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Physical and chemical characterisation of PM emissions from two ships operating in European Emission Control Areas

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Abstract

Emissions of particulate matter (PM) from shipping contribute significantly to the anthropogenic burden of PM. The environmental effects of PM from shipping include negative impact on human health through increased concentrations of particles in many

- ⁵ coastal areas and harbour cities and the climate impact. The PM emitted by ship engines consists of organic carbon (OC), elemental or black carbon (EC/BC), sulphate, inorganic compounds containing V, Ni, Ca, Zn and other metals and associated water. The chemical composition and physical properties of PM vary with type of fuel burned, type of engine and engine operation mode. While primary PM emissions of species like
- ¹⁰ V, Ni and Ca are supposed to be determined by composition of fuel and lubricant oil, emissions of particulate OC, EC and sulphate are affected both by fuel quality and by operation mode of the engine.

In this paper a number of parameters describing emission factors (EFs) of gases and of particulate matter from ship engines were investigated during 2 on-board measure-

- ¹⁵ ment campaigns for 3 different engines and 3 different types of fuels. The measured EFs for PM mass were in the range 0.3 to 2.7 g/kg-fuel with lowest values for emissions from combustion of marine gas oil (MGO) and the highest for heavy fuel oil (HFO). Emission factors for particle numbers EF(PN) in the range 5×10^{15} – 1×10^{17} #/kg-fuel were found, the number concentration was dominated by particles in the ultrafine mode
- ²⁰ and ca. 2/3 of particles were non-volatile. The PM mass was dominated by particles in accumulation mode.

Main metal elements in case of HFO exhaust PM were V, Ni, Fe, Ca and Zn, in case of MGO Ca, Zn and P. V and Ni were typical tracers of HFO while Ca, Zn and P are tracers of the lubricant oil. EC makes up 10–38% of the PM mass, there were not found large differences between HFO and MGO fuels. EC and ash elements make up

found large differences between HFO and MGO fuels. EC and ash elements make up 23–40 % of the PM mass. Organic matter makes up 25–60 % of the PM. The measured EF(OC) were 0.59 ± 0.15 g/kg-fuel for HFO and 0.22 ± 0.01 g/kg-fuel for MGO. The measured EF(SO₄²⁻) were low, ca. 100–200 mg/kg-fuel for HFO with 1 % fuel sulphur



content (FSC), 70–85 mg/kg-fuel for HFO with 0.5 % FSC and 3–6 mg/kg-fuel for MGO. This corresponds to 0.2–0.7 % and 0.01–0.02 % of fuel S converted to PM sulphate for HFO and MGO, respectively.

The (scanning) transmission electron microscopy (TEM and STEM) images of the collected PM have shown three different types of particles: (1) soot composed mainly of C, O, sometimes N, and with traces of Si, S, V, Ca and Ni; (2) char and char-mineral particles composed of C, O, Ca and S (sometimes Si and Al) with traces of V and Ni and sometimes P and (3) amorphous, probably organic particles containing sulphur and some vanadium. The maps of elements obtained from STEM showed heterogeneous composition of primary soot particles with respect to the trace metals and sulphur. Composition of the char-mineral particles indicates that species like CaSO₄, CaO and/or CaCO₃, SiO₂ and/or Al₂SiO₅, V₂O₅ and Fe₃O₄ may be present; the last two were also confirmed by analyses of FTIR spectra of the PM samples.

The TPO of PM from the ship exhaust samples showed higher soot oxidation reactivity compared to automotive diesel soot, PM from the HFO exhaust is more reactive than PM from the MGO exhaust. This higher oxidation reactivity could be explained by high content of catalytically active contaminants; in particular in the HFO exhaust PM for which the energy-dispersive X-ray spectroscopy (EDXRF) analyses showed high content of V, Ni and S.

Oxidative potential measured as a rate of consumption of consumption of Dithiothreitol (DTT) was for the first time measured on PM from ship exhaust. The obtained values were between 0.01 and 0.04 nmol-DTT/min/µg-PM, quite similar to oxidative potentials of PM collected in urban and traffic sites.

The data obtained during the experiments add information on emission factors for ²⁵ both gaseous and PM-bound compounds from ship engines using different fuels and under different engine load conditions. Observed variability of the EFs illustrates uncertainties of these emission factors as a result of measurement uncertainties, influences from trace components of fuels and lubricants and from differences between individual engines.



1 Introduction

Emissions of particulate matter (PM) from shipping contribute significantly to the anthropogenic burden of PM on global, regional and urban scales, the last two mainly in coastal and harbour regions. The recent emission inventories indicate that on Eu-

- ⁵ ropean level international shipping in seas surrounding Europe emits over 20% of the EU-27 anthropogenic PM emission totals (www.emep.int). In many harbour cities the PM emissions from shipping make significant contribution to land-based sources (e.g. Snijder et al., 2008; Haeger-Eugensson et al., 2010; Hong Kong EPD, 2005). In addition to the primary emitted PM the gaseous emissions contribute to air pollution with secondary PM formed after being processed in the atmosphere. The environmental effects of PM from shipping include negative impact on human health through increased concentrations of particles in many coastal areas and harbour cities and the climate impact (Eyring et al., 2010 and references therein).
- The increasing both relative and absolute contributions of emissions from shipping to the anthropogenic emission burden and its negative environmental impacts have been recognised for some time (Endresen et al., 2003; Eyring et al., 2005; Corbett et al., 2007). The main gaseous species emitted by shipping are CO₂, NO_X and SO₂ (CO and volatile organic compounds, VOCs, are of minor importance). The reason for the high contribution of navigation to the emission totals is the fact that shipping emissions have been, in difference from the land sources, unregulated for a long time and only in
- have been, in difference from the land sources, unregulated for a long time and only in last few years regulation is gradually entering into force through Annex VI of the MAR-POL convention that was adopted by the Marine Environmental Protection Committee (MEPC) of the International Maritime Organisation (IMO). Annex VI which came into force in May 2005 (IMO, 2008) is targeting emissions of sulphur through maximum al-
- ²⁵ lowed fuel sulphur content (FSC) and to some extent emissions of NO_X. Emissions of PM are addressed only indirectly through decrease of formation of secondary PM from the reductions in SO₂ and NO_X. Regulations introduced by Annex VI will also impact emissions of the primary PM due to enforced improvements in fuel quality associated



with reduction of the fuel sulphur content and effect of engine improvements as well as installations of emission cleaning technologies. These effects are, however, very uncertain as only few measurements of PM mass and PM composition providing this information are available. MEPC has been recently discussing impact of black carbon

- (BC) on the Arctic, potentially considering future regulation in the region. While development of distinct exhaust aftertreatment systems for the reduction of PM emissions is well-progressed in automotive industry, maritime applications are rare. In order to set and in consequence meet limitations on particulate exhaust an extensive characterisation of such emission is essential.
- The PM emitted by ship engines consists of organic carbon (OC), elemental or black carbon (EC/BC), sulphate, inorganic compounds V, Ni, Ca, Zn and other metals and sulphate-associated water (Agrawal et al., 2008; Petzold et al., 2008; Moldanová et al., 2009). The chemical composition and physical properties of PM vary with type of fuel burned, type of engine and engine operation mode. While primary PM emissions of species like V, Ni and Ca are supposed to be determined by composition of fuel and lubricant oil, it has been shown that emissions of particulate OC, EC and sulphate are effected bath by fuel curling and by energine meda of the engine (Datable et al., 2010).

affected both by fuel quality and by operation mode of the engine (Petzold et al., 2010; Ristimaki et al., 2010).

Chemical and microphysical properties have also implications for the climate impact
 of shipping. BC is an important climate warming compound with both direct climate effect and indirect effect through decreased albedo of bright surfaces in Polar Regions. The BC emission factors for shipping have recently been reviewed by Lack et al. (2012) who found rather complex relations between BC emissions from heavy fuel oil (HFO) and marine distilled fuels showing often, but not always, decrease of BC emissions
 with improved fuel quality from HFO to distilled fuel. The chemical composition of PM affects also hygroscopic properties of the emitted particles and with that their ability to

form cloud condensation nuclei (CCN) and modify clouds (Lauer et al., 2007). In this study composition of PM and emission factors (FE) of different PM co

In this study composition of PM and emission factors (EF) of different PM compounds from several in-operation ship engines burning different marine fuels have



been investigated. The chemical characterisation of PM was complemented with transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) analyses and with investigation of the toxic properties of the PM. Further, oxidation reactivity of exhaust particles has been investigated with temperatureprogrammed oxidation (TPO), information especially needed for design of particulate mass reducing units.

2 Methods

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2.1 The measurement campaigns

Two measurement campaigns were performed within EU FP7 project TRANSPHORM, the second was joined with a research project funded by SIVL and Stena AB. The 10 first measurement campaign was performed on a RoRo/cassette carrier ship in October 2010. The ship was travelling in the Baltic Sea. The measurements were performed on a 4-stroke diesel main engine (ME) Wärtsilä Vasa 12V32D with a maximum rated power (MRP) of 4440 kW and a nominal engine speed of 750 rpm and on a Wärtsilä auxiliary engine (AE) with a MRP of 870 kW. The exhaust compounds were probed for 15 the ME at engine loads of 80 and 30% of MRP, and for the AE at 47% of MRP. The engine load and fuel consumption were measured manually with help of the fuel rack and a fuel flow meter. Both parameters were stable during the measurements. Data on technical parameters and engine operation conditions are presented in Tables S1 and S2 in the Supplement. During the campaign the main engine was burning heavy 20 fuel oil (HFO) with $\sim 1 \text{ wt\%}$ fuel sulphur content (FSC) and the auxiliary engine ma-

rine gas oil (MGO) with FSC of ~0.1 wt%. Fuel and lubricant from ME and fuel from AE were analysed for elemental composition, density and other parameters by DNV Petroleum Services. Results of these analyses are summarized in Table S3 in the Supplement. Throughout this report, the different measurements will be abbreviated as



with heated cleaned air (primary dilution) and thereafter with non-heated cleaned air

The measurements were carried out on exhaust that was extracted from the exhaust channel with an isokinetic probe. The probe was connected to a Dekati Fine Particle Sampler (FPS-4000) system. In the FPS system, the warm exhaust was first diluted

- (ejector dilution). The temperature of the sampled gas was monitored after the heated dilution (temperature T1) and in the outlet of the FPS (T2). For sampling of PM mass and composition, PM_{2.5} and PM₁₀ cyclones (Apex Instruments) followed by filter holders, vacuum pumps and gas meters were connected to the FPS system (Fig. S1).
- Dilution ratios were monitored by FPS and by parallel measurement of NO_x in the ex-25 haust channel and after the FPS instrument. Dilution ratios during the filter sampling were 15-20. The dilution ratios and T1 and T2 temperatures for all experiments are presented in Table 1.



S1_HFO1%_ME-full (ME at engine load 80%), S1_HFO1%_ME-low (ME at engine load 30 %) and S1_MGO_AE (AE at engine load 47 %).

The second measurement campaign was performed on a cargo/passenger ferry on line traffic between Sweden and Germany in March-April 2010. Basic information ⁵ about the ship is provided in Table S1 in the Supplement. The ship machinery comprised four 4-stroke diesel engines, Sulzer 8ZAL40S, with a MRP of 6000 kW each and a nominal engine speed of 510 rpm. All measurements were performed on one of the engines. The measurements were completed on an engine operating on 57% engine

- load. The engine load was monitored continuously through the scavenge air pressure. The fuel consumption was calculated from the engine trial report data provided by the 10 engine producer. During the campaign three different fuels were tested: HFO with S content 1 wt%, HFO with S content 0.5 wt% and MGO (FSC ~ 0.1 wt%). For further engine and fuel details, see Tables S2 and S3, respectively. The different measurements from this vessel will be abbreviated as S2_HFO1%_ME-full (ME at engine load 57%). S2 HF00.5% ME-full and S2 MGO ME-full.

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2.2 Sampling conditions and online measurements

For measurements of particle number concentrations (PN) and particle size distributions online instruments were used. Particles in a size range of 5.6–560 nm were monitored with an EEPS (Engine Exhaust Particle Sizer, Model 3090, TSI Inc.). The EEPS measures particles in this size range in 32 channels, 1-s time resolution mode ⁵ was used in this study. Before the EEPS the sample flow optionally passed through a thermodenuder (TD, Dekati) to measure the ratio of volatile to non-volatile particles. Particles in the size range > 300 nm were measured with aerosol spectrometer GRIMM 1–108 that detects particles in the size range 300 nm–20 µm with 1-s time resolution in 15 size channels. The 2 aerosol instruments were coupled in parallel after the secondary dilution (Dekati Axial Diluter, DAD-100) and Dekati thermodenuder ELA 423, if used (Fig. S2). Different dilution conditions during sampling with the online instruments were tested with dilution ratios between 300 and 800.

Concentrations of a number of gas constitutes were measured continuously in the hot exhaust. Nitrogen oxides (Horiba PG-250 chemiluminescence instrument), carbon monoxide and carbon dioxide (Horiba PG-250 NDIR), oxygen (Horiba PG-250 galvanic cell), total hydrocarbons (Bernath Atomic BA 3006 FID), and sulphur dioxide (Horiba PG-250 NDIR) were monitored.

The temperature and humidity of the engine inlet air were monitored. The exhaust gas flow was measured with a pitot tube during each sampling experiment. The exhaust temperature was measured several times during each sampling period. Further details on the gas measurement methodologies can be found in Cooper (2001, 2003).

2.3 PM filter analyses

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Several sets of filter samples were collected during the campaigns. Table 1 summarizes filter samples and analyses performed at different laboratories. The goal of the sampling was to obtain the emission factors for the following PM parameters: PM mass, Elemental carbon (EC), Black Carbon (BC), Organic Carbon (OC), elemental composition and ionic composition. These emission factors further distinguish between EFs for total suspended particulate matter (TSP), PM₁₀ and PM_{2.5} or PM₁. Additional analyses



for oxidative potential, microphysical and chemical characterisation and for oxidation reactivity by TPO were performed.

Some analyses were done by several techniques or at several laboratories to address uncertainties of the analyses. BC/EC was analysed as EC with Sunset technique and also as BC by 2 optical methods using transmissometer and reflectometer.

In this way some uncertainties of both methods were addressed. Elemental composition was analysed by energy dispersive X-ray fluorescence (EDXRF) and supported by ion chromatography.

For all analyses, multiple samples were taken for at least one experiment and one PM metric. The sampling matrix is not full for all analyses due to the time and budget constraints of the measurement campaigns. More details of individual analyses are given further down in this chapter.

For *gravimetric analyses* a Mettler Toledo model MT5 balance was used. The balance was calibrated to an uncertainty limit of $\pm 3 \,\mu g$ in the range 0–10 000 μg and $\pm 7 \,\mu g$ in the range 10 000–100 000 μg . The gravimetric analyses were performed with PTFE Mitex membrane filters.

15

The *analysis of EC/OC* is based on the thermal optical method as described in the American Standard Method NIOSH 5040 (NIOSH 2003). The EUSAAR 2 protocol (Cavalli et al., 2010) was used for the temperature settings. A 1 cm² piece of the sample taken on quartz fibre filters was used for the measurement. OC is removed from the filter in the temperature range of 200–650 °C in a non-oxidising carrier gas (helium). EC is then removed in the temperature range of 500–850 °C making use of a mixture of helium and oxygen. The originated CO₂ is then converted to methane and detected by flame ionisation detection (FID). Correction for pyrolysis is carried out by

measurement of light transmission. Quantification takes place based on a gas mixture of 5 % methane in helium. Sucrose is used as a control standard. The total uncertainty of the method amounts 31 %.

For *analyses of black carbon (BC)* a Soot Scan Transmissometer Model OT21 (Magee Scientific, Berkeley, USA) was used. Attenuation of light of two wavelengths,



880 and 370 nm, passing the examined filter sample is measured and compared with attenuation by a blank filter. The detected attenuation of IR-light (880 nm) comes from absorption and scattering of PM and is proportional to the surface density of BC mass on the filter with a factor σ (absorption cross section). The absorption cross section is

- ⁵ dependent of the filter material and also type of the PM analysed. In this study σ = 12.6 has been used. This σ has been developed by US EPA for ambient urban air BC samples from Improve network taken on PTFE membrane filters similar to those used in our study. Attenuation in wavelength 370 nm has not been evaluated as the OC obtained from this measurement is only indicative.
- BC has been also analysed with reflectometer of the type Smokestain EEL M43D. In the reflectometer a white light source is placed on top of the filter. The light passes through the filter and thereafter reflects back through the filter to a detector. On the double pass-way through the filter, light is absorbed by all black constituents on the filter. The amount of light that is detected after the double pass through the filter is compared with a blank filter of the same type which is set to 100% reflection. The absorbed light can be converted to BC given in μg m⁻³ (Quincey, 2007; Butterfield et al., 2010). Detection limit of 13 ng cm⁻² of filter area was determined by analysis of blank polycarbonate membrane filters at University of Gothenburg (Pettersson et al.,
- 2011).
 The PM deposits on PTFE Mitex membrane filters were analysed with *ion chromatography (IC)*. The filters were first extracted in an ultrasonic bath with Milli-Q water and the extracts were analysed on Dionex anion chromatograph for sulphate (SO₄²⁻) and on Dionex cation chromatograph for sodium (Na⁺), potassium (K⁺), magnesium (Mg²⁺) and calcium (Ca²⁺). The sample was driven through an anion exchange column together with a carbonate eluent for analysis of anions and through a cation exchange
- together with a carbonate eluent for analysis of anions and through a cation exchange column together with a methylsulphonic acid eluent for analysis of cations. In the ion exchange columns the ions are separated, conductivity of the eluent is reduced with a suppressor and afterward the ions are detected with a conductivity detector.



The sampled PM deposits on PTFE Mitex membrane filters were analysed with *Energy Dispersive X-ray Fluorescence (EDXRF)* to obtain concentrations of the trace elements in the PM. XRF is a non-destructive method analysing elements from Si to U in atomic weight. For experiments S1 the XRF analyses were performed at the Department of Chemistry, University of Gothenburg with a laboratory-built EDXRF, the samples from the S2 experiments were analysed at Cooper Environmental Services L.L.C., US as the GU instrument was not available at that time. Some samples from the S1 campaign were analysed also at Cooper Environmental Services L.L.C. to get intercomparison of results from the 2 laboratories. Agreement between the 2 labs was good considering that different filter samples taken during the respective experiments were compared (see Fig. 9 in Results and discussion part).

Analyses at University of Gothenburg were made with a voltage of 50 kV and a current of 25 mA applied to the silver X-ray tube and spectra were collected for 1000 s. The data from the XRF analyses were processed and quantified with the Quantita-

- tive X-ray Analysis System (QXAS) software developed by the Atomic Energy Agency (IAEA), Vienna, Austria. For quantification of the detected elements a calibration file was needed. The calibration file was created from single element standards during previous XRF sample analyses at the University of Gothenburg (Molnár et al., 2006). Detection limits were determined by analysis of blank membrane filters (Boman et al., 2006).
- ²⁰ 2009). They depend on the element under analysis and vary between 0.60 ng cm⁻² and 90 ng cm⁻² of filter area for the elements.

Analyses performed at Cooper Environmental Services L.L.C., US were done on Quanx EDX-771 energy dispersive X-ray spectrometer with a 200 Watt rhodium target tube as an excitation source. The machine operation, data acquisition and spectral processing were handled by Kevex's software. Analyses followed EPA compendium IO 3.3 (US EPA, 1999).

25

For measurement of *oxidative potential* samples taken on PTFE membrane filters as well as pieces of the quartz fibre filters were used. The samples were tested with the dithiothreitol (DTT) assay based on the method described by Cho et al. (2005). Earlier



studies showed the correlation between DTT results and EC, OC and PAH's (Cho et al., 2005; Jeng, 2010; Li et al., 2003). First the filters were extracted with ethanol for 90 minutes in ultrasonic bath. Further, the extracts were dried and re-dissolved in 100 μ L ethanol and 900 μ L Milli-Q water. The PM mass in the suspension obtained from PTFE

- ⁵ filters was determined by weighing the filters before and after extraction in a conditioned weighing room. Quartz filters' extracts were filtered in order to remove quartz fibres which interfere with DTT measurement. As a result quartz filters' extracts contain only extractable fraction of collected PM. To calculate DTT results per PM mass the total PM mass sampled on quartz filter is used. While the results are compared, mea-
- ¹⁰ surements on PTFE filters are higher than DTT measured on quartz filters. This is due to the different extraction procedure and lower extraction efficiency for the quartz filters. The outcome is in line with results published by Yang et al. (2013). 100 μ L of the sample extract with known concentration of PM was incubated with 200 μ L of 0.5 mM DTT in 0.1 M potassium phosphate buffer (pH 7.4) at 37 °C. The incubation time for the assay
- ¹⁵ was 0, 10, 20, 30, 40, 50 min. After the incubation time 300 µL of 10 % trichloroacetic acid was added. Next, 1 mL of 0.4 M Tris-HCl, pH 8.9, with 20 mM EDTA was mixed with 0.5 mL of the incubation mixture. Finally 30 µl of 10 mM DTNB was added. Absorption of the formed 5-mercapto-2-nitrobenzoic acid was measured at 412 nm by spectrophotometry. The soot sample was used as a quality control. All results were corrected with
- DTT depletion rate of blanks, where instead of PM suspension Milli-Q water was used. Three Milli-Q blanks were measured for each set of measurements. Coefficient of variance of Milli-Q blank analyses was 1 %. The expanded uncertainty of the method is 35%. In addition 3 PTFE filter and 2 quartz filter field blanks were analysed. Average DTT depletion rate of the PTFE filter field blanks was 18% higher and of the quartz
 filter field blanks was 2% higher than the Milli-Q blanks.

Microphysical and chemical analyses of PM samples were performed using several microscopic techniques. Special devices, each holding 4 Cu microgrids with amorphous carbon holey film for electron microscopy and a Ge window for Fourier transform infrared spectroscopy (FTIR) were prepared. The transmission electron microscope



(TEM) analyses of the samples collected on carbon holey film were done on TEM Philips CM20 FEG (CEMES, Toulouse) working at accelerating voltage 200 kV in transmission bright field mode and in scanning transmission mode (Scanning Transmission Electron Microscopy, STEM). Other pictures were taken on the TEM JEOL JEM 3010

- ⁵ microscope (CINaM, Marseilles). Elemental composition was obtained by EDS (Bruker AXS Microanalysis "Quantax") coupled to the TEM Philips CM20 FEG. Elemental analysis in STEM mode allows us to create maps of the distribution of each element presented in the sample. In the TEM mode the elemental composition is obtained from the whole selected area.
- ¹⁰ The chemical nature of the particles was studied by FTIR. Spectra were measured at 4 cm⁻¹ resolution using a Bruker Equinox 55 FTIR spectrometer (CINaM, Marseilles) equipped with a deuterated triglycine sulfate (DTGS) detector. For this analysis, Ge windows were exposed to the diluted exhaust in a similar way as filters for other PM analyses. The spectra were also measured on a bulk soot powder collected on a metal
- ¹⁵ sampling probe placed inside the exhaust duct during the entire PM sampling period. Prior to the analysis the powder was deposited directly on a bare Ge window without dilution into a solvent. Transmission spectra were recorded by averaging 400 scans in a typical wave number range from 4000 to 400 cm⁻¹.

Raman spectra were taken on XploRA Raman Microscope (Horiba Jobin Yvon, CEMES, Toulouse) with an excitation wavelength of 532 nm. The objective of ×100 and the grating of 1800 lines per mm were used. Spectra were taken at several areas of the sample and each spectrum is accumulated for 30 s. The sample consists of PM collected on a sampling probe stacked into the exhaust channel of the investigated main engine on S1 and covers both S1_HFO1%_MEfull and S1_HFO1%_MElow. The collected powder was placed on the glass slide without any solvent in order to avoid its

influence on the Raman spectra. PM collected on guartz fibre filters was investigated by *temperature-programmed ox-*

idation (TPO). A diesel exhaust after-treatment model system (Messerer et al., 2006; Schmid et al., 2011) was used for oxidation of the soot samples in the temperature



range from 100 to 700 °C. A total gas flow of 3.0 Lmin^{-1} of nitrogen including 5 % of oxygen was streamed through the filter. The temperature of the gas was raised at a rate of 5 K min⁻¹. Adjustment and control of the gas temperature were carried out using a type K thermocouple (HKMTSS-150, Newport Omega, Germany) placed in an immediate proximity of the filter surface. Combustion products CO and CO₂ were analysed by FTIR spectroscopy (FTIR spectrometer IFS 66/s, Bruker, Germany) equipped with a 2-L gas flow cell with an optical path length of 6.4 m. Before the experiments, the filters were pre-treated at 150 °C under air for 30 min to remove residual water that would interfere with the FTIR analysis.

10 3 Results and discussion

3.1 Emissions of gas phase species and PM mass

The emission factors for the measured gas phase species and for PM mass obtained from gravimetry analyses of PTFE filters during the 6 experiments are shown in Table 2. The actual measured NO_X emission factors are shown together with EF(NO_X) corrected for ambient conditions (humidity and temperature) as in ISO 8178-1 1996 clause 13.3 and with the maximum allowed EF(NO_X) for the engine calculated according to the TIER I NO_X emission standard. A comparison of these two shows that the measured EFs were 16–35 % lower on investigated MEs and ~ 7 % higher on the AE (S1_MGO_AE) than the TIER I standard maximum emission factors (Fig. S3 in the Supplement). Ship S1 is a pre-TIER ship while S2 is of TIER I standard. For S1 there is almost no difference between EF(NO_X) at full load of the engine and at low (30 %) load. In data from S2 one can see a decrease of EF(NO_X) when HFO fuel is changed to MGO which is in agreement with a report of EC and ENTEC UK Limited (2002).

The EFs for SO₂ are presented both as measured and as calculated from the ²⁵ fuel S content. For S1 experiments the measured $EF(SO_2)$ were ~5% lower than the calculated, the differences between measured and calculated $EF(SO_2)$ in the S2



experiments were -20 - -30 % (~ 4 g kg⁻¹ fuel for HFO in absolute numbers) for the 3 fuels tested. The observed sulphate in particulate phase corresponded to less than 1 % of fuel S and could not explain the discrepancy in the S2 experiment. This large discrepancy between the measured and calculated EF(SO₂) persists also when ratios of

- SO₂ and CO₂ concentrations in the exhaust are compared to ratios of S and C content in the fuel (adjusted for molar weight differences) eliminating possible uncertainties in fuel consumption. Uncertainties of the fuel S and C analyses are for S 9, 11 and 20 % for fuel S content of 1, 0.5 and 0.1 %, respectively, and for C is 3 % (Table S3). Combination of these uncertainties gives maximum uncertainties for the S/C ratio of ± 12,
- ¹⁰ \pm 13 and \pm 20% for fuels with FSC 1, 0.5 and 0.1%, respectively. Uncertainties of the exhaust measurements are \pm 2% for both CO₂ and SO₂, i.e. much smaller. Assuming all these uncertainties we can conclude that the difference between the measured and calculated EF(SO₂) is larger and systematically negative to be explained with the analytical uncertainties. Large differences between the measured and calculated EF(SO₂)
- ¹⁵ were found on the same ship during earlier measurement campaign coordinated by JRC (Hjorth, personal communication) and also in measurements on other ships. This issue has been a subject of scientific discussion during the past 2 yr. While the fuel separators remove mainly water and mineral particles, not largely affecting the S content, some S could be lost in the engine in reaction with lubricant Ca additive followed
- ²⁰ by removal of the solid reaction product (CaSO₄) to the lubricant sludge tank. A rough estimate of lubricant needed to react with 10% of the fuel S based on measured lubricant Ca concentration and assumption of 100% reaction efficiency gives lubricant consumption needed ~ 100 kg h⁻¹, a factor of 40–300 higher than lubricant consumption of 0.1–0.8 kg kWh⁻¹ given for a wide range of marine engines by engine producers
 ²⁵ (www.doosan.com). Hence, this study has not resulted in a satisfactory answer to the question of the missing S.

Emission factors for gaseous emissions measured under different engine loads were available for S1_HFO1 but also for S2_HFO1 and S2_MGO (Table 2). EF(CO₂) and EF(SO₂) as $g kg^{-1}$ fuel did not show a dependence on engine load which is in



agreement with what was expected. Also $EF(NO_X)$ and EF(HC) did not differ significantly between the different engine loads, while CO showed increasing EFs with decreasing engine load (Fig. 1).

- The emission factors for PM mass obtained for TSP, PM₁₀ and PM_{2.5} or PM₁ are presented in Fig. 2. All these EFs were somewhat larger for HFO on ship S1 comparing to ship S2. EFs for MGO fuel were similar for the 2 investigated engines. In S1 the EF(PM) decreased with decreased engine load. This is in agreement with earlier measurements performed by e.g. Fridell et al. (2008), Agrawal et al. (2010) and Petzold et al. (2010). Analyses of elemental composition of the sampled PM (Fig. 9 further in the text) confirmed that this decrease in EF(PM) is due to lower conversion of sul-
- phur to sulphate in the exhaust at low engine load that exceeds the opposite trend in the BC/EC emissions with load. Comparing the different fuels, EF(PM) is decreasing from HFO with FSC 1 % over HFO with FSC 0.5 % to MGO with FSC 0.1 %. We could see an increase in PM mass from $PM_{2.5}$ or PM_1 to PM_{10} and TSP indicating presence
- of coarse and giant particles. It should be noted that large particles can come from re-entrained soot and ash particles inside the exhaust channel as was indicated by the online measurements which showed the occasional presence of large particles not observed during the rest of the monitoring time period. Variability (coefficient of variance) of the EF(PM_X) obtained from PM mass on different filter samples taken during acceleration of the end 18.0% on average. Uncertainty of the
- 20 each individual experiment was between 4 and 18.9% on average. Uncertainty of the gravimetrical analysis as such for the investigated filters was less than 1% on average.

3.2 Emission factors for PN and particle size distributions

Data from the EEPS and GRIMM 1108 instruments for particle number concentrations and size distributions are available for the S1 experiments only. The online PM ²⁵ measurements involve a set of instrumentation coupled either in series (FPS dilution system, DAD-100 secondary dilution, thermodenuder, EEPS) or in parallel (EEPS, GRIMM, tracer gas monitoring) (Figs. S1 and S2). Uncertainties of individual instruments, time resolution and time coordination of the data as well as different dilution



ratios of online instruments and filter sampling all contribute to the overall uncertainty. The consistency of the instruments could roughly be checked by comparison of particle numbers measured by the GRIMM and EEPS instruments in the particle size range that is covered by both instruments, i.e. 300–500 nm and by comparison of PM mass calculated from size distributions (assuming PM specific mass of 1 g cm⁻³) with the filter gravimetry results. The first comparison is between 2 parallel instruments, each using different physical principles for particle sizing, coupled to the same serial line for sampling. Considering that the size interval overlap of the online instruments does not match exactly (300–500 nm GRIMM, 294–564 nm and 340–564 nm EEPS) the agreement was good with GRIMM/EEPS PNC mean values of 0.7 and 1.5 for the 294–564

- 10 ment was good with GRIMM/EEPS PNC mean values of 0.7 and 1.5 for the 294–564 and 340–564 nm EEPS intervals, respectively, during the first day (S1_HFO1%_ME-full and _low) and 1.6 and 3.8 mean values during the second day (S1_MGO_AE). The second comparison is between the parallel online instruments and measurements performed in different serial line and shifted in time. Comparison of PM mass calculated
- from the online instrument data (assuming unit particle density) agreed within a factor of 4 with data obtained from the filter gravimetry with online data showing a lower mass than gravimetry data for both HFO tests and a higher mass than gravimetry data for MGO test. Considering the different physical principles of these two analyses, unknown specific density of the PM and uncertainty brought by the exhaust dilution and particle condensation incurse we consider this being a consistent result. At the same time the
- ²⁰ condensation issues we consider this being a consistent result. At the same time the difference is demonstrating the uncertainties inherent in the PM measurements.

The EFs for particle numbers EF(PN) are presented in Fig. 3 as PN/kg-fuel. For S1_HFO1%_full experiment, i.e. for the full engine load the EF(PN) was 1.1 × 10¹⁷ #/kg-fuel and for the S1_HFO1%_low the EF(PN) was 4.9 × 10¹⁵ #/kg-fuel. EF(PN) for the auxiliary engine burning MGO was 9.5 × 10¹⁵ #/kg-fuel. The EF(PN) for S1_HFO1%_full is ca. a factor of 2 higher than EFs found by Petzold et al. (2010) for full load operation of ship engine using HFO and factor 3–5 higher than EF(PN) measured by Jonsson et al. (2011) in plumes of 4 individual ships passing their on-shore measurement station. The drop in EF(PN) with engine load is larger in our measurements (factor 22) than



in Petzold et al. (2010) (factor 4–5). Figure 3 shows also contribution of ultrafine (UF), accumulation mode (Acc), and coarse mode (Co) particles to the total particle number. One can see that the total is largely dominated by ultrafine particles. This can be also seen in number size distributions shown in Fig. 4. The PM mass is on the other hand

- often dominated by particles in accumulation mode as can be seen in the second panel of Fig. 4. In Fig. 4 a large difference between concentrations of particles with diameter above ca. 500 nm can be seen. Figure S4 in the Supplement displays the same number size distributions together with ± standard deviation intervals showing variance of the S1 measurement data. One can see that variability increases for large
- particles and also that measurement under full-load conditions with higher flux and more turbulence in the exhaust channel displays more variability than measurement conducted under the low-load conditions. This indicates importance of swirling and re-entrance of particles from the exhaust channel walls.

The volatility of particles was investigated with thermodenuder (TD) in experiment
S1_HFO1%_ME-full. We found that 33% of the particles (PN) and 42% of the PM mass were volatile. Figure 5 shows fraction of PN and PM mass that was removed by the thermodenuder at 3 TD temperatures. The observed volatile PN fractions are on the low end of earlier published data. Petzold et al. (2010) found in their on-board measurements ~ 66% of particles volatile, Jonsson et al. (2011) found in measurements in passing plumes of 4 identified ships 34–61% of particles being volatile and Pirjola et al. (2011) found in similar in-plume measurements that the volatile particles were responsible for 55–61% of the total particulate number. The differences can be result

of differences between the investigated engines and fuels as well as of differences in sampling conditions (dilution and temperature of sampled exhaust).

25 3.3 PM composition

The main components of the analysed PM are organic carbon (OC), elemental carbon (EC) and sulphate. The elements like V, Ni, Ca and Zn make up proportionally only a small part of the total PM mass. The mass closure of PM in our measurements



has relatively large uncertainties since EC and OC were measured on different filter samples (quartz) than sulphate and other elements (PTFE). The ash residuals left on quartz filter punches after the temperature program of the Sunset analysis could not be defined due to uncertainties in the gravimetrical analysis of these punches.

- Figure 6 presents composition of the sampled PM with respect to EC, organic mass (OM = OC*1.2, Petzold et al., 2008), sulphate and associated water as well as other elements measured by ED XRF. Contributions of EC to the PM mass were between 10 and 35 %, contributions of OM 25–60 %. The sum of volatiles (OM, sulphate and associated water) forms between 30 and 70 % of the total PM (including the unidentified
- ¹⁰ mass UIM). For the S1_HFO1%_ME-full measurement the composition-based volatile part is ca. 50% (including UIM) or 75% (excluding UIM). This is more than the 42% observed with thermodenuder experiment. Assuming differences in these 2 methods and the fact that the ash elements are associated in mineral species like CaSO₄, CaO, CaCO₃, V₂O₃, Fe₂O₃ and NiS (results of microchemical analyses later in the text, Moldanová et al., 2009; Popovicheva et al., 2012), taking up part of the assumed "volatiles" i.e. C and SO₄^{2–} and some additional mass in form of unanalysed species.
- "volatiles", i.e. C and SO_4^{2-} and some additional mass in form of unanalysed species, the difference is not very surprising.

The emission factors for EC and OC analysed by Sunset are presented in Fig. 7. The EF(OC) based on all samples taken in HFO exhaust was 0.59±0.15 g/kg-fuel
with somewhat higher EF(OC) for the HFO with 1% sulphur (0.64±0.12 g/kg-fuel) and lower for 0.5% S (0.43±0.13 g/kg-fuel). The 2 samples from the auxiliary engine running on MGO showed lower EF(OC) 0.22±0.01 g/kg-fuel. Emission factors for OC can be compared with EF(HC) expressed as HC-C measured in the exhaust. For HFO experiments the EF(OC)/EF(HC-C) was 58±21%, for MGO the ratio was lower, ca. 14±0.5% (for EF(HC-C) see Table 2). The EF(EC) for all samples in HFO exhaust was 0.34±0.15 g/kg-fuel with higher EF(EC) for the HFO with 1% FSC (0.40±0.12) g/kg-fuel and lower for 0.5% FSC (0.17±0.02 g/kg-fuel). The

2 MGO samples showed EF(EC) 0.14 ± 0.04 g/kg-fuel. The variability includes impact of different PM metrics and different engines investigated. An increasing EF(EC) and



EF(PM-mass) can be seen from PM_1 ($PM_{2.5}$) over PM_{10} to TSP. This is, however, not true for EF(OC) where in some cases EF(OC) for PM_{10} were lower than those for PM_{25} . This is illustrating uncertainties associated with sampling of volatile PM. Coefficient of variation of EF(EC) and EF(OC) measured on multiple samples taken from the same ⁵ experiment was 7.4 and 4.2%, respectively.

The EF(EC) obtained from Sunset analyses were compared with corresponding EF(BC) calculated from Transmissometer analyses and also with the few EF(BC) calculated from analyses with reflectometer. In Fig. 8 the relative contributions of EC and of BC characterised by the 2 different analytical methods to the PM mass on the anal-

- ysed filters are compared (the relative contribution is chosen in order to eliminate un-10 certainties coming from different EF(PM-mass) obtained on the different filter samples). Figure 8 shows a very good agreement between the 2 different BC optical methods. Comparing to these optical methods EC analysed with thermal-optical method gives higher contribution to the total PM in all samples originating from HFO exhaust where
- EF(EC)/EF(BC) is 2.32 ± 0.64. Two EC samples taken in MGO exhaust show closer 15 agreement with the BC analyses, EF(EC)/EF(BC) is 0.97 ± 0.24. Petzold et al. (2010, 2011) found higher EF(EC) comparing to EF(BC) both for HFO, MGO and for a series of investigated biofuels. In his data the EF(EC)/EF(BC) ratios show strong positive correlation with engine load with values at 100% load ~4 for HFO and ~9 for MGO and

at 10% load 0.7–1.4 for HFO and 1.9 for MGO. 20

Emissions of elements were calculated from masses obtained with XRF analyses of the PM sampled on PTFE filers. Emission factors for the most important species are presented in Fig. 9 and more detailed information is shown in Table S4 in the Supplement. As for some experiments 2 samples analysed at 2 different laboratories

are available, these are both presented in the Table to enable the comparison. It can 25 be concluded that the results from the double samples are in a good agreement. Some filter samples were also analysed with ion chromatography performed on PM extracted from filters by Milli-Q water. These analyses gave results for EFs of PM sulphate and calcium consistent with the EDXRF analyses. Table S4 shows also uncertainties of the



EDXRF analysis for different types of samples as well as coefficient of variance for analysed multiple samples.

Emissions of S, V and Ni are mainly associated with fuel and comparison of the obtained emission factors in g/kg-fuel with the fuel content of these species is therefore

- interesting. For S the EFs of PM-bound S emitted in the HFO exhaust corresponded to 0.1–0.8% of the S content of the fuel. The lowest ratio of EF(PM-S)/Fuel-S 0.1% was measured for the low-load operation mode in S1_HFO1%_ME-low. The full load mode on the same engine showed EF(PM-S)/Fuel-S ~ 0.6% (0.4–0.8%). The samples from the S2 campaign taken in exhaust from HFO with 1 and 0.5% S content combusted
- under full load conditions showed EF(PM-S)/Fuel-S 0.3–0.4 %. All these ratios are on the low end of values of 1-5% S oxidised in exhaust that were found earlier (Moldanová et al., 2009; Petzold et al., 2010) and agree with the finding of Petzold et al. (2010) that oxidation of S to sulphate and hence PM-bound S increases with increasing engine load. For MGO the EF(PM-S)/Fuel-S were 0.6% for the investigated auxiliary engine
 (S1_MGO_AE) and 0.1% for the main engine S2_MGO_ME-full.

For V and Ni the ratios of the measured EFs for these elements (in mg/kg-fuel) to their content in HFO were 43 ± 14 and 66 ± 18 %, respectively (for MGO fuel content of metals was below the detection limit). Also emissions of Fe seem to be associated to large extend with fuel Fe as the EF(PM-Fe)/Fuel-Fe ratio was 21 ± 11 % (mean value for HEO experimente). The S1 HEO1% ME full experiment with high EEs for menu elements.

for HFO experiments). The S1_HFO1%_ME-full experiment with high EFs for many elements had also significantly higher ratios of EF(x)/Fuel-x, x being V, Ni and Fe (60 ± 1 , 90 ± 8 and $34 \pm 2\%$ for V, Ni and Fe, respectively).

Analyses of lubricant oils in engines have shown high contents of Ca, P and Zn. Emissions of these species can be thus associated with the lubricant. If we assume

that a fixed part of Ca in fuel and in lubricant is found in the analysed PM (e.g. 20% in S1_HFO1%_ME-full and 10% in other experiments) we can estimate the respective contributions of fuel and lubricant to the emission of Ca and Zn (P is below the detection limit in fuel analyses). With this estimate it appears that Ca in the sampled PM is dominated by the lubricant origin (factor 1–15, average 8) while for Zn contributions



from fuel (HFO) and from the lubricant are similar (factor 0.3–1, average 0.6). The fuel and lubricant compositions are shown in Fig. 9 together with the emission factors for analysed elements, S shown as S/100 and lubricant concentrations in 100 mg kg^{-1} . This scaling fits all elements and sources on one scale but also should be seen in context with the found ~ 1 % S conversion to particulate sulphate and the ratio of fuel to lubricant consumption which was in order of magnitude *n**100–2000.

Among EFs for elements analysed with EDXRF three different groups with high correlation (r > 0.85) were found: First group includes V, Ni, Fe and Si which has also high correlation coefficient with EF for PM mass ($r \sim 0.9$) second is Cr, Al and Mg which has lower correlation with EF(PM-mass) ($r \sim 0.4$ –0.7) and third is Ca and Zn with lowest

- ¹⁰ lower correlation with EF(PM-mass) ($r \sim 0.4-0.7$) and third is Ca and Zn with lowest correlation to EF(PM-mass), 0.3 and 0.4, respectively. Correlation of the particulate sulphur with any other element was not as high, likely due to the fact that it is in difference from metals largely affected by engine operation conditions. Highest correlation of S was found with the elements in the first group with r 0.7–0.8. Table S5 in the Supplement presents sample Pearson correlation coefficients r for the emission factors for
 - different elements and PM mass.

Oxidative potential calculated as DTT depletion rate normalised for the PM mass measured on PTFE filter samples was found to be between 0.01 and 0.04 nmol-DTT/min/µg-PM (Fig. 10a). The highest value was found for a PM sample in exhaust

- from MGO combustion in experiment S2, 0.038 nmol-DTT/min/µg-PM. PM from MGO exhaust in experiment S1 showed a mean value of 0.020 nmol-DTT/min/µg-PM, close to the average of all analysed samples. It is therefore not possible to draw the conclusion that there is a systematic difference between oxidative potential of PM from MGO and HFO fuels based on our experiments. Oxidative potential measured on PM
- samples from HFO exhaust was between 0.01 and 0.02 nmol-DTT/min/µg-PM with lowest value measured on PM from HFO with FSC 0.5 wt%. Biswas et al. (2009) and Cheung et al. (2009) found similar levels of DTT oxidation rate for emissions from road diesel vehicles, both falling into a range 0.01–0.025 nmol-DTT/min/µg-PM. Figure 10b shows oxidation potential calculated as rate of DTT depletion per kg fuel



consumed. With this metrics oxidative potential of PM in exhaust from HFO with 1 wt% FSC combustion was 30–40 μ mol-DTT/min/kg-fuel. Oxidative potential of PM in HFO with 0.5 wt% FSC exhaust was lower, 9.6 μ mol-DTT/min/kg-fuel. Mean DTT depletion rate found for PM in MGO exhaust was 6.8 μ mol-DTT/min/kg-fuel.

- ⁵ The absolute values of oxidative potential found on quartz fibre filters were low due to the low extraction efficiency for PM on this material; however, these results were still suitable to study correlation with OC and EC, especially as the EC/OC analyses were performed on the same filters. It is known that organic components can catalyse DTT oxidation (Li et al., 2003). On quartz filter samples high correlation between oxidative potential and OC (Pearson correlation coefficient r = 0.77) and low correlation between
- oxidative potential and EC (r = 0.374) was found (Fig. S5 in the Supplement). Similar correlation levels between OC, EC and oxidative potential were found by Jeng (2010) and Biswas et al. (2009). In our study there was found a low negative correlation between oxidative potential measured on PTFE filters and SO₄²⁻ and metals. This is consistent with results presented by Biswas et al. (2009), Cheung et al. (2009) and
- Ntziachristos et al. (2007).

Morphology, microstructure and chemical microcomposition of PM have been studied on samples taken in the diluted exhaust in experiments S1_HFO1%_ME-full and S1_MGO_AE. Both samples have shown presence of small, almost spherical particles ²⁰ (soot-type particles) forming agglomerates, bigger spherical particles: char or charmineral particles, big particles without any regular shape: mineral particles and small (~ 10–30 nm) amorphous organic particles. These particle types have been already observed in PM samples from ship exhaust by Popovicheva et al. (2009) and Moldanová et al. (2009). A global view TEM image of the PM sampled in the main engine exhaust ²⁵ is presented in Fig. 11.

Size distributions of the primary soot particles in agglomerates have been calculated for both experiments from ca. 500 images of primary soot particles representing 15–20 agglomerates. The experimental data were fitted with lognormal functions, the mean particle diameter was 37 nm with standard deviation 0.7 for S1_HFO1%_ME-full and



30 nm with a standard deviation 1.1 for S1_MGO-AE. The primary soot particle size distributions are presented in Fig. S5 in the Supplement. In the sample from HFO combustion in the main engine also different clusters of larger primary soot-type particles with 60–70 nm in diameter were observed. Presence of these larger primary soot particles are shown as zone 2 in Fig. 11b while zone 1 in the same figure shows the more

abundant primary soot particles with mean Dp 37 nm.

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The selected area electron diffraction (SAED) pattern of soot-type particles in both samples showed broad and diffuse rings (Fig. S6a in the Supplement) which correspond to randomly distributed crystallites of graphite also observed on soot samples by Murr and Soto (2005) and Chen et al. (2005). From this pattern interreticular distances d_{hkl} between crystallographic planes (h, k, l) were calculated: For the S1_HFO1%_ME-full sample $d_{002} = 3.74 \pm 0.19$ Å, $d_{10} = 1.98 \pm 0.10$ Å, $d_{11} = 1.14 \pm 0.06$ Å; for S1_MGO_AE sample $d_{002} = 3.79 \pm 0.19$ Å, $d_{10} = 1.94 \pm 0.10$ Å, $d_{11} = 1.13 \pm 0.06$ Å. These values are typical for graphite microcrystallites with a turbostratic

- order (Vander Wal, 1997). In S1_HFO1%_ME-full sample a different type of primary soot particles with small dark points on the surface or inside them was observed (Fig. S6b in the Supplement). The diffraction pattern of these polluted soot-type particles exhibits the diffused rings 10 and 11 with light dots on and between the rings. The ring 002 of graphite microcrystallites is not visible indicating that the primary soot particles con-
- sist of randomly distributed graphene layers and do not possess any intergraphene layer long range order (Chen et al., 2005). Thus, we should assume almost disordered carbon structure, already observed on soot-type particles sampled in heavy fuel oil exhaust (Popovicheva et al., 2009).

Figure 12 shows an example of a STEM image and of an elemental composition map of soot-type particles. More images are presented in the Supplement (Figs. S7– S11). Elemental composition of the primary soot particles from the S1-HFO1%_ME-full experiment was found to be quite variable, some particles being composed of mainly C and O (example in Fig. S6 with 92.6 wt% C, 6.9 wt% O and <0.1 wt% traces of Si, S, V, Ni and Al), some showing high content of nitrogen (10–15%) together with



traces of V, Ca, S, Ni and Si (e.g. Figs. 12, S7 and S8). The elemental composition maps show different areas where N, V, S and Ca are dominating indicating different genesis of the individual primary soot particles. The soot-type particles collected in experiment S1_MGO_AE were mainly composed of C (77 wt%), O (17 wt%), Si (5 wt%), and aluminium (1.5 wt%) with traces of S and Ca (Fig. S9).

The char and char-mineral particles come from incomplete combustion of fuel or lubricant droplets. The quantitative analysis of the EDS spectra of char-mineral and mineral particles showed carbon content of 50–70%, oxygen content of 25–40% and traces of S, Ca, Al, Si, V, Ni, Zn, and P. Elements Ca, Zn and P typically indicate origin of the particles from lubricant, while V, Ni and S are typical tracers of the HFO fuel. Many char-mineral particles collected in HFO exhaust show traces of elements from

- Many char-mineral particles collected in HFO exhaust show traces of elements from both groups (Fig. S8) which could either be result of internal mixing of elements in the exhaust into these particles or of the fact that both HFO and lubricants actually have some traces of all these species (Table S3). Assignment of fuel or lubricant origin to the char-mineral particles collected in MGO exhaust is easier as Ca, Zn and P in this
 - case come only from the lubricant (Figs. S10, S11).

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The TEM images have also shown amorphous organic particles (no SAED pattern), smaller than soot particles with traces of S, V, Ca and Al. On images of these particles one can see dark points, probably mineral impurities (Fig. S12). It is difficult to deter-

²⁰ mine their exact elemental composition as they are located on the carbon amorphous film and are likely formed from carbon. The sulphur-rich areas outside soot clusters in Figs. 12 and S7b, often on the boarder of the carbon film, are probably these organic particles. One can notice that the particles interact with the high-energy electron beam of the microscope which can be explained by the presence of semi-volatile compounds and absence of crystallized structure.

The elemental composition maps support the bulk EDXRF elemental analyses where weaker correlation between groups of elements V, Ni, Fe on one side, Ca, Zn on the second and S on the third were found as both the primary soot particles and the charmineral particles show variability in composition between these groups of elements.



The FTIR spectra measured on the S1_HFO1%_ME-full and S1_MGO_AE samples were very similar and showed presence of aromatic compounds, C-O and C=O group, vanadium oxide V_2O_5 , iron oxide, nitrogen-containing compounds, very strong peaks for sulphide compounds and another at 1108 cm⁻¹ indicating sulfone, thiocarbonyl or ⁵ C-O-C compounds (Fig. S14). These findings are supported by elemental composition obtained with EDS. The Raman spectra measured on cumulative PM sample collected on S1_HFO1%_ME is presented in Fig. S15 in the Supplement. Five bands were identified, one G band corresponds to the graphite lattice and 4-D bands correspond to the disordered graphite structure and amorphous carbon. The ratio of the intensities of band D₁ and band G is related to the average in-plane length L_a of a microcrystallite of graphite (Larouche et al. 2010; Ferrari et al. 2000). For the investigated sam-

- lite of graphite (Larouche et al., 2010; Ferrari et al., 2000). For the investigated samples $L_a = 6.3$ nm, a value typical for carbon black particles (Larouche et al., 2010). The observed FTIR and Raman spectra are generally in agreement with results of Popovicheva et al. (2012) who measured these spectra on different samples from the
- same campaign. N-species observed in this work were not detected by their system due to sensitivity limitations. Their analyses of Raman spectra showed in addition to the signature of graphitic soot also numerous inorganic compounds. These spectra were obtained on the ash residue after partial burn-out of the soot, a method not used in this work.
- The oxidation reactivity of the main engine exhaust (S1_HFO1%_MEfull) and the auxiliary engine exhaust (S1_MGO_AE50) were measured by TPO. The corresponding TPO profiles (plots of CO + CO₂ emissions against the sample temperature) for TSP and PM_{2.5} are shown in Fig. 13. The TPO profiles for various carbonaceous samples observed by Schmid et al. (2011) generally show an emission shoulder or minor peak
- ²⁵ at lower temperatures, followed by a main emission peak at higher temperatures. The shoulder or minor peak is assigned to amorphous or highly disordered soot structures, whereas the main emission peak is related to soot structures of higher structural order. The temperature of maximum CO and CO₂ emission (T_{max}) of the main peak is defined as reactivity parameter. The TPO profile of pure graphite demonstrated by Schmid



et al. (2011) shows almost no emission up to 500 °C and T_{max} of 760 °C. For spark discharge soot they observed a pronounced emission shoulder due to amorphous and highly disordered domains and a comparatively broad main emission peak with T_{max} at 515 °C representing the combustion of highly ordered soot structures. They also found that typical automotive diesel soot samples start to oxidize at ~ 250 °C and reveal maximum emission temperatures T_{max} between those of graphite and spark discharge soot, i.e. 515 and 760 °C. Bladt et al. (2012) demonstrated that the iron oxide internally mixed with soot, especially at low concentrations (below 10 wt% Fe) shifts strongly T_{max} towards lower temperatures. Other contaminations, such as heavy metal oxides or salts, may also enhance soot reactivity (Neeft et al., 1997; Ciambelli et al., 1996; Castoldi et al., 2009). Thus, soot oxidation reactivity is influenced by both soot particle structure and content of metal elements.

The TPO profile of PM from HFO exhaust, S1_HFO1%_MEfull, consists of two emission peaks. Whereas the low temperature emission peak starts at 250 °C and reaches its maximum at 366 and 407 °C for the TSP and PM_{2.5} sample, respectively, the maximum of the high temperature peak is at 452 and 463 °C, respectively. Both highertemperature peaks in the two profiles have maxima at similar temperatures and probably present combustion of similar structural domains in soot, namely higher ordered soot structures also observed with SAED patterns with TEM (Fig. S6a). Compared to

- ²⁰ automotive diesel soot samples (Schmid et al., 2011) the temperatures of the emission maxima are very low. It is highly possible that the oxidation is catalysed by inorganic salts and/or oxides. Especially vanadium oxides and iron oxides are known for their strong catalytic activity in soot oxidation (Bladt et al., 2012; Neeft et al., 1997) and these metals were found both by the EDXRF analyses of bulk PM (Fig. 9, Table S4)
- and with the microchemical analyses in STEM (Figs. 12 and S7–S11). Temperature at the maximum of the lower-temperature emission peak is lower for the TSP sample comparing to the PM_{2.5} sample. Hence, these peaks belong to the combustion of different structural domains and/or are influenced differently by oxidation catalysts of different quantity or effectiveness.



The TPO profiles of S1_MGO_AE exhibit the main higher-temperature emission peak at 532 and 527°C in the TSP and PM₂₅ samples, respectively, and broad emission shoulders starting at around 250 and 290 °C, respectively. Thus, there are soot components in S1_MGO_AE that start combusting at similar temperatures as in S1_HFO1%_MEfull. Nevertheless, T_{max} of the S1_MGO_AE sample of TSP and PM_{2.5} 5 are 80 and 64°C, respectively, higher compared to the S1_HFO1%_MEfull samples and combustion is completed at temperatures about 50 °C higher. These findings can be explained by a lower reactivity of soot in S1_MGO_AE samples compared to the S1_HFO1%_MEfull due to higher structural order of the soot and/or by lower content of oxidation catalysts. The structural order of the soot was analysed with the SAED 10 patterns which, however, could not give any evidence of difference in degree of crystallinity between the S1_HFO1% and S1_MGO samples. Further, the results of XRF analyses support the lower content of oxidation catalysts in the MGO sample as the concentrations of V. Ni and S are low in the MGO exhaust sample relative to that from HFO. The relative intensity of the emission shoulders to their respective main peaks 15 in S1_MGO_AE is lower for PM_{2.5} than for TSP and starts at a higher temperature. Accordingly, PM_{2.5} mostly contributes to the structural domains of higher order rather

4 Conclusions

The measurement campaigns investigated a number of parameters describing emission factors of gases and of particulate matter from ship engines. The measured EFs for PM mass were in the range 0.3 to 2.7 g/kg-fuel with lowest values for emissions from combustion of MGO and the highest for HFO. An increase of EF(PM-mass) with increasing FSC was observed. For the dependence of EF(PM-mass) on engine load role of re-entrainment of soot and ash particles inside the exhaust channel walls at higher exhaust flow rates has been indicated by the online PM measurements.

than to the structural domains of lower order in the TSP.



The emission factors for particle numbers were measured for 2 different fuels and 2 engine operation modes. EF(PN) in the range 5×10^{15} – 1×10^{17} #/kg-fuel were found, the number concentration is dominated by particles in the ultrafine mode and ca. 2/3 of particles are non-volatile. The data are consistent with earlier studies by Petzold et al. (2010) and Jonsson et al. (2011).

The PM mass is dominated by particles in accumulation mode and it consists of EC, OC, sulphate with associated water and various metal elements. Main metal elements in case of HFO are V, Ni, Fe, Ca and Zn, in case of MGO Ca, Zn and P. V and Ni are typical tracers of HFO while Ca, Zn and P are tracers of the lubricant oil. EC makes up 10–38 % of the PM mass, there were not found large differences between HFO and MGO fuels. This finding is consistent with measurements published by e.g. Petzold et al. (2010). EC and ash elements make up 23–40 % of the PM mass, measurements with online instruments and thermodenuder indicated that ca. 60 % of mass is

non-volatile. These two results have been found consistent when uncertainties asso-

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- ¹⁵ ciated with mass closure gap and differences in sampling techniques are assumed. In exhaust from HFO combustion emission factors for BC measured with 2 different optical methods showed substantially lower values comparing to those EF(EC) obtained from thermo-optical method. Ratio EF(EC)/EF(BC) was 2.3 ± 0.6 . For MGO exhaust EF(EC)/EF(BC) was 0.97 ± 0.24 . This discrepancy between EF(EC) and EF(BC) can
- ²⁰ also be found in data in Petzold et al. (2010, 2011) and there it seems to be associated rather with combustion conditions (engine load) than with the fuel type. Organic matter makes-up 25–60% of the PM. The measured EF(OC) were 0.59 ± 0.15 g/kg-fuel for HFO and 0.22 ± 0.01 g/kg-fuel for MGO. The measured EF(SO₄²⁻) were low, ca. 100–200 mg/kg-fuel for HFO with 1% FSC, 70–85 mg/kg-fuel for HFO with 0.5%
- ²⁵ FSC and 3–6 mg/kg-fuel for MGO. This corresponds to 0.2–0.7 and 0.01–0.02 % of fuel S converted to PM sulphate for HFO and MGO, respectively. For the low engine load experiment the $\text{EF}(\text{SO}_4^{2-})$ was 18 mg/kg-fuel corresponding to 0.06 % fuel S conversion.



The TEM and STEM images of collected PM have shown three different types of particles: (1) soot composed mainly of C, O, sometimes N, and with traces of Si, S, V, Ca and Ni; (2) char and char-mineral particles composed of C, O, Ca and S (sometimes Si and Al) with traces of V and Ni and sometimes P and (3) amorphous, probably organic

- ⁵ particles containing sulphur and some vanadium. The maps of elements obtained from STEM showed heterogeneous composition of primary soot particles with respect to the trace metals and sulphur. SAED patterns of different soot particles show presence of soot particles composed of microcrystallites with a turbostratic order and in the HFO sample also of particles of almost disordered carbon structure with light dots on and between the ringe from impurities. Composition of the other mineral particles indicates
- between the rings from impurities. Composition of the char-mineral particles indicates that species like CaSO₄, CaO and/or CaCO₃, SiO₂ and/or Al₂SiO₅, V₂O₅ and iron oxide may be present, the last two were also confirmed by analyses of FTIR spectra of the PM samples.
- The temperature-programmed oxidation (TPO) of PM from the ship exhaust sam-¹⁵ ples showed higher soot oxidation reactivity compared to automotive diesel soot, PM from the HFO exhaust is more reactive than PM from the MGO exhaust. This higher oxidation reactivity could be explained by high content of catalytically active contaminants; in particular in the HFO exhaust PM for which the EDXRF analyses showed high content of V, Ni and S. Analyses of PM from the MGO exhaust identified only
- ²⁰ Zn, Ca, presumably less catalytically active species, and small amounts of S. It could be demonstrated that PM_{2.5} more dominantly contributes to the main emission peak related to soot structures of higher structural order than to the minor emission peak related to highly disordered soot.

Oxidative potential measured as a rate of consumption of DTT was for the first time measured on PM from ship exhaust. The obtained values were between 0.01 and 0.04 nmol-DTT/min/µg-PM, quite similar to oxidative potentials of PM collected in urban and traffic sites.

The data obtained during the Transphorm experiments add information on emission factors for both gaseous and PM-bound compounds from ship engines using different



fuels and under different engine load conditions. Observed variability of the EFs illustrates uncertainties of these emission factors as a result of measurement uncertainties, influences from trace components of fuels and lubricants and from differences between individual engines.

⁵ Supplementary material related to this article is available online at: http://www.atmos-meas-tech-discuss.net/6/3931/2013/ amtd-6-3931-2013-supplement.pdf.

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3965

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Table 1. Matrix of analyses performed on filter samples from ship campaigns S1 and S2. DR – dilution ratio used during the sampling, T1 and T2 – sample temperatures after primary and secondary dilution in the FPS instrument. Filter material: PTFE – PTFE membrane filters, Quartz – quartz fibre filters, CF&Ge – holders with Cu microgrids with amorphous carbon holey film and Ge windows. Analyses: grav. – gravimetry, BC – analysis for BC with transmissometer, IC – ion chromatography, EC/OC – Thermal optical analysis for EC and OC, ox. pot. – oxidative potential tested with DTT assay, microscopy – transmission electron microscopy, FTIR and Raman.

Experiment	DR	T1 [°C]	T2 [°C]	Filter	Analyses	PM metrics
S1_HFO1%_ME-full	28.3	136.2	40.1	PTFE	grav., BC, XRF, IC	TSP, PM ₁₀ , PM ₁
S1_HFO1%_ME-full	28.3	136.2	40.1	PTFE	XRF	PM_{10}, PM_{1}
S1_HFO1%_ME-full	28.3	136.2	40.1	Quartz	EC/OC, ox. pot.	TSP, PM ₁₀ , PM ₁
S1_HFO1%_ME-full	28.3	136.2	40.1	PTFE	ox. pot.	TSP, PM ₁
S1_HFO1%_ME-full	28.3	136.2	40.1	CF&Ge	microscopy	TSP
S1_HFO1%_ME-low	26.0	89.7	35.1	PTFE	grav., BC, XRF, IC	TSP, PM ₁₀ , PM ₁
S1_HFO1%_ME-low	26.0	89.7	35.1	Quartz	EC/OC	TSP, PM ₁
S1_MGO_AE	31.5	105.0	29.2	PTFE	grav., BC, XRF, IC	TSP, PM ₁₀ , PM ₁
S1_MGO_AE	31.5	105.0	29.2	PTFE	XRF	PM ₁
S1_MGO_AE	31.5	105.0	29.2	Quartz	EC/OC, ox. pot.	TSP, PM ₁₀ , PM ₁
S1_MGO_AE	31.5	105.0	29.2	PTFE	ox. pot.	TSP, PM ₁
S1_MGO_AE	31.5	105.0	29.2	CF&Ge	microscopy	TSP
S2_HFO1%_ME-full	17.9	106.8	39.1	PTFE	grav., BC, XRF	PM ₁₀ , PM _{2.5}
S2_HFO1%_ME-full	17.9	106.8	39.1	PTFE	ox. pot.	PM _{2.5}
S2_HFO0.5%_ME-full*	23.5/27.7	132.9/ 149.0	39.0/ 50.1	PTFE	grav., BC, XRF	PM ₁₀ , PM _{2.5}
S2_HFO0.5%_ME-full*	23.5/27.7	132.9/ 149.0	39.0/ 50.1	Quartz	EC/OC	PM ₁₀ , PM _{2.5}
S2_HFO0.5%_ME-full*	23.5/27.7	132.9/ 149.0	39.0/ 50.1	PTFE	ox. pot.	PM _{2.5}
S2_MGO_ME-full	28.8	141.4	41.9	PTFE	grav., BC, XRF	PM ₁₀ , PM _{2.5}
S2_MGO_ME-full	28.8	141.4	41.9	PTFE	ox. pot.	PM _{2.5}

* Sampling in 2 periods with different sampling conditions.

AN 6, 3931–3	ITD 8982, 2013
European Contro	er Emission End Emission
J. Moldar	nová et al.
Title	Page
Abstract	Introduction
Conclusions	References
Tables	Figures
I	▶1
•	•
Back	Close
Full Scre	een / Esc
Printer-frier	ndly Version
Interactive	Discussion
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Discussion Paper

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Discussion Paper

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Experiment	S1₋HFO1 %_ME-full	S1_HFO1 %_ME-low	S2₋HFO1 %₋ME-full	S2_HFO0.5 %_ME-full	S1_MGO _AE	S2₋MGO- ME-full
EF	[gkWh ⁻¹]	[g kWh ⁻¹]	[g kWh ⁻¹]	[g kWh ⁻¹]	[g kWh ⁻¹]	[g kWh ⁻¹]
CO ₂	678	617	610	592	642	572
0, -	1054	1127	841	786	1084	913
οō	1.17	1.82	0.96	0.92	0.60	0.64
HC (C)	0.27	0.30	0.10	0.07	0.32	0.07
NO _x	9.6	9.6	12.5	10.1	13.2	9.3
NO _X corr.*	8.2	8.1	11.2	9.4	12.1	8.4
NO _X TIER I**	12.0	12.0	12.9	12.9	11.3	12.9
SO ₂	3.65	3.24	2.8	1.5	0.12	0.27
SO_2^- calc.***	3.84	3.50	3.6	2.2	0.12	0.36
TSP	0.58	0.34	0.37	0.23	0.07	
PM ₁₀	0.41	0.35	0.27	0.19	0.06	0.06
PM _{2.5}	-	_	0.27	0.15	-	0.04
PM ₁	0.41	0.27	-	-	0.06	-
EF	[g kg ⁻¹ fuel]					
CO ₂	3204	3206	3219	3189	3151	3161
0 ₂ -	4983	5862	4442	4235	5318	5043
cō	5.52	9.46	5.06	4.98	2.92	3.55
HC (C)	1.28	1.58	0.52	0.40	1.59	0.39
NO _x	45.2	49.7	66.1	54.2	64.6	51.6
SO ₂	17.3	16.8	14.9	8.2	0.57	1.51
TSP	2.7	1.8	1.97	1.22	0.33	-
PM ₁₀	1.9	1.8	1.44	1.00	0.28	0.34
PM _{2.5}	-	_	1.41	0.79	-	0.23
PM₁	1.9	1.4	-	-	0.27	-

Table 2. Emission factors for gas phase species and mass of TSP, $\rm PM_{10},\ \rm PM_{2.5}$ and $\rm PM_{1}$ measured during the experiments.

* NO_x corrected with factor for ambient conditions as in ISO 8178-1 1996 clause 13.3 version (b). ** NO_x EF calculated according to the IMO TIER I standard, EF = $45^*n^{-0.2}$ g kWh⁻¹, n = engine speed in rpm. *** SO₂ calculated from fuel sulphur content assuming complete oxidation to SO₂.





Fig. 1. EF(CO) (green) and EF(HC) (violet) at different engine loads. The red ellipses couple experiments performed on same engine and with the same fuel at different engine loads.





Fig. 2. EFs (in $g kg^{-1}$ fuel) for total suspended particulate matter (TSP), PM_{10} and $PM_{2.5}$ obtained from gravimetric analyses of exposed PTFE filters.





Fig. 3. Emission factors (in #/kg fuel) for particle numbers in 3 different size intervals. UF – ultrafine mode, 6 nm < Dp < 100 nm, Acc – accumulation mode, $100 \text{ nm} < \text{Dp} < 2.5 \mu\text{m}$, Co – coarse mode, $2.5 \mu\text{m} < \text{Dp} < 10 \mu\text{m}$.





Fig. 4. Particle number and mass size distributions measured in the exhaust on S1 (recalculated for in-stack exhaust concentrations).



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Fig. 5. Part of PM mass and PM number volatilized at 90 °C (Vol. 90), 150 °C (Vol. 150) and 300 °C (Vol. 300) in the thermodenuder and the non-volatile part (Nonvol.).





Fig. 6. Composition of PM sampled during S1 from the Sunset (EC, OM = OC*1.2) and XRF (SO₄²⁻, other elements) analyses. Sulphate-bound H₂O is calculated as SO₄2-*0.8 (after Petzold et al., 2008).





Fig. 7. Emission factors for elemental carbon (EC) and organic carbon (OC) analysed by Sunset on exposed quartz filters.





Fig. 8. Relative contributions of EC and BC to the PM mass on the analysed filters. BC was analysed with 2 different instruments, Smokestain reflectometer (reflect.) and Soot Scan transmissometer (transmiss.).





Fig. 9. Emission factors for elements based on XRF and IC analyses of PM filter samples. (a) Samples taken in HFO exhaust, (b) samples taken in MGO exhaust, (c) concentrations in fuel (mg kg⁻¹, S 100 mg g⁻¹) and in lubricant (100 mg kg⁻¹, S 10 g kg⁻¹).



Fig. 10. Oxidative potential of investigated PM measured on PTFE membrane filter samples. (a) Specific for the emitted PM in nmol DTT/(min $\times \mu g$ PM), (b) calculated for the emission source as nmol DTT/(min $\times kg$ -fuel).





Fig. 11. TEM image of PM from the S1_HFO1%_ME-full experiment. (a) Global view showing soot-type, char-mineral and mineral particles. (b) Primary soot-type particles of 2 different sizes, zone 1 - soot particles with Dp ~ 30-40 nm, zone 2 -Dp 60-70 nm.







Fig. 12. (a) STEM image of an agglomerate of soot-type particles from the S1_HFO1%_ME-full experiment. Composition: C 77.1 wt%, N 15.7 wt% and O 6.9 wt% and traces of V, Ca and S (about 0.1 wt% of each element). **(b)** Elemental composition map of V, Ca and S for the soot-type particles in **(a)**.





Fig. 13. Oxidation behaviour of PM (TSP in black and $PM_{2.5}$ in red) sampled in (a) S1_HFO1%_ME-full, (b) S1_MGO_AE experiments.

