



Real-world particle emissions and secondary aerosol formation from a diesel oxidation catalyst and scrubber equipped ship operating with two fuels in a SECA area[☆]

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ABSTRACT

SO_x Emissions Control Areas (SECAs) have been established to reduce harmful effects of atmospheric sulfur. Typical technological changes for ships to conform with these regulations have included the combustion of low-sulfur fuels or installation of SO_x scrubbers. This paper presents experimental findings from high-end real-time measurements of gaseous and particulate pollutants onboard a Roll-on/Roll-off Passenger ship sailing inside a SECA equipped with a diesel oxidation catalyst (DOC) and a scrubber as the exhaust aftertreatment. The ship operates between two ports and switched off the SO_x scrubbing when approaching one of the ports and used low-sulfur fuel instead. Measurement results showed that the scrubber effectively reduced SO₂ concentrations with over 99% rate. In terms of fuel, the engine-out PM was higher for heavy fuel oil than for marine gas oil. During open sea cruising (65% load) the major chemical components in PM having emission factor of 1.7 g kg_{fuel}⁻¹ were sulfate (66%) and organics (30%) whereas the contribution of black carbon (BC) in PM was low (~4%). Decreased engine load on the other hand increased exhaust concentrations of BC by a factor exceeding four. As a novel finding, the secondary aerosol formation potential of the emitted exhaust measured with an oxidation flow reactor and an aerosol mass spectrometer was found negligible. Thus, it seems that either DOC, scrubber, or their combination is efficient in eliminating SOA precursors. Overall, results indicate that in addition to targeting sulfur and NO_x emissions from shipping, future work should focus on mitigating harmful particle emissions.

1. Introduction

Shipping emissions consisting of gaseous and particulate species affect both local air quality (Ault et al., 2009; Viana et al., 2020) and climate (Eyring et al., 2010). In order to reduce the environmental burden of marine traffic, global sulfur regulation decreased the sulfur content in fuel from 3.5% to 0.5% starting January 1st 2020 (IMO, 2021). In specific SO_x Emissions Control Areas (SECAs) like the Baltic Sea or coasts of North America, the current sulfur limit stands at 0.1% (IMO, 2021). For ship operators to comply with sulfur limits, the first option is a shift to low sulfur fuels, which has been considered as a very expensive option because of large difference in price of low and high

sulfur level fuels. Second method is the introduction of liquefied natural gas (LNG) as fuel, but this mainly concerns newbuilds, because retrofitting existing vessels has not been considered as a viable option. The third method concerns installing exhaust abatement techniques, which reduce sulfur emissions to levels as required in the EU sulfur directive (European Parliament and the Council of the European Union, 2012). The adoption of SO_x scrubber devices instead of low sulfur fuel largely depends on the cost (Jiang et al., 2014). If a vessel mainly operates in SECAs and annual fuel consumption is high, scrubber use may prove to be the cheapest option. An open loop mode can be used in regions where wash water release is within International Maritime Organization (IMO) limits. In areas where sea water salinity is too low, additional chemicals (NaOH, caustic soda) may be needed for sulfur capture and closed loop

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Abbreviations		LNG	Liquefied Natural Gas/MGO Marine Gas Oil
BC	Black Carbon	OC	Organic carbon
DOC	Diesel Oxidation Catalyst	PAH	Polycyclic Aromatic Hydrocarbons
DR	Dilution Ratio	PAM	Potential Aerosol Mass
EC	Elemental carbon	PM	Particulate matter
ECA	Emission Control Area	PM-SDS	Particulate Matter Ship Dilution System
EF	Emission Factor	PN	Particulate number
FPS	Fine Particle Sampler	RoPax	Roll-on/Roll-off passenger
FSN	Filter Smoke Number	SECA	SO _x Emissions Control Area
FTIR	Fourier transform infra-red	SOA	Secondary Organic Aerosol
HFO	Heavy Fuel Oil	SMPS	Scanning Mobility Particle Sizer
IMO	International Maritime Organization	SP-AMS	Soot Particle Aerosol Mass Spectrometer
		TD	Thermodenuder

operation may be applied. In 2019, over 2000 vessels worldwide were equipped with open, closed or hybrid scrubbers (Jalkanen et al., 2021). The sulfur limits reduce efficiently sulfur emissions and particulate matter (PM), providing significant health benefits (Sofiev et al., 2018). Shipping is expected to still remain a globally significant source of particle number (PN) emissions in the near future (Kuittinen et al., 2021) despite the stricter sulfur reduction, whereas the cloud forming potential of emission particles may reduce 80% (Yu et al., 2020).

As another mean to reduce harmful particle emissions, IMO is preparing to limit BC emissions of ships. IMO has agreed on a technology-neutral definition for BC covering different properties according to Bond et al. (2013); BC is defined as a distinct type of carbonaceous material, formed only in combustion of carbon-based fuels (Bond et al., 2013). BC particles are aggregates of small carbonaceous spherules that are refractory and water insoluble, absorbs strongly in visible wavelengths. In this study, term BC or elemental carbon (EC) are used to denote particulate material with the above characteristics. From environmental perspective, BC is problematic since it absorbs solar radiation, thus warming the atmosphere, but also affects cloud formation and cloud properties. When deposited on icy surface, BC changes the surface albedo and accelerates melting (Bond et al., 2013; IPCC, 2014).

Scientific literature reports only handful of cases of scrubber performance under realistic operating conditions, and only a few publications exist where particle emissions are covered. This campaign, briefly and partly covered in Lehtoranta et al. (2019), provides a study of a vessel equipped with an open loop scrubber and aims to fill this gap in knowledge. Lehtoranta et al. (2019) observed that fuel change to lower sulfur level fuels or to natural gas and the use of scrubbers significantly decreased the PM emissions. However, this was not directly linked with nonvolatile particle number (PN) emission reductions, and low PN levels were associated with low EC. Winnes et al. (2020) observed lower particle emissions at the use of low sulfur fuel than high sulfur fuel downstream the scrubber. The scrubber removed between 32% and 43% of PM, but levels equivalent to those in low sulfur fuel exhaust were not reached. Some decreases in the emissions of polycyclic aromatic hydrocarbons (PAH-16) and PM as BC, organic carbon (OC) and EC, over the scrubber were observed. Fridell and Salo (2016) observed that the scrubber reduced the emissions of PM by 75%. The total particle number was reduced by about 92% whereas the solid fraction by 48% in the scrubber. In addition, the content of polycyclic aromatic compounds in the exhaust was significantly reduced in the scrubber.

Currently, it is not well known how large the emissions of combustion originated particles are during variable operating conditions, that occur especially close to harbors, of marine engines, although at least one study exists (Hallquist et al., 2013). Most studies report results under laboratory conditions or during steady operation of a real ship. Moreover, it is unknown how large the secondary aerosol formation potential in the scrubbed marine exhaust can be and how the real-time chemical composition of exhaust PM varies during a voyage.

This paper describes results from a measurement campaign executed onboard a large Roll-on/Roll-off Passenger (RoPax) ship equipped with a diesel oxidation catalyst (DOC) and an open-loop scrubber. The vessel operates on a regular route between two ports and must switch off the scrubber when approaching the other port and use low sulfur fuel instead. The aim of this article is to study broad range of real-world emission components of a ship that operates inside SECA and applies both scrubber and low sulfur fuel strategies to conform with emission regulations. In the experimental work, the stack emissions were extensively characterized for gases (CO₂, CO, SO₂, NO_x, HC) and particles for their physical (PM, PN, size distribution, volatility, ageing effect) and chemical properties (organics, sulfates, black carbon, PAH) with high-end online and offline methods.

2. Materials and methods

2.1. Studied ship

Measurements were conducted on-board a RoPax ship during two consecutive cruises inside the Baltic SECA area. On-board the ship, exhaust was sampled from one of the ship's four main engines (Wartsila 9L46D). The studied engine had nine cylinders, maximum speed of 514 rpm and maximum power rating of 10.4 MW. The engine was equipped with an open loop scrubber (ECO-DeSO_x, Ecospray Technologies), and a DOC (Ecospray Technologies). Both the scrubber and DOC were retrofitted in the ship in 2016, about one year before the experiments.

Ship navigated normally and thus engine load varied during the measurements. Majority of the ship operation consisted of open-sea cruising where the typical engine load varied between 60 and 70%. During the arrivals and departures to ports (port A and port B), engine load was lowered to 15–20%. Engine load data was received from the ship operator. Variable load conditions also occurred during short intervals, but time periods during which load remained stable around 65% and 17% were chosen for more detailed analysis. In addition, transient conditions including load and fuel changes as well as switching the scrubber on or off were studied.

2.2. Fuels

During the cruises, the ship mainly burned Heavy Fuel Oil (HFO) with a sulfur content of 1.9 wt-%. However, due to regulations related to sea water quality, the open loop scrubber was turned off while maneuvering inside the harbor area in port B. To still comply with the SECA regulation, the ship switched into burning Marine Gas Oil (MGO) with 0.02 wt-% sulfur before entering the area. Samples of both fuels and engine oil were collected during the campaign and the analyses are shown in Tables S1 and S2. Properties of engine oil resembled those of SAE 40 oil for HFO applications.

2.3. Sampling locations and probes

On the ship, exhaust was sampled from three locations – from the engine exhaust channel before DOC (“Engine-out”), after DOC and before scrubber, and after scrubber. Schematic describing the sampling locations and instruments is shown in Fig. 1. Some other parameters were recorded from the sampling locations such as humidity, pressure, and temperature of the exhaust gas.

Gaseous compounds as well as filter collections of the exhaust PM were conducted at all three sampling locations. Probe before the scrubber was unheated, but heated lines, filters and diluters were connected immediately to the probe outlet and the connections were isolated for avoiding any “cold spots”. The probe after the scrubber was heated to 250 °C to avoid the formation of water droplets on sampling surfaces. Based on probe temperature tests, heating the probe did not affect the particulate matter results.

2.4. Measurements from undiluted exhaust

Gaseous compounds were measured on-line at 20 s intervals using three Fourier transformation infrared (FTIR) devices (Gasmeter DX-4000) placed at different sampling locations. Raw exhaust sample was drawn and conditioned to 180 °C. Compounds measured were SO₂, H₂O, CO₂, CO, NO, NO₂, CH₄, N₂O, NH₃, ethylene, formaldehyde, acetaldehyde, and octane. NO_x was calculated as a sum of NO and NO₂.

AVL 415S Filter Smoke Meter was applied to measure Filter Smoke Number (FSN, ISO 10054) from raw exhaust gas. Conversion from FSN to BC concentration was done according to the equation provided by the manufacturer. In these measurements, 2 m transfer line (70 °C) was used; temperature of the instrument cabin was 63 °C.

2.5. PM filter collections

An ISO 8178 compliant Ship Dilution System (PM-SDS) which can be moved between the ship decks was designed and built-up to collect PM samples. In PM sampling, a partial flow from the exhaust was taken for dilution with filtered air (dilution ratio, DR 10), after which the flow was drawn through filter. Heating of transfer line (6 m) was set to 250 °C, filter was held between 42 and 52 °C. PM samples were collected on filters and three replicate tests were conducted to validate the results. The PM filters were analyzed with EC/OC method as well as for metals, analysis details are given in SI.

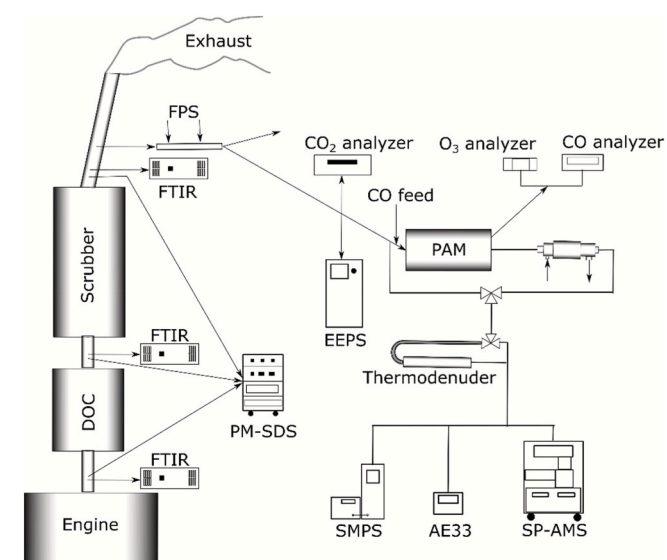


Fig. 1. Measurement setup for gaseous and particulate phase instrumentation.

2.6. Online aerosol instruments after scrubber

Additional online particle instruments were located after the scrubber. For these instruments, the sampling was performed with a Fine Particle Sampler (FPS, Dekati Oy) equipped with a stack heater probe. In the FPS, the first stage dilution is performed with a perforated tube diluter whereas ejector is used for the second dilution stage. The dilution air was set to the temperature of about 25 °C which was higher than the temperature of the exhaust downstream the scrubber. Total DR was determined with trace gas CO₂ measurements in both raw and diluted exhaust. SIDOR CO₂ analyzer (Sick Maihak GmbH) was used to measure the concentration of CO₂ downstream the FPS dilution system. The applied DR range was between 200 and 300.

Soot Particle Aerosol Mass Spectrometer (DeCarlo et al., 2006; Onasch et al., 2012) (SP-AMS; Aerodyne Inc.) was used for real-time measurement of submicron PM chemical composition. The SP-AMS was operated in both Mass Spectrum and epTOF (efficient particle time-of-flight) mode alternately with time resolution of 2 min to measure several chemical components like refractory black carbon (rBC), organics, sulfates, nitrates, chloride, and ammonium. The elaborated details of SP-AMS operation principle and usage in these experiments are given in SI. In addition to SP-AMS, the concentration of BC was measured using a dual-spot aethalometer (Drinovec et al., 2015) (AE33, Magee Scientific). The flow rate was set to 5 L min⁻¹ and the time-resolution of measurement was 1 min.

Particle number size distributions was measured using Scanning Mobility Particle Sizer (SMPS) (Wang and Flagan, 1990). SMPS has a Differential Mobility Analyzer (Model 3071 Electrostatic Classifier, TSI Inc.) for particle size selection and a Condensation Particle Counter (Model 3775, TSI Inc.) to measure particle number size distribution (range 10–400 nm). The engine conditions were stable during SMPS measurements, and 3-min sampling time was used. Number size distributions were converted to mass using particle density of 1.6 g cm⁻³ on average. The real-time density values were calculated based on the chemical composition measured by SP-AMS and densities of single compounds during each measurement condition (Salcedo et al., 2006).

2.7. Studying aerosol aging and volatility

The potential aerosol mass (PAM (Kang et al., 2011)) chamber (Aerodyne Inc.) was used to simulate aerosol aging in the atmosphere. The PAM chamber is a small flow-through reactor with two UV lamps positioned inside to produce photons at two wavelengths 185 and 254 nm. Photolysis of O₂ and H₂O produced the oxidants O₃, OH and HO₂. The flow through the PAM chamber was ~9 L min⁻¹ composed of the ring flow (1.5 L min⁻¹) and central flow (7.5 L min⁻¹). The aging potential of PAM chamber was varied in sequences according to the used voltage: 0 V, 2.9, and 9 V corresponding to 0, 0.5, and 5 days of atmospheric aging, respectively. Photochemical age was calibrated against the decay of CO which was continuously injected into the sample line before the PAM and measured by CO analyzer (Environnement S.A. CO12) after setting the chamber UV lights on/off (similar approach as in Lambe et al. (2011)). An additional ejector diluter (DR 6–10) was used downstream the PAM. The SP-AMS, aethalometer, and SMPS were placed downstream this ejector.

The volatility of the exhaust particles was measured using a thermodenuder (TD) (Heikkilä et al., 2009). TD removes semi-volatile material by adsorption of gaseous compounds. In the TD, the aerosol is heated to 265 °C, and then the evaporated material is adsorbed by activated carbon. TD was used periodically upstream the SP-AMS, aethalometer, and SMPS. The SMPS size distributions were corrected for the losses (Heikkilä et al., 2009). The thermodenuded aerosol is later referred to as ‘Primary’ aerosol in contrast to ‘Fresh’ aerosol including also the semi-volatile material.

2.8. Emission factor calculation

For calculating emission factors (EFs), engine load was available from ship data. Fuel consumption recorded by ship was a sum for two engines, and thus not useful for the calculations of the results for the measured engine. Based on the theoretical fuel consumption of 170 g kWh⁻¹, measured exhaust CO₂ concentrations and fuel composition, fuel consumption (1110 and 300 kg h⁻¹) and exhaust flows (42,400 and 24,400 kg h⁻¹) were calculated at 60–65% (power 6550 kW) and at 17% engine load (1770 kW). These values were used in the calculations of emissions as mass per kg_{fuel} or kWh.

3. Results

3.1. Standard PM and gaseous emissions

Results for gaseous emissions, PM concentration and composition (sulfate, EC, OC, metals) and PAH compounds analyzed from filter samples collected during ~65% load operation of the engine running with HFO fuel at three different measurement points (engine-out, before and after scrubber) are shown in Fig. 2. The PM collected from the engine out exhaust was mainly composed of sulfate, with around one third

of the analyzed mass composed of organic carbon (OC) and elemental carbon (EC) as well as metals (Fig. 2A). High sulfate originates from combustion where part of fuel sulfur form SO₃ which then can form sulfuric acid the particulate phase when the exhaust cools. It can be observed that both the DOC (before scrubber) and scrubber reduced the PM and PAH concentrations. The DOC and the scrubber each halved the concentration of collected sulfate as well as the unanalyzed part of the PM, typically composed of sulfate associated water and ash. The DOC reducing PM phase sulfate is unexpected, compared to previous findings with road vehicles (Karjalainen et al., 2014). The DOC also reduced the concentrations of organic and elemental carbon by 37% and 50%, respectively. In particular, the total concentration of the 7 priority PAHs (Fig. 2B) was reduced by 68% in the DOC by oxidation and further by 40% in the scrubber probably by adsorption to water droplets. Chrysene remained the main PAH compound found after scrubber.

Metals, particularly vanadium (5.62 mg m⁻³), nickel (1.42 mg m⁻³), sodium (0.52 mg m⁻³), iron (0.81 mg m⁻³) and calcium (0.27 mg m⁻³) (Fig. 2A) were present in the engine-out PM when the engine was fueled with HFO. The DOC reduced the metal concentrations (also same after the scrubber) to below detection limit, indicating high filtration efficiency of metal containing particles in the DOC. Also, the EC concentration was observed to decrease ~50% in the DOC calculated from

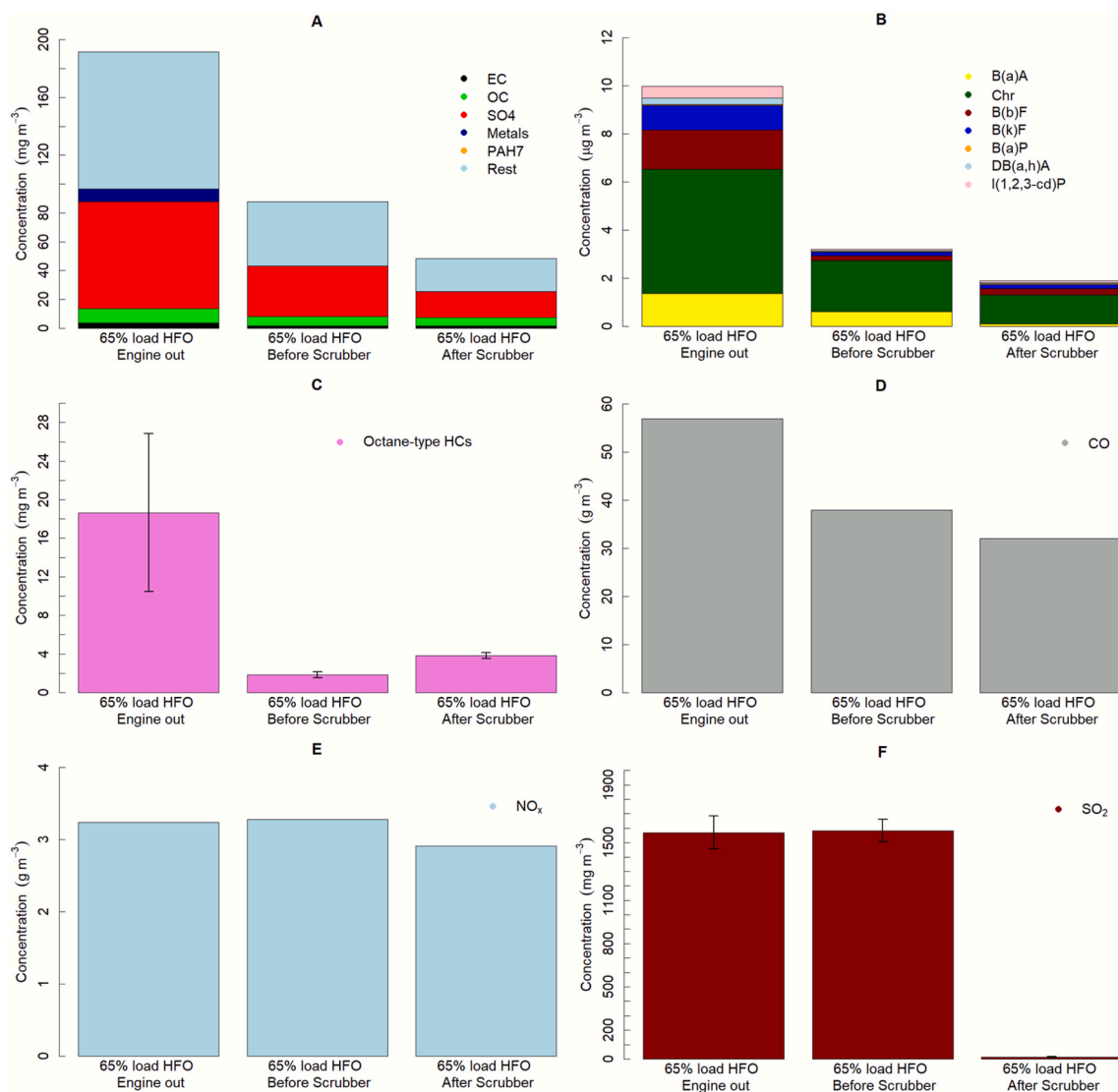


Fig. 2. Chemical composition and PAH compounds in PM analyzed from filter samples (A–B) as well as gaseous emissions measured before DOC (Engine out) (C–F), and before and after scrubber. The results for PM concentration and gaseous compounds after scrubber have been previously reported in Lehtoranta et al. (2019).

comparing engine-out (pre-DOC) and before scrubber (post-DOC) locations.

The results for the gaseous emissions (Fig. 2A–D) show that the DOC effectively oxidized octane-type hydrocarbons present in the exhaust, but less optimally reduced the concentration of CO. This can be explained by different oxidation efficiency, chemical transformation of octane-type VOCs in the DOC or adsorption of these VOCs on the DOC surfaces. Scrubber reduced effectively the SO₂ concentrations from the exhaust gas (Fig. 2F). Effective fuel sulfur content calculated from the measured SO₂ and CO₂ concentrations was on average 2.0–2.5% (m/m) before scrubber, while it was only below 0.02% (m/m) after scrubber, which correspond to over 99% SO_x removal rate. The scrubber also had small effects on the concentrations of octane-type HCs, CO, and NO_x but these effects are within uncertainty of the measurements. The NO_x concentrations were observed to remain stable over the sampling points which was expected since the ship was not equipped with de-NO_x devices. Some degree of NO_x reduction over the scrubber could be explained by absorption of NO₂ to water droplets as suggested by Yang et al. (2021) during low load conditions.

3.2. Fresh and aged aerosol emissions

Besides particulate matter samples collected to filter substrates, detailed real-time composition analysis of submicron PM in the exhaust after scrubber was conducted with the SP-AMS (Fig. 3). We note that the conditions in the FPS sampling system described above favor condensation of semi-volatile constituents of aerosol, and therefore are not

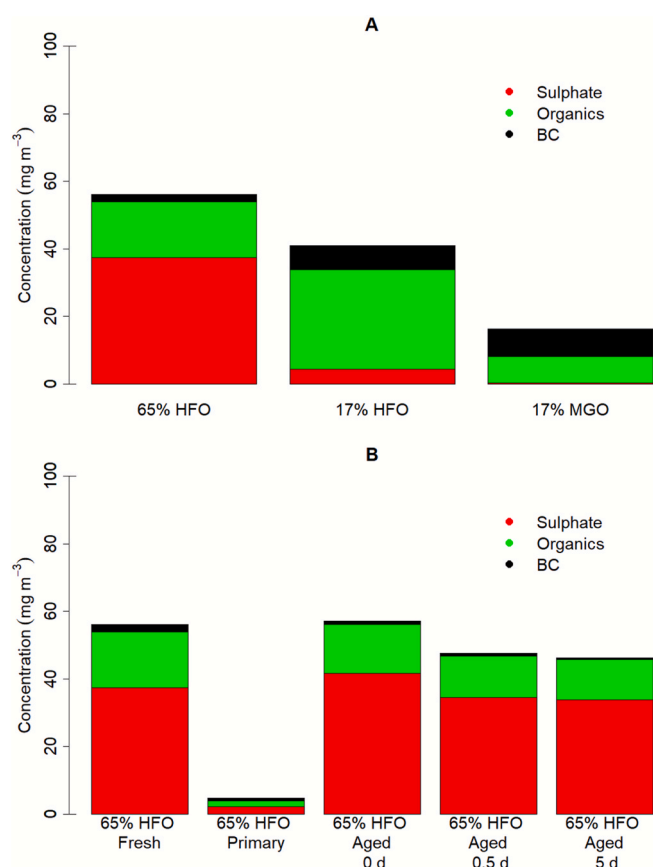


Fig. 3. Concentrations of major chemical components (BC, organics, sulfate) measured with the SP-AMS and an aethalometer (BC) at open sea run and arrivals and departures Port A and B. At open sea the average engine load was 65% and at ports 17%. At port B the used fuel was MGO and open-loop scrubber was turned off. PAM was operated at different lamp voltages corresponding average atmospheric ageing of 0, 0.5, and 5 days.

directly comparable with the results discussed above. However, PM concentrations after scrubber using HFO at 65% load (48 mg m⁻³) were relatively close to the total mass measured by SP-AMS (AE33 for BC) sum concentration shown in Fig. 3A (56 mg m⁻³).

Fig. 3A presents the chemical composition results for HFO fuel under two engine loading conditions (65% and 17%), and the effect of fuel switch from HFO to MGO under 17% engine loading. We can observe that the load decrease from 65% to 17% decreased the total particle concentration by 27% but the observed change in composition was more drastic. With lower load, the sulfate concentrations were 88% lower, but the organics and BC concentrations increased by 78% and 224%, respectively. Reduction in engine load leads to lower combustion temperatures preventing SO₂ oxidation to SO₃ of which the latter will reach particle phase when the exhaust eventually cools explaining the change in observed sulfates level. At the same time, the levels of organics and BC can increase since the lower in-cylinder temperatures lead to more incomplete combustion. Higher BC emissions at low load conditions have been reported e.g. by Gysel et al. (2017) and Zhao et al. (2020). The fuel change from HFO to MGO, lead to almost entire vanishment of sulfates (as in Lehtoranta et al., 2019), a significant decrease in organics (73%) but an increase in BC concentration (13%). All in all, between different fuel and loading conditions there was an inverse relation between BC and sulfates.

In Fig. 3B the open sea cruising with 65% load (HFO fuel, scrubber on) was analyzed and measured with multiple sampling condition: as is (Fresh), downstream thermodenuder (Primary), downstream the PAM with three ages. The most significant change between sampling conditions was observed between “Fresh” and “Primary” condition. All the components, BC, organics, and sulfates were observed to decrease in the TD treatment. In principle, “Fresh” and “Aged 0 d” results should be similar, only difference being blank PAM chamber and an additional diluter. With respect to total concentration these measurement points were quite similar, however there was some difference in BC levels, probably due to variation in engine operation. The effect of ageing in PAM to PM concentrations was observed to be very small, in fact, smaller PM concentrations after ageing were observed than with lamps off. Looking at organic fraction, it appears that no new particle mass (secondary organic aerosol, SOA) is formed in the PAM with lamps on with both settings, instead some losses occur possibly due to fragmentation of organic molecules or evaporation of organics due to heat caused by the lamps.

Another aspect to discuss regarding the properties of particles in the diluted exhaust sample is the particle size distribution measured with the SMPS. Information on how changing the fuel or load affect the particle size distributions is shown in Fig. 4A, changes in sampling conditions (TD, different PAM settings) are shown in Fig. 4B. High particle number concentrations were detected in the exhaust in 65% HFO case, the particles were dispersed over a seemingly unimodal particle mode with GMD of c. 80 nm. When the engine load was decreased from 65% to 17%, the particle size increased, but concentration levels were reduced by 81%. Also, the “right shoulder” of the size distribution is showing higher concentrations possibly due to higher level of soot (BC rich) particles that are generally found in these sizes (Ntziachristos et al., 2016). When fuel was changed to MGO, the particle size distribution peak shifted to smaller sizes, however, the particle number concentration remained constant.

A bimodal size distribution was observed for non-volatile particles with smaller mode in ~25 nm and larger mode in ~80 nm. Without TD, a seemingly unimodal size distribution with maximum at ~80 nm was observed. In addition, the size of the larger mode was decreased. Aged zero days should be similar as the “Fresh” case but there were smaller concentration levels downstream the PAM. This may be caused by losses in the PAM associated with extra tubing and Nafion humidifier. When moderate photochemistry was applied (Aged 0.5 days case) there was no changes in the main particle mode at (~100 nm), however, as the amount of oxidants was increased, we started to observe a nucleation

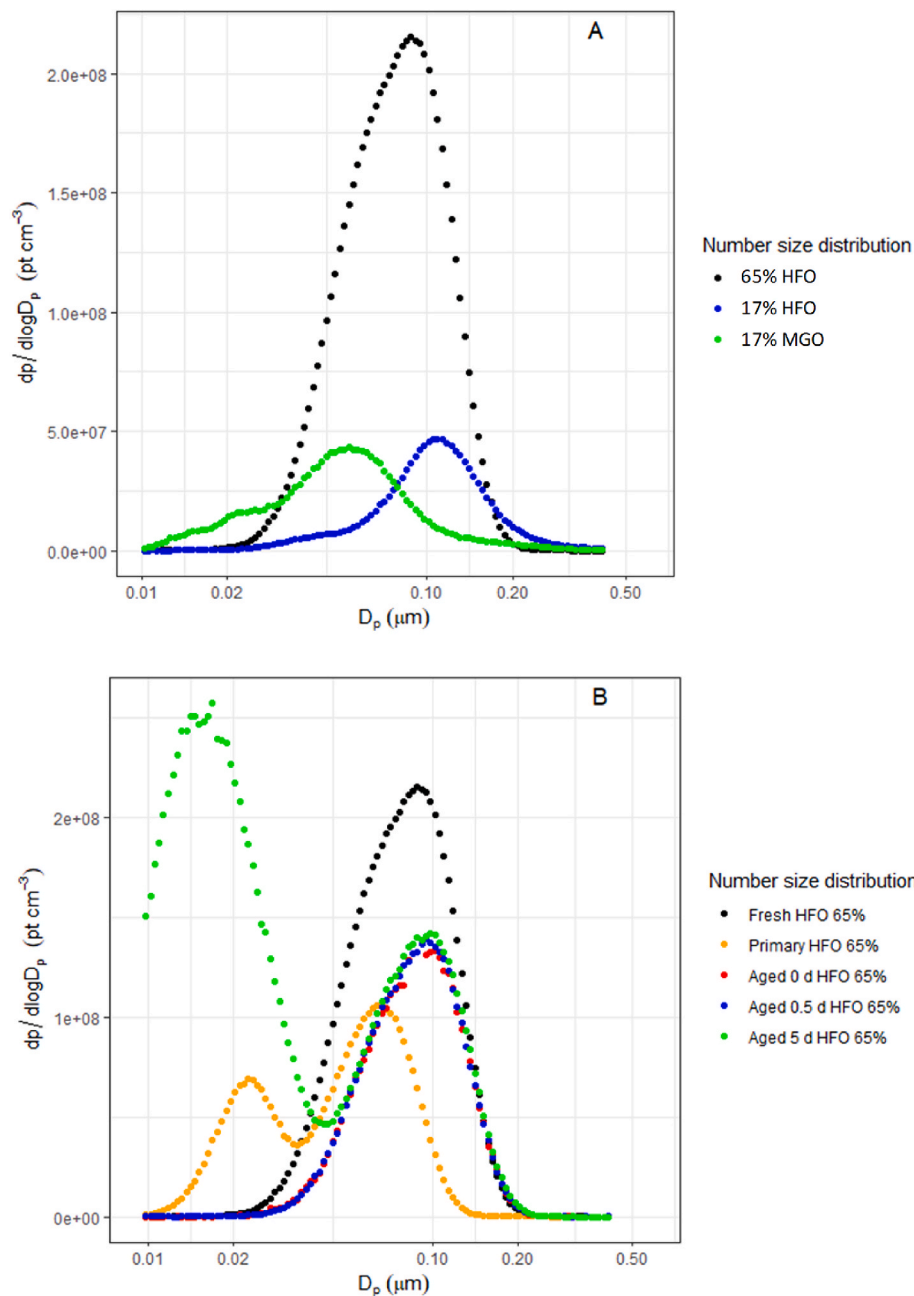


Fig. 4. Particle size distributions measured with an SMPS at open sea run and arrivals and departures Port A and B. At open sea the engine load was 65% and at ports 17% (A). At port B the used fuel was MGO and open-loop scrubber was turned off. In (B), “Fresh” was measured directly downstream the FPS dilution, “Primary” downstream a thermodeuder, and “Aged 0, 0.5 d, and 5 d” downstream the PAM chamber with different lamp voltages corresponding to different photochemical ages in days.

mode (in “Aged 5 d” case). Formation of new nucleation particles due to remaining impurities is typical behavior in the PAM when photochemistry is active, however, these small particles do not necessarily affect the total PM. Especially they cannot be observed in the SP-AMS due to losses of nanoparticles in the aerodynamic lens.

3.3. Emission profiles close to harbors

Most of the cruising time was spent on the open sea where the ship mostly stabilizes the engine loading to a constant setting (~65% here). However, in proximity to the harbors, the operation of the engine in question was dramatically changed, as well as usage of the fuel and scrubber. In port A, the arrival and departure were operated with the scrubber on and with HFO fuel but in port B the fuel was first changed to MGO, after this the scrubber was deactivated (Fig. 5). When the ship departed from port B, MGO fuel was used during the first hour, after this the scrubber and fuel switch to HFO were simultaneously activated.

Additionally, related to port B, the fuel change takes approximately 1 h before which was detected e.g. in sulfate concentration data of SP-AMS in Fig. 5 (bottom panel) during both arrival and departure. This way it was ensured that the engine was not combusting HFO fuel when the scrubber was deactivated.

In data related to operation close to port A (Fig. 5, top panel), there is a significant change in concentrations and composition measured with the SP-AMS when the engine load was changed. With decreased load, the sulfate concentrations merely vanished but the level of BC was increased. Close to harbor, the loading profile did not remain constant since this engine was used to generate steady low power and occasionally load spikes were caused by maneuvering. Load switches were clearly detectable in the particle levels measured with the SP-AMS. The levels of SO_2 in the exhaust were low, but somehow increased after the departure when engine load was increased.

Compared to the port A, the engine operation in port B was much more diverse. The changes in fuel, scrubber operation and engine load

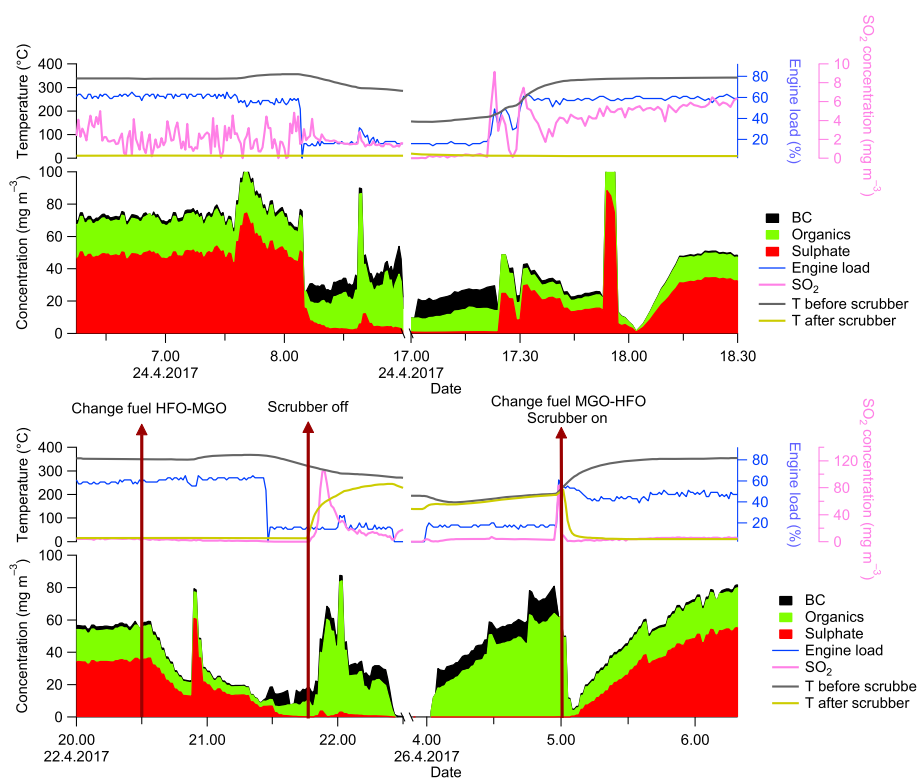


Fig. 5. Real-time concentrations of chemical compounds measured by the SP-AMS, together with engine load and SO₂ concentration of the exhaust during arrivals and departures to and from harbor A (top) and to and from harbor B (bottom).

were clearly detectable in the PM chemical composition results of the SP-AMS. The fuel change from HFO to MGO was visible in sulfate levels that decrease when more and more HFO is replaced with MGO. When the load was dropped, there was an increase in BC levels due to e.g. lower combustion temperature, similarly as reported (Aakko-Saksa et al., 2016; Winnes et al., 2020). But when scrubber was deactivated, surprisingly the SO₂ emission rapidly increased and stayed on a higher level for the rest of the journey. After departure, there was an increase in the particle mass, due to constant increase in the organics signal. When fuel was switched and scrubber activated, there was another SO₂ spike. After this, the concentrations gradually increased mainly because the fraction of combusted HFO fuel increased gradually, and thus higher sulfate shares were measured with the SP-AMS.

3.4. Emission factors

Concentrations (m⁻³) and emissions factors (kWh⁻¹ or kg_{fuel}⁻¹) for gaseous and particulate exhaust components at high/low load with HFO fuel and at low load for MGO fuel are given in Table 1. Gaseous emission factors are given for CO₂, CO, NO_x, SO₂ and octane-type HC. Emission factors show high mass for NO_x (56.5–83.5 g kg_{fuel}⁻¹) but relatively lower masses for CO (0.9–8.7 g kg_{fuel}⁻¹) and SO₂ (0.2–4.0 g kg_{fuel}⁻¹). Most compounds have higher emission factors for low load compared to high load where in NO_x concentrations opposite trend is shown.

Particulate phase analysis includes emission factors for particle number (PN), mass (PM, with several methods), and composition (off-line/online methods). PN emission factors are found in the range of 0.35–2.9 × 10¹⁵ kg_{fuel}⁻¹, highest with HFO high load and lowest with MGO low load. PM emission factor levels were 1.9 g kg_{fuel}⁻¹, 2.3 g kg_{fuel}⁻¹ and 1.7 g kg_{fuel}⁻¹ for HFO high, HFO low and MGO low load cases respectively, indicating only minor influence of fuel switch from HFO to MGO. Fuel change had larger effects in PN than in PM. In the case of HFO fuel, the emission factors of PM were larger calculated from SMPS compared to the sum of chemical components (SP-AMS + AE33).

But for MGO fuel, the sum of chemical components showed higher result.

The dominant contributor to PM was sulfates with HFO but with EF of 1100 mg kg_{fuel}⁻¹ (high load) but decreased down to 2.2 mg kg_{fuel}⁻¹ with MGO at low load. Emission factor of total organics however increased from 886 mg kg_{fuel}⁻¹ to 3450 mg kg_{fuel}⁻¹ over the fuel switch from HFO to MGO at low load. BC concentrations measured with different devices at ship exhaust emissions were generally low, below 5 mg/m³. For example, at 65% engine load using HFO, BC was 2.9 mg/m³ (87 mg kg_{fuel}⁻¹, 15 mg kWh⁻¹). Only at the lowest engine load (17%), BC concentrations were high (up to 30 mg m⁻³). Larger BC concentrations when engine was operating 17% load compared to 65% load were observed for both fuels. Concentration of total organics were quite similar for both engine loads when HFO fuel was used but lower when MGO fuel was used. The BC measured by AE33 showed higher emission factors than EC measured from filter samples (65 mg kg_{fuel}⁻¹ vs. 51.4 mg kg_{fuel}⁻¹).

4. Discussion

4.1. Gaseous emissions

Measurements showed that scrubber effectively reduced the SO₂ concentrations from the exhaust gas mainly by dissolving gaseous SO₂ molecules into sprayed sea water droplets. Calculated fuel sulfur content was on average 2.0–2.5% (m/m) upstream the scrubber, but below 0.02% (m/m) downstream the scrubber, which corresponds to over 99% SO₂ reduction rate. Scrubber also reduced the NO_x concentrations of exhaust to some extent. CO and HC concentrations on the other hand were reduced already in the DOC unit.

When the low-sulfur fuel was used, the scrubber was deactivated while approaching harbor B which led to a rapid increase in the exhaust temperature at the scrubber location. This phenomenon increased the gaseous SO₂ concentrations measured downstream the scrubber, first

Table 1

Emission factors for particulate and gaseous emissions with 65% and 17% loads and HFO and MGO after scrubber. Following components were below detection limit and are not included: Metals, Methane CH₄, Ethylene C₂H₄, Formaldehyde HCHO, Acetaldehyde CH₃CHO, Ammonia NH₃, Nitrous oxide N₂O.

Dry, STP 273.15 °C & 101.323 kPa		On-sea	Close to harbor	Close to harbor
		~65% load HFO	~17% load HFO	~17% load MGO
Gaseous				
CO ₂	g/m ³	108.4	61	54
	g/kWh	528.6	646	566
	g/	3110.3	3806	3331
CO	kg _{fuel} g/m ³	0.03	0.14	0.08
	g/kWh	0.2	1.5	0.9
	g/	0.9	8.7	5.2
NO _x	kg _{fuel} g/m ³	2.9	0.9	0.9
	g/kWh	14.2	9.7	9.6
	g/	83.5	56.7	56.5
SO ₂	kg _{fuel} g/m ³	0.015	0.003	0.065
	g/kWh	0.071	0.03	0.68
	g/	0.419	0.2	4.0
Octane-type HC	kg _{fuel} g/m ³	0.004	0.004	0.029
	g/kWh	0.019	0.043	0.31
	g/	0.110	0.3	1.8
Particulate				
PN All (SMPS)	1/cm ³	9.77 × 10 ⁷	1.90 × 10 ⁷	5.62 × 10 ⁶
	1/kWh	4.89 × 10 ¹⁴	2.03 × 10 ¹⁴	6.01 × 10 ¹³
	1/	2.88 × 10 ¹⁵	1.20 × 10 ¹⁵	3.54 × 10 ¹⁴
PM (SMPS)	kg _{fuel} mg/m ³	65.3	37.2	27.1
	mg/	327	397	290
	kWh			
	mg/	1925	2337	1706
PM (filter)	kg _{fuel} mg/m ³	48.2	n/a	n/a
	mg/	235.0		
	kWh			
	mg/	1382.9 (n = 9)		
EC (filter)	kg _{fuel} mg/m ³	1.8	n/a	n/a
	mg/	8.7		
	kWh			
	mg/	51.4 (n = 3)		
OC (filter)	kg _{fuel} mg/m ³	5.6	n/a	n/a
	mg/	27.2		
	kWh			
	mg/	159.8 (n = 3)		
SO ₄ (filter)	kg _{fuel} mg/m ³	18.2	n/a	n/a
	mg/	88.6		
	kWh			
	mg/	521.1 (n = 2)		
PAH7 (filter)	kg _{fuel} mg/m ³	0.0	n/a	n/a
	mg/	0.0		
	kWh			
	mg/	0.1 (n = 2)		
Rest, mainly oxygen (filter)	kg _{fuel} mg/m ³	20.4	n/a	n/a
	mg/	99.3		
	kWh			
	mg/	584.6 (n = 2)		
PM (SP-AMS, BC from AE33)	kg _{fuel} mg/m ³	56.2	26.7	68.4
	mg/	281	285	731
	kWh			
	mg/	1655	1680	4305
SO ₄ (SP-AMS)	kg _{fuel} mg/m ³	37.5	1.0	0.0
	mg/	188	10.6	0.4

Table 1 (continued)

Dry, STP 273.15 °C & 101.323 kPa		On-sea	Close to harbor	Close to harbor
		~65% load HFO	~17% load HFO	~17% load MGO
	mg/ kWh			
	mg/	1105	62.2	2.2
	kg _{fuel} mg/m ³			
Organics (SP-AMS)	mg/	16.5	14.1	54.9
	kWh	82.4	150	586
	mg/	485	886	3451
	kg _{fuel} mg/m ³			
BC (FSN-based, AVL 415S)	mg/	2.9	n/a	19.4
	kWh	14.3		205
	mg/	84.1 (n = 29)		1210 (n = 1)
	kg _{fuel} mg/m ³			
BC (AE33)	mg/	2.5	11.6	13.2
	kWh	11.1	124	141
	mg/	65	732	828
	kg _{fuel}			

the concentrations increased followed by a decrease. Apparently, dissolved sulfur compounds are released back in the gaseous phase due to heat on the scrubber and surrounding surfaces. Later all available excess SO₂ gets consumed, and concentrations begin to decrease and eventually reach fuel originated levels. In principle, this phenomenon is directly connected to the scrubber deactivation process, hence the SO₂ peak cannot be easily avoided. However, in some cases ships should emit this excess SO₂ emission before entering a SECA area to reduce local emissions in coastal regions. The calculated SO₂ level corresponding to the SECA limit value was exceeded over a period of 15 min so that the SO₂ emission during this period corresponds to 30 min of emissions at the limit value. During the whole cruise the SO₂ emission is on average well below the SECA regulation. However, this type of exceeding during fuel change may have local importance.

4.2. Particulate emissions

Conducted measurements show that PM in ship exhaust emissions consisted of sulfates, elemental and organic carbon, metals, and associated oxygen. In terms of fuel, the engine-out PM was higher for HFO than for MGO. The DOC seemed to reduce particulate sulfate and associated oxygen, and also OC of PM, and scrubber seemed to further reduce their concentrations. Especially the DOC seemed to reduce the metal concentrations to below detection limit, which is surprising since one usually does not consider high filtration efficiencies for DOC system, especially as systems in road vehicles have shown (Johnson and Kittelson, 1996). Differences in BC concentrations before and after emission control devices were within the standard deviation, although a slight decrease over scrubber was indicated.

The particle number size distributions were unimodal at (~80 nm) but the application of the TD showed a bi-modal size distribution so that the smaller particle mode was at ~25 nm size in the HFO 65% case. This would indicate that there are two independent formation pathways for these particle modes. This phenomenon of a single mode splitting into two separate mode has been previously observed in the laboratory for a marine engine running with HFO type fuel (Amanatidis et al., 2018; Ntziachristos et al., 2016). Additionally, it appears that nonvolatile particle number equals the total particle number observed, even though total PM contains mainly semi-volatile species. Since the TD is a strong evaporator, particle number is not expected to reduce by evaporation in any plume under realistic atmospheric conditions. The fuel switch from

HFO to MGO resulted in smaller exhaust particle sizes as reported (Anderson et al., 2015).

During open sea cruising (65% engine load, scrubber on) the major chemical components in particulate phase were sulfate (66%) and organics (30%). The sulfate concentrations measured from sampled filters showed slightly lower concentrations which are due to the differences in sampling, dilution, and measurement principles. The contribution of BC at open sea cruising was low (4%), majorly agreeing with previous findings (Lehtoranta et al., 2019; Winnes et al., 2020; Zhang et al., 2021). BC on the other hand showed increased concentrations when the engine load was decreased, similarly as previously reported (Lack and Corbett, 2012). This mainly relates to more effective combustion when higher engine loads are used.

Exhaust aftertreatment (DOC + scrubber) effectively removed gaseous components like SO₂ and hydrocarbons, which via oxidation steps can form secondary PM in the atmosphere. The measurements using PAM chamber, which simulates the formation of secondary PM in the atmosphere, showed that no new PM was formed in the photo-oxidation process which has been observed previously for plumes measured with a PAM reactor in an ambient monitoring site in Baltic SECA area (Ausmeel et al., 2020). It seems that the exhaust aftertreatment is effective to eliminate secondary PM formation in the atmosphere. SOA precursors may have been removed e.g., in the DOC mainly via oxidation of organic molecules or in the scrubber by dissolving into cold water droplets (~5 °C), or by combined effects of these two units.

This study shows that many emission components of modern ship equipped with DOC + scrubber aftertreatment like SO₂, metals, and secondary aerosol are very low. However, the gaseous NO_x emissions and the particle emissions like PN, PM, and BC are relatively high. Therefore, we see that the next steps in the development of emissions control systems and emission regulations should focus on the particle emission reduction to improve air quality in coastal regions and reduce adverse climate effects. One must bear in mind that scrubber effluent emission (Jalkanen et al., 2021) can have a major influence in the sea ecosystem which has to be considered in the total comparison of low sulfur fuels and scrubber system alternatives.

5. Conclusions

This paper presents experimental findings from high-end real-time measurements of gaseous and particulate pollutants onboard a RoPax ship inside a SECA equipped with a diesel oxidation catalyst and a scrubber as an exhaust aftertreatment. Measurements showed that the scrubber effectively reduced SO₂ concentrations with over 99% rate, which indicates that scrubbers are very effective in real-world sulfur control. Controlled switching off the scrubber after change to low sulfur fuel increased SO₂ concentrations for a brief time but this doesn't represent significant emissions over the whole cruise. In terms of fuel, the engine-out PM was higher for heavy fuel oil than for marine gas oil. During open sea cruising (65% load) the major chemical components in particulate phase were sulfate (66%) and organics (30%). The contribution of black carbon (BC) was low (~4%). Decreased engine load on the other hand increased exhaust concentrations of BC by a factor exceeding four due to worse fuel combustion conditions. It is obvious that sulfate in PM is related to combustion of fuel sulfur. It appears that BC and organic PM formation are occurring with marine fuels. Hence, particulate free exhaust is not reached with DOC and scrubber solutions, instead, more efficient particle filtration would be needed. In the sense of air quality, PM abatement is important especially close to harbor where BC related emission factors are over 10-fold compared to open sea. The secondary aerosol formation potential of the emitted exhaust measured with an oxidation flow reactor and an aerosol mass spectrometer was found negligible. Thus, either DOC, scrubber, or their combination is efficient in eliminating SOA precursors. Overall, in addition to targeting sulfur and NO_x emissions from shipping, future efforts on airborne emission prevention should focus on to mitigate

harmful particle emissions which remain as a challenge for marine fleets.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

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