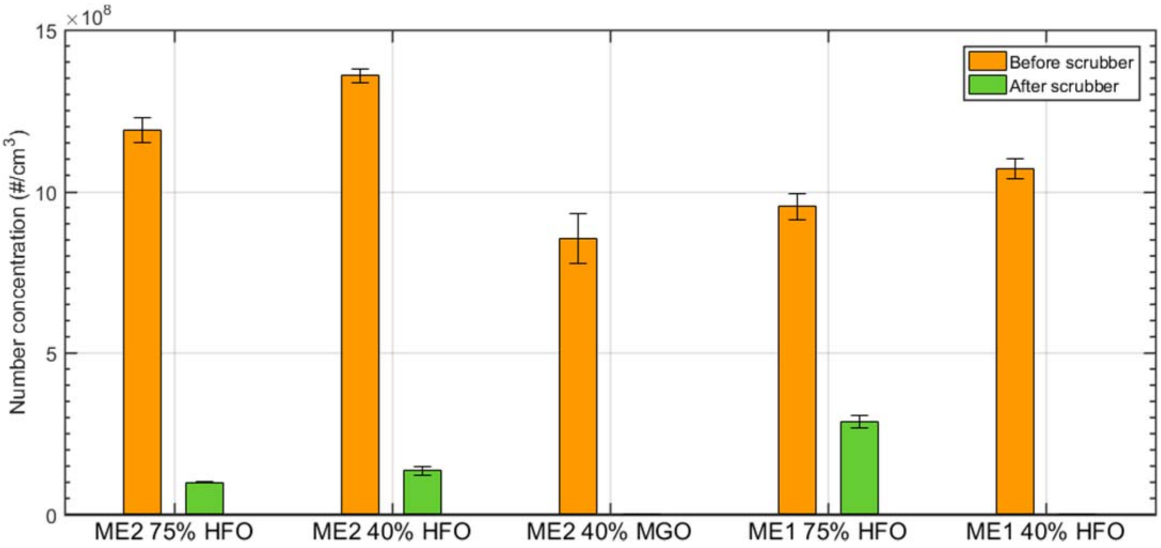


Figure 3.18 Particle number concentrations with CPC before and after scrubber for ME1 and ME2 engines.

3.8 Particle size distributions

Particle number size distributions were measured using scanning mobility particle sizers (SMPS and Nano-SMPS, TSI). Both SMPSs were measuring PM concentrations after PTD dilution that mimics atmospheric dilution and allows the formation and growth of particles by nucleation and condensation of volatile gases.

Diesel engines typically emit particles that can be seen in particle number size distribution as one, two or three separate modes. Soot mode particles consist of agglomerates that can have volatile condensates on them. In ship emission, nucleation mode particles can be typically seen in under 50 nm size, and they can consist of volatile compounds such as water, sulphur compounds and hydrocarbons, but also include fuel ash components or soot spherules (Kasper et al., 2007; Fridell et al., 2008).

In the measurements conducted before scrubber, the particle number size distributions consisted of three modes, which indicated three particle types. Peaks of these particle modes were typically seen around 20-40 nm, 60-80nm, and around 70-100 nm for soot particles. For MGO the two first particle modes were seen in smaller sizes, with peaks around 15 nm and 35 nm. The soot mode was best visible for measurements with MGO.

In the measurements after scrubber, the number size distributions included up to four modes (Figure 3.19-3.20). The particle number concentrations were generally lower after scrubber but the average particle diameter was shifted to larger size (Figure 3.21). The scrubber especially decreases the amount of particles seen in the mode around 20-30 nm in size. For ME1 the peak concentrations of particles in this mode were reduced to a level of 10^7 -10^8 #/cm^3 and for ME2 to a level of 10^6 -10^7 #/cm^3, when concentrations before scrubber were in order of 10^9 #/cm^3. This could indicate that the scrubber effectively removed particles of precursor gases that would form these particles during dilution.

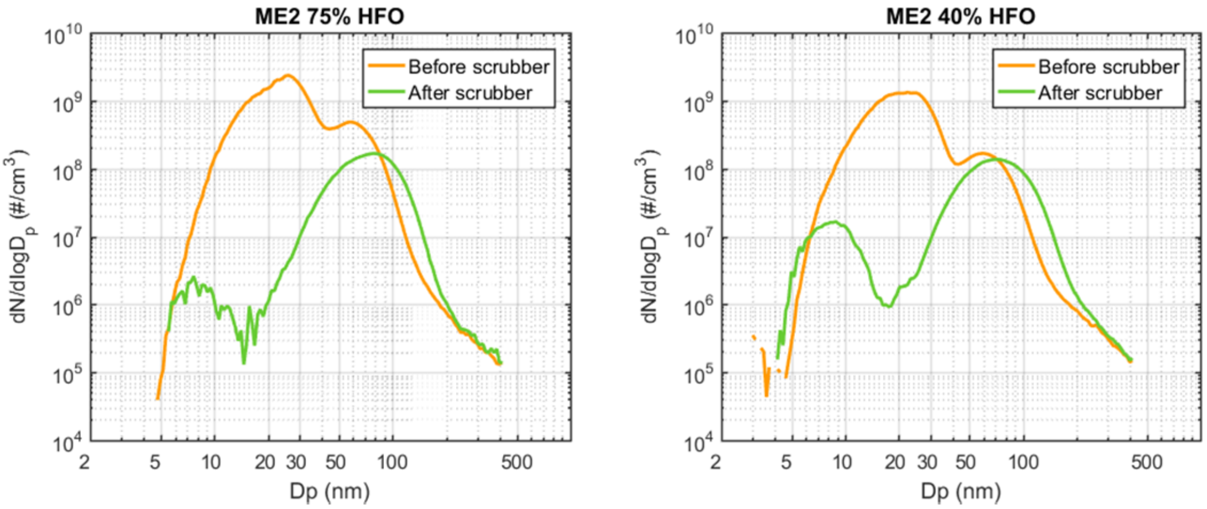


Figure 3.19 Particle number size distributions before and after scrubber for ME2 engine at 75% and 40% loads when using HFO.

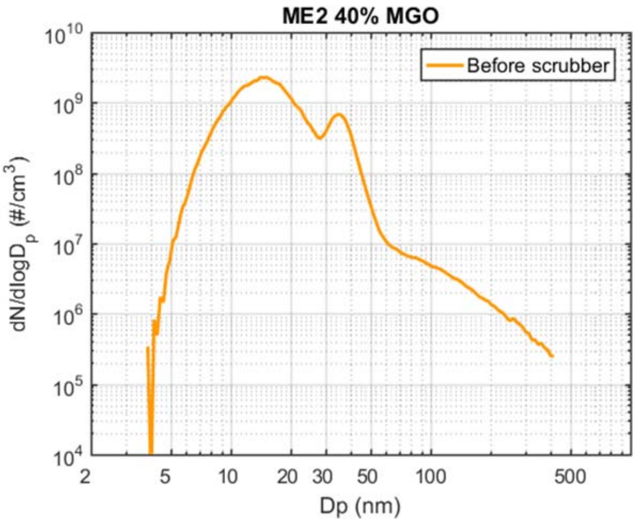


Figure 3.20 Particle number size distributions before for ME2 engine at 40% loads when using MGO.

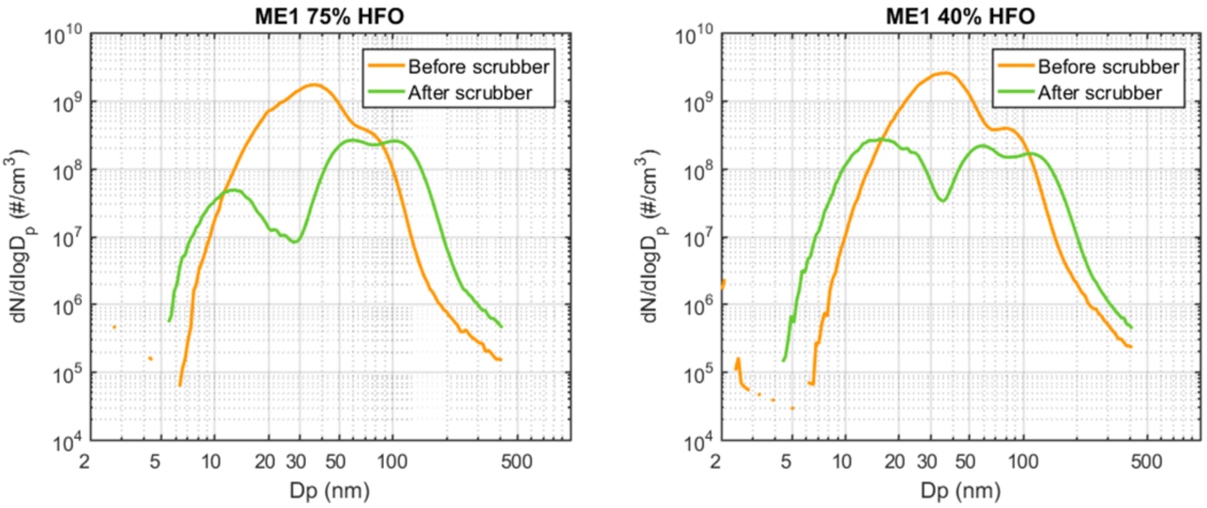


Figure 3.21 Particle number size distributions before and after scrubber for ME1 engine at 75% and 40% loads.

3.9 Particle morphology

The transmission electron microscopy (TEM) images showed three distinct particle types in the analysed samples (Figure 3.22). The samples were collected after thermal treatment at 350 °C and therefore the images only include non-volatile particulate matter.

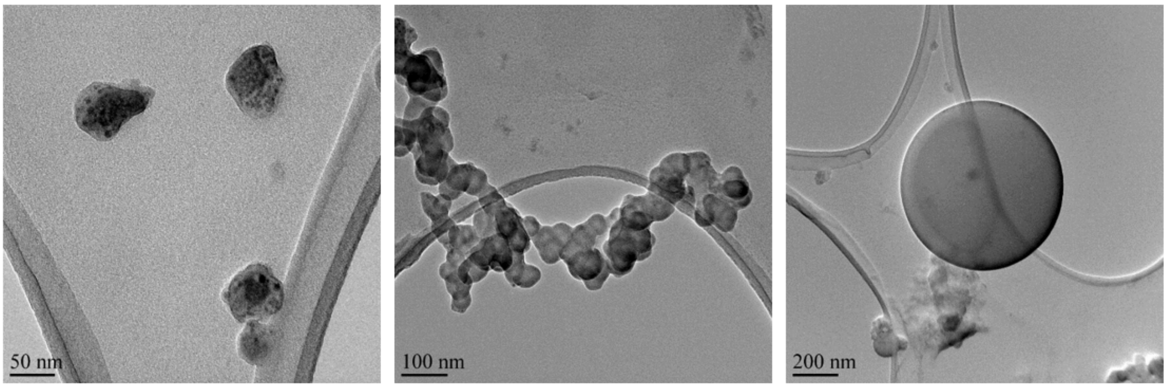


Figure 3.22 Examples of the three particle types detected from TEM analyses.

The first image on the left shows particles that were dominating in all samples collected during HFO operation. They are asymmetrical in shape and the sizes vary in 50-150 nm range. The particles seem to have smaller and denser spherical particles merged either inside or on top of them. According to the EDS analysis these particles included elements O, C, Si, S, Na, Al, Ca, V, Fe, Ni and Zn. These particles weren't observed in the MGO sample.

The middle figure shows a typical soot agglomerate that were found in all the samples. In the sample collected during MGO operation these soot particles were the dominant particle type. Elements O, C, Si and S were found in EDS analysis.

The rightmost image shows an example of the third particle type: spherical particles with diameters in the 500-600 nm range. The number of these particles was very low compared to the other particle types but they were found in at least four of the samples, with HFO operation and both before and after scrubber. Elements O, C, Si and S were analysed also from these particles. In some cases, these particles hade material similar to the first particles attached on top of them.

3.10 Comparison to WP1 results

Ship in WP2 represents modern technology and has new engines and after treatment systems. When compared to old marine engine used in WP1 where BC concentrations were up to 35 mg m^{-3}, the observed BC levels in this campaign were very low (BC < 5 mg m^{-3}) (Figure 3.23). Especially notable is that in WP1 the engine load had a clear influence to BC emissions. With 75% load BC concentrations were below 10 mg m^{-3}, whereas for 25% load concentrations were mostly ranging from 10 to 35 mg m^{-3}. In WP2 for modern engine this was not observed, as the BC concentration in the exhaust was fairly independent of the load.

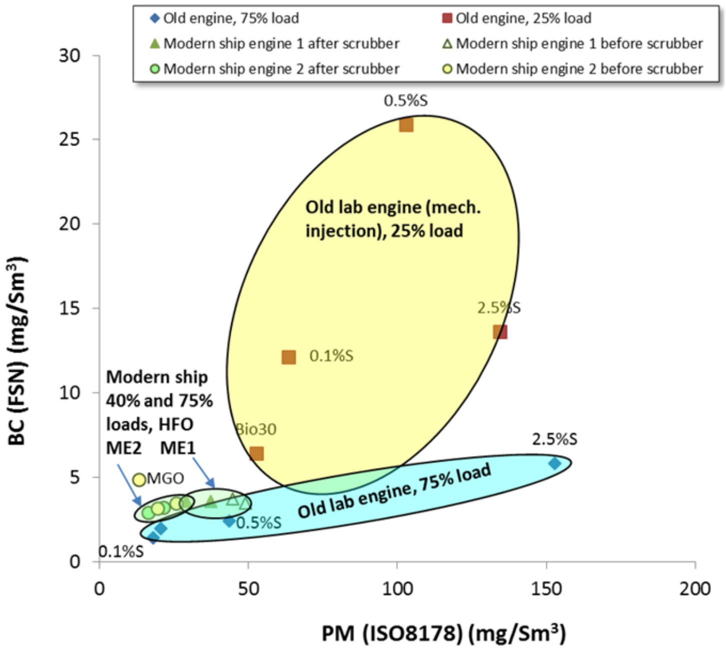


Figure 3.23. BC concentration measured for old engine (red, blue) and for new engine (green).

4 Conclusions

Overall, the onboard measurement campaign was a success. All instruments worked well, almost all intended measurements were accomplished and the campaign provided scientifically interesting results.

New engine, aftertreatment technology (Scrubber + SCR catalyst) and used lower sulphur (~0, 7% S) fuel dramatically reduced the particulate and gaseous exhaust emissions of a ship when compared to emissions of an old ship engine. Also, engine load was observed to have less influence to emissions for this newly build ship when compared to old ship engine emissions. The influence of scrubber or catalyst to BC emissions was observed to be small. Also, fuel had only a relatively small influence to BC emissions.

The main focus of this campaign was to test different BC measurement methods at onboard conditions. Although the results from different instruments were similar, the application of instruments designed for ambient measurements e.g. MAAP was challenging and required a high dilution ratio.

Acknowledgements

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APPENDIX 1

Average concentrations (mass per Sm^3 dry). ME1 after scrubber, ME2 after SCR and scrubber. HFO fuel.*

Component	Instrument/ standard	Unit	ME2 75% load	ME2 40% load	ME1 75% load	ME1 40% load
NOx		g/Sm3 (dry)	0,21	0,76	2,19	3,10
CO		g/Sm3 (dry)	0,10	0,14	0,07	0,10
CO2		g/Sm3 (dry)	114	98	119	104
O2 (dry)		vol%	12,8	14,2	12,9	13,7
H2O	FTIR	g/Sm3 (wet)	15,3	27,6	17,7	15,4
NO2	FTIR	mg/Sm3 dry	1,2	4,2	50,1	133,6
CH4	FTIR	mg/Sm3 dry	bd	bd	bd	bd
N2O	FTIR	mg/Sm3 dry	bd	bd	bd	bd
NH3	FTIR	mg/Sm3 dry	0,0	0,3	1,3	0,0
SO2	FTIR	mg/Sm3 dry	1,1	2,1	6,3	3,0
Formaldehyde	FTIR	mg/Sm3 dry	bd	bd	bd	bd
Acetaldehyde	FTIR	mg/Sm3 dry	bd	bd	bd	bd
PM	ISO 8178 (SPC)	mg/Sm3 dry	21,7	16,9	29,9	38,1
BC	AVL 415SE	mg/Sm3 dry	3,3	3,0	3,6	3,6
BC	AVL MSS	mg/Sm3 dry	1,5	2,1	2,4	2,6
BC	MAAP	mg/Sm3 dry	2,1	2,2	3,5	3,2
BC	AE33	mg/Sm3 dry	2,9	2,5	4,0	4,5
EC (EUSAAR2)	PM: ISO8178	mg/Sm3 dry	1,4	1,5	1,9	2,1
PM: SO4		mg/Sm3 dry	4,9	4,2	4,7	5,8
PM: NO3		mg/Sm3 dry	0,0	0,1	0,1	0,1
PM: PO4, Br, Cl, F		mg/Sm3 dry	0,8	0,2	0,4	0,4
PM: OC		mg/Sm3 dry	7,3	4,5	13,5	16,4
PM: metals		mg/Sm3 dry	3,4	2,2	2,1	3,5
PM: EC		mg/Sm3 dry	1,4	1,5	1,9	2,1
Rest of PM		mg/Sm3 dry	3,9	4,2	7,3	9,9
Ca		mg/Sm3 dry	0,38	0,26	0,26	0,47
Fe		mg/Sm3 dry	0,31	0,27	0,23	0,35
Mg		mg/Sm3 dry	0,08	0,05	0,05	0,10
Mo		mg/Sm3 dry	0,08	0,07	0,04	0,11
Na		mg/Sm3 dry	0,40	0,36	0,23	0,46
Ni		mg/Sm3 dry	0,27	0,20	0,25	0,28
P		mg/Sm3 dry	0,01	0,01	0,01	0,02
V		mg/Sm3 dry	0,38	0,28	0,41	0,43
benz(a)antracene*		µg/Sm3 dry	0,1	0,0	0,1	0,4
chrysene*		µg/Sm3 dry	1,7	1,2	1,7	4,2
benzo(b)fluoranthene*		µg/Sm3 dry	0,3	0,2	0,3	0,8
benzo(k)fluoranthene*		µg/Sm3 dry	0,2	0,2	0,2	0,5
benzo(a)pyrene*		µg/Sm3 dry	0,0	0,0	0,0	0,1
indeno(1,2,3-cd)pyrene*		µg/Sm3 dry	0,0	0,0	0,1	0,2
dibenz(a,h)antracene*		µg/Sm3 dry	0,1	0,0	0,1	0,4
PAH6		µg/Sm3 dry	2,3	1,7	2,6	6,5

* Before scrubber (ME1/HFO, ME1/MGO, ME2/HFO) and before SCR (ME2/HFO) in the Figures.

Average emissions (mass per kg oil equivalent). ME1 after scrubber, ME2 after SCR and scrubber. HFO fuel.*

Component	Instrument/ standard	Unit	ME2 75% load	ME2 40% load	ME1 75% load	ME1 40% load
NOx		g/kgoe	6,1	24,8	59,8	97,1
CO		g/kgoe	2,9	4,6	1,8	3,0
CO2		g/kgoe	3259	3199	3249	3255
O2 (dry)		vol%	12,8	14,2	12,9	13,7
H2O	FTIR	g/kgoe	428	892	483	477
NO2	FTIR	mg/kgoe	33	131	1349	4092
CH4	FTIR	mg/kgoe	bd	bd	bd	bd
N2O	FTIR	mg/kgoe	bd	bd	bd	bd
NH3	FTIR	mg/kgoe	1,3	8,5	35	0,0
SO2	FTIR	mg/kgoe	31	67	170	92
Formaldehyde	FTIR	mg/kgoe	bd	bd	bd	bd
Acetaldehyde	FTIR	mg/kgoe	bd	bd	bd	bd
PM	ISO 8178 (SPC)	mg/kgoe	624	552	815	1195
BC	AVL 415S	mg/kgoe	94	98	100	114
BC	AVL MSS	mg/kgoe	44	68	67	80
BC	MAAP	mg/kgoe	61	71	94	102
BC	AE33	mg/kgoe	82	81	109	140
EC (EUSAAR2)	PM: ISO8178	mg/kgoe	41	48	51	65
PM: SO4		mg/kgoe	141	138	127	181
PM: NO3		mg/kgoe	0,6	2,2	1,8	4,1
PM: PO4, Br, Cl, F		mg/kgoe	23	5,1	10	13
PM: OC		mg/kgoe	209	148	369	513
PM: metals		mg/kgoe	99	72	56	109
PM: EC		mg/kgoe	41	48	51	65
Rest of PM		mg/kgoe	111	138	199	311
Ca		mg/kgoe	10,9	8,5	7,1	14,7
Fe		mg/kgoe	8,8	8,7	6,3	11,0
Mg		mg/kgoe	2,2	1,6	1,4	3,1
Mo		mg/kgoe	2,2	2,4	1,1	3,5
Na		mg/kgoe	11,5	11,9	6,2	14,4
Ni		mg/kgoe	7,6	6,5	6,8	8,9
P		mg/kgoe	0,3	0,2	0,3	0,5
V		mg/kgoe	11,0	9,1	11,2	13,4
benz(a)antracene*		µg/kgoe	1,8	0,6	2,7	12,5
chrysene*		µg/kgoe	48,6	40,3	47,4	130,9
benzo(b)fluoranthene*		µg/kgoe	7,5	5,2	8,4	26,4
benzo(k)fluoranthene*		µg/kgoe	5,1	5,0	6,8	15,2
benzo(a)pyrene*		µg/kgoe	1,1	0,6	0,5	4,1
indeno(1,2,3-cd)pyrene*		µg/kgoe	1,1	0,2	1,7	5,2
dibenz(a,h)antracene*		µg/kgoe	1,8	0,6	2,7	12,5
PAH7		µg/kgoe	65	56	72	205

* Before scrubber (ME1/HFO, ME1/MGO, ME2/HFO) and before SCR (ME2/HFO) in the Figures.

Average emissions (mass per kWh). ME1 after scrubber, ME2 after SCR and scrubber. HFO fuel.*

Component	Instrument/ standard	Unit	ME2 75% load	ME2 40% load	ME1 75% load	ME1 40% load
NOx	ISO 8178	g/kWh	1,2	5,0	11,4	19,5
CO	ISO 8178	g/kWh	0,56	0,94	0,34	0,61
CO2	ISO 8178	g/kWh	627	650	620	653
vol%	ISO 8178	%	12,8	14,2	12,9	13,7
H2O	FTIR	g/kWh	84	178	93	97
NO2	FTIR	mg/kWh	6	26	260	831
CH4	FTIR	mg/kWh	bd	bd	bd	bd
N2O	FTIR	mg/kWh	bd	bd	bd	bd
NH3	FTIR	mg/kWh	0,2	1,7	6,7	0,0
SO2	FTIR	mg/kWh	6,1	13	33	19
Formaldehyde	FTIR	mg/kWh	bd	bd	bd	bd
Acetaldehyde	FTIR	mg/kWh	bd	bd	bd	bd
PM	ISO 8178 (SPC)	mg/kWh	120	112	156	240
BC	AVL 415S	mg/kWh	18	20	19	23
BC	AVL MSS	mg/kWh	8,4	14	13	16
BC	MAAP	mg/kWh	12	14	18	20
BC	AE33	mg/kWh	16	16	21	28
EC (EUSAAR2)	PM: ISO8178	mg/kWh	7,8	9,7	9,7	13
PM: SO4		mg/kWh	27	28	24	36
PM: NO3		mg/kWh	0,1	0,4	0,4	0,8
PM: PO4, Br, Cl, F		mg/kWh	4,3	1,0	1,9	2,5
PM: OC		mg/kWh	40	30	70	103
PM: metals		mg/kWh	19	15	11	22
PM: EC		mg/kWh	7,8	9,7	9,7	13
Rest of PM		mg/kWh	21	28	38	62
Ca		mg/kWh	2,1	1,7	1,4	2,9
Fe		mg/kWh	1,7	1,8	1,2	2,2
Mg		mg/kWh	0,4	0,3	0,3	0,6
Mo		mg/kWh	0,4	0,5	0,2	0,7
Na		mg/kWh	2,2	2,4	1,2	2,9
Ni		mg/kWh	1,5	1,3	1,3	1,8
P		mg/kWh	0,1	0,0	0,1	0,1
V		mg/kWh	2,1	1,8	2,1	2,7
benz(a)antracene*		µg/kWh	0,4	0,1	0,5	2,5
chrysene*		µg/kWh	9,3	8,2	9,0	26
benzo(b)fluoranthene*		µg/kWh	1,4	1,1	1,6	5,3
benzo(k)fluoranthene*		µg/kWh	1,0	1,0	1,3	3,0
benzo(a)pyrene*		µg/kWh	0,2	0,1	0,1	0,8
indeno(1,2,3-cd)pyrene*		µg/kWh	0,2	0,1	0,3	1,0
dibenz(a,h)antracene*		µg/kWh	0,4	0,1	0,5	2,5
PAH7		µg/kWh	13	11	14	41

* Before scrubber (ME1/HFO, ME1/MGO, ME2/HFO) and before SCR (ME2/HFO) in the Figures.