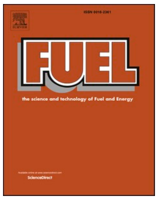
Fuel 304 (2021) 121323

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel



Full Length Article

Controlling emissions from an ocean-going container vessel with a wet scrubber system

Jiacheng Yang[a,b], Tianbo Tang[a,b], Yu Jiang[a,b], Georgios Karavalakis[a,b], Thomas D. Durbin[a,b], J. Wayne Miller[a,b], David R. Cocker III[a,b], Kent C. Johnson[a,b,*]

[a] University of California, Bourns College of Engineering, Center for Environmental Research and Technology (CE-CERT), 1084 Columbia Avenue, Riverside, CA 92507, USA
[b] Department of Chemical and Environmental Engineering, Bourns College of Engineering, University of California, Riverside, CA 92521, USA

ARTICLE INFO

Keywords:
Ship emissions
Scrubber
$PM_{2.5}$ emissions
SOx emissions
Heavy fuel oil

ABSTRACT

This study assessed the real-world gaseous and particulate emissions for a wet scrubber retrofit to an existing container ocean-going vessel as it cruised from Tacoma Washington to Anchorage Alaska. The vessel was operated with a high sulfur heavy fuel oil and testing was performed following the ISI 8178 E2 steady test cycle. The scrubber unit provided more than a 95% removal efficiency of sulfur dioxide (SO_2) emissions across all engine loads. In contrast to the higher removal efficiencies for SO_2 emissions, the scrubber only removed approximately 10% (ISO weighted reduction) of particulate matter ($PM_{2.5}$) emissions. $PM_{2.5}$ composition was primarily composed of sulfate, followed by organic carbon (OC) and elemental carbon (EC). Pre- and post-scrubber sulfate levels were similar, indicating why the $PM_{2.5}$ removal efficiencies were low. This phenomenon was likely due to the formation of small sulfuric acid particles in the scrubber fluid that were not efficiently removed by impaction, influencing $PM_{2.5}$ mass emission measurements.

1. Introduction

Ocean going vessels (OGVs) transport more than 80% of global trade by volume, with international maritime transport significantly contributing to pollutants related to global warming, air quality and visibility, and human health for coastal communities [1–4]. Ships are responsible for about 1 billion tons of carbon dioxide (CO_2) emissions, a strong greenhouse gas, representing approximately 3% of global CO_2 emissions, with further projections showing that the international maritime sector could reach up to 17% of global CO_2 emissions in 2050 [5,6]. Shipping is also a significant source of anthropogenic emissions, including nitrogen oxides (NOx), sulfur oxides (SOx), particulate matter (PM), carbon monoxide (CO), and volatile organic compounds [7–10]. These emissions are important sources for secondary organic and inorganic aerosol formation on local and regional scales, and also contribute to increased ozone (O_3) levels in the atmosphere [11,12].

Efforts to reduce environmental pollution from maritime transport have been a priority in recent years, with the International Maritime Organization (IMO) adopting strict regulations under Annex VI of the International Convention for the Prevention of Marine Pollution from Ships (MARPOL) by implementing Emission Control Areas (ECAs). These ECAs include the North Sea and English Channel, Baltic Sea, North America, and United States Caribbean Sea for all vessels over 300 gross tons (GT). The North America and United States Caribbean Sea ECAs have also set limits for NOx emissions. Emissions of SOx are more strictly controlled within these areas by indirectly regulating the upper limit for sulfur content in marine fuels. From January 1, 2020 the current global sulfur limit in marine fuels dropped to 0.50% from 3.5%. For ships operating within designated ECAs, the sulfur limit was further reduced to 0.1% from a limit of 1.0%, with this stricter legislation coming into effect after January 1, 2015.

Traditionally, marine low-speed two-stroke engines are designed to burn heavy fuel oil (HFO) or marine gasoil (MGO). HFOs are produced from residuals of the crude oil refining process and include residuums of the thermal and catalytic cracking, visbreaking, and coking processes. HFOs usually contain higher concentrations of sulfur, ash, metals, heavy hydrocarbons (aromatics and asphaltenes), and water than middle distillate MGOs. Elevated SOx and PM emissions from HFO combustion

---

[*] Corresponding author at: University of California, Bourns College of Engineering, Center for Environmental Research and Technology (CE-CERT), 1084 Columbia Avenue, Riverside, CA 92507, USA.

E-mail address: kjohnson@cert.ucr.edu (K.C. Johnson).

https://doi.org/10.1016/j.fuel.2021.121323
Received 23 April 2021; Received in revised form 17 June 2021; Accepted 20 June 2021

are mainly dependent on the concentration of sulfur in the fuel [10,13,14]. Sulfur dioxide (SO_2), the prime constituent of SOx, is oxidized in the exhaust to form sulfur trioxide (SO_3), which is subsequently combined with water to form sulfates that contribute to total PM emissions [15]. A number of studies have shown important SOx, NOx, and PM emissions benefits from the application of two strategies: fuel switching and the use of new generation ultra-low sulfur heavy fuel oils (ULSHFO) [14,16–18]. Recent studies conducted by McCaffery et al. [10] and Gysel et al. [19] on a Tier 2 container vessel and a very large crude carrier vessel, respectively, using ECA compliant ULSHFO fuels, reported reductions in NOx, PM, SOx, and carbon monoxide (CO) emission levels compared to other studies utilizing marine fuels with high sulfur contents [7,9,16,20,21].

An attractive and widely used emissions abatement technology to primarily control SOx emissions and to some degree PM and NOx emissions, is to employ an exhaust gas cleaning system (EGCS) or a scrubber [22–24]. This alternative allows ships to use high sulfur and considerably less expensive HFOs instead of higher quality ULSHFOs in designated ECAs. The economic feasibility to install a scrubber on-board is not entirely clear in the current environment, where the COVID-19 pandemic significantly slowed global shipping trade, oil prices dropped significantly, and shippers reached an overcapacity in storing ECA compliant ULSHFO. For the maritime sector, wet scrubbers are mostly used to remove SOx emissions, which pass the exhaust through a liquid media (sea water or chemically treated fresh water) [25,26]. Wet scrubbers normally include open loop and closed loop systems, as well as hybrid systems [27]. In open loop systems, sea water is used to neutralize SOx in the exhaust and then is discharged from the system to the sea with minimal or no treatment [25]. This process will likely result in a release of CO_2 emissions, as well as the release of organic and inorganic pollutants suspended in the washwater discharged in the aquatic ecosystem [22,26]. In the closed loop systems, the fresh or sea water enhanced with sodium hydroxide is used to reduce SOx emissions and continuously cleaned and recirculates in the system. Small amounts of discharged water typically occur in closed loop systems (bleed off), although this water is purified in a treatment plant to remove the residue sludge containing PM, polycyclic aromatic hydrocarbons (PAHs) [27–29]. This residual sludge is usually temporarily stored on board for on-land disposal. Hybrid systems can operate in both open and closed loop modes, where ships utilizing these systems can operate in open loop when cruising in open sea and in closed loop when operated in ECAs or at berth [27,28].

There are several studies in the open literature focused on the investigation of scrubber systems installed in the main and auxiliary engines, and boilers for the reduction of gaseous and PM emissions from ships [24,25,30–33]. Caiazzo et al. [34] demonstrated SO_2 emissions reductions of up to 93% from a marine diesel engine operated on HFO and retrofitted with an open loop scrubber system. Winnes and coworkers [32] reported reductions in SO_2, SO_3, non-methane hydrocarbon, PAHs, and PM emissions when they tested a RoPax ferry with a four-stroke engine operated on HFO equipped with seawater scrubber. In their experiments, SO_2 emissions reduced up to 99% by the scrubber at all engine loads. Similar findings were seen in a different study employing a two-stroke, slow-speed diesel (SSD) marine engine with low sulfur HFO and a wet scrubber providing desulfurization efficiencies above 99% [30].

The present study investigates the effectiveness of a hybrid wet scrubber system designed and operated in both open loop and closed loop modes when retrofitted on a D7 Class contained vessel while running on high sulfur HFO. In-use gaseous and particulate emissions were measured pre and post the scrubber system from the main and auxiliary engines at different engine loads while the vessel was operated in a designated ECA and during cruising from the port of Tacoma, Washington to the port of Anchorage, Alaska. Results reported here are intended to provide information on the performance of a commercially available EGCS used in marine applications and to help understand their impact on the environment.

2. Experimental

2.1. Test platform: vessel and fuels

Testing was performed on a D7 Class container vessel that was built in 1987 and moves up to 1676 twenty-foot equivalent units (TEUs) and 249 reefers with a gross tonnage of 20,965. The vessel was equipped with one main engine (ME), two main generators (MGs), two auxiliary engines (AEs), and one boiler. The ME was a Tier 0 1986 build Mitsui B&W 7L70 two-stroke SSD engine with 7 cylinders, 16.6 megawatts (MW), and with 177,962 operation hours. The main generators were both Tier 0 model year 1986 Wartsila 6R32D, equipped with 6 cylinders, 2.1 MW medium-speed, 4-stroke diesel engines with 70,096 and 79,020 operation hours, respectively. During normal at sea operation, the main generators represent approximately 7% of the total exhaust flow compared to the main engine, indicating that the main engine dominates the contribution of emissions from this vessel.

Commercial marine high sulfur content HFO meeting RMG-380 specifications was used during testing, with the main properties shown in Table 1. The lubricant oil used for the main engine cylinder was MobilGard® 300, and for the main engine camshaft was MobilGard® 560.

2.2. Scrubber system

The vessel was retrofitted with a wet scrubber system to allow the use of high sulfur HFO fuels while operating in designated ECAs. Only the main engine and the two larger main generators were connected to the scrubber system, whereas the two auxiliary engines and the boiler were not designed to operate with the scrubber, as shown in the experimental setup in Fig. 1. The scrubber system was designed by Alfa-Laval and included an exhaust gas inlet section, a high-pressure spray nozzle to create small droplets (~100 μm), a jet section, and an absorber section. The jet section was designed to accelerate particles and gases to create greater mixing and a chance for SOx to be removed via absorption, and $PM_{2.5}$ by diffusion/impaction mechanisms. In the absorber section, the flow is slower, allowing time for collecting the mist with absorbed SOx and the $PM_{2.5}$ by diffusion to the droplets [33]. Demister pads follow the absorption section to remove larger water droplets before the gas is vented to the atmosphere.

The scrubber on this vessel was designed for both an open loop mode at-sea where the ocean water provides the alkalinity needed to meet the scrubber design and a closed loop mode during operation with low-alkalinity water. During closed loop mode, the scrubber water is fortified with added caustic solutions to boost alkalinity and re-circulated. This scrubber was designed to work with up to 3 wt% sulfur in the fuel. Above 3 wt%, the SOx absorption efficiency decreases with both decreasing salinity and alkalinity [25].

2.3. Testing protocol

Normally, the main propulsion engine while at sea operates at 80–85% load, which represents a time fraction of about 90% of the total trip. Higher main engine loads are uncommon, but are possible for short durations of the trip if requested. While on the voyage, one main

Table 1
Selected properties of the HFO.

Fuel properties	Test method	Result	Specification
Density at 15 °C (kg/m^3)	ISO 12185	989.3	991.0 max
Viscosity at 50 °C (mm^2/s)	ASTM D445	306.6	380.0 max
Micro carbon residue (mass %)	ASTM D524	12.59	18.00 max
Sulfur (mass %)	ASTM D2622	1.89	3.5 max
Calculated carbon aromaticity index (CCAI)	ISO 8217	825.5	870 max

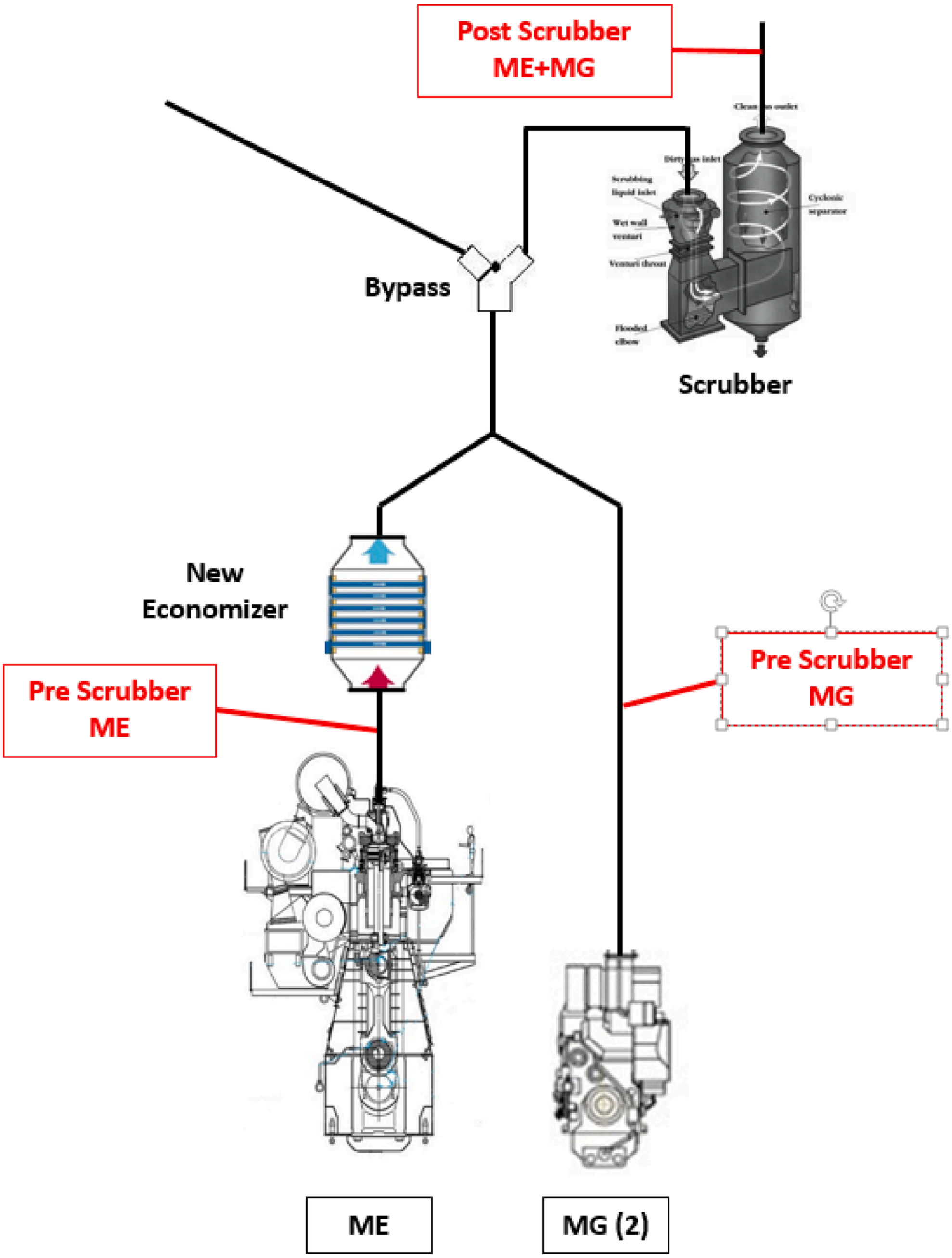


Fig. 1. Schematic diagram of the experimental setup showing the OGV engine layout.

generator is typically operated for ship services, hotel, maneuvering, and reefer power. The generator load typically varies from 45% to 65% and depends on the reefer's needs. During berth entry and exit maneuvers, the main engine power is reduced between 25% and 50% load, while the main generator remains at 45%-65% load. While in port and during loading and unloading goods, the main generator is typically at a load between 45% and 65% (i.e., without shore power), with the main engine turned off. Ship operation during berth entry, exit, and maneuvering usually represents about 1% (or less) of the total trip, while dock conditions account about 9% of the total trip.

For this study, emissions measurements for the main generators were conducted with the generator turned off and 50% load. At sea, main engine operation followed the certification loads for the E3 cycle in International Organization for Standardization (ISO) 8178-4, as closely as possible during ship operations. The load/power points for the main engine were with the engine turned off and at 50%, 75%, and maximum load (92%), which represented 4%, 48%, 70%, and 85%, respectively, of the scrubber's maximum flow capacity. Table 2 lists the engine load points, percent of scrubber capacity, and tunnel dilution where pre-scrubber emissions were measured separately for the main engine and main generators, and post-scrubber emissions measured for the combined exhaust of the main engine and main generators.

The test points covered the range of the normal scrubber exhaust flow and represented about 85% of the weighting factor used for determining the overall emission factor. Prior to the first test, the engine was operated for 30 min at maximum power to stabilize emissions. At subsequent scrubber capacity points, measurements for gaseous and $PM_{2.5}$ mass emissions were conducted when the gas concentration values stabilized. Gaseous and $PM_{2.5}$ mass emissions measurements were made for 5–20 min to allow sufficient time for $PM_{2.5}$ mass filter loading. Testing was conducted in triplicate. It should be noted that testing on the main generator pre-scrubber was conducted in Tacoma,

Table 2
Test matrix and sampling conditions.

Mode	Location	Source	Scrubber	Me load	MG load	Scrubber capacity	Dilution ratio
4	At-berth	MG	Pre	0%	50%	–	20:1
3	At-sea	ME	Pre	50%	50%	–	12:1
2	At-sea	ME	Pre	75%	50%	–	8:1
2	At-sea	ME	Pre	75%	50%	–	8:1
1	At-sea	ME	Pre	92%	50%	–	6:1
1	At-sea	ME + MG	Post	92%	50%	85%	6:1
2	At-sea	ME + MG	Post	75%	50%	70%	8:1
2	At-sea	ME + MG[1]	Post	75%	50%	70%	8:1
3	At-sea	ME + MG	Post	50%	50%	48%	11:1
1	At-sea	ME-only	Post	92%	0%	n/a	6:1
2	At-sea	ME + MG*	Post	75%	50%	70%	8:1
4	At-berth	MG	Post	0%	50%	4%	20:1

*Closed loop vs. open loop scrubber control evaluated at two conditions 85 and 70% scrubber flow percent.

Washington, whereas testing on the main generator post-scrubber was conducted in Anchorage, Alaska. The scrubber was operated in an open loop mode during at sea operation and a closed loop mode at berth.

2.4. *Emissions sampling and measurement*

The exhaust duct configuration allowed the engine-out emissions from the main engine and main generator to be measured separately; however, both streams were combined before the scrubber unit, so only combined emissions were monitored after the scrubber. The post-scrubber sampling port was located approximately 1 m above the absorber section of the scrubber unit and 0.5 m below the vessel's continuous emissions monitor (CEM).

Exhaust concentrations of CO, CO_2, NOx, oxygen (O_2), and SOx emissions were continuously measured following the ISO 8178-2 protocol with a Horiba PG-350 portable multi-gas analyzer. The PG-350 utilizes Non-Dispersive Infra-Red (NDIR) detectors to measure CO, CO_2, and SO_2 and a chemiluminescence detector (CLD) for NOx measurement. The PG-350 analyzer was calibrated using EPA protocol gases several times during the testing and measured drift was accounted for during the analysis of the data. Instrument drift met the manufacturer's specification.

The $PM_{2.5}$ mass emission measurements were made using a partial flow dilution system design based on the ISO 8178-1 protocol and on conditioning the diluted exhaust gas, as per 40 CFR Part 1065. The dilution ratio ranged from 6:1 for the highest flow rate on the scrubber system to 20:1 for the lower flow conditions on the scrubber, as recommended in 40 CFR Part 1065. The residence time was approximately 1.5 s, a filter flow rate of 15 slpm, with a dilution tunnel of two inch outside diameter, no transfer line (direct coupled to the exhaust) and mass flow controllers sampling through URG filter holders equipped with Delrin cassettes housed for Whatman Teflon filters and Quartz filters. The dilution system maintained the $PM_{2.5}$ sampling to 47 °C± 5 °C for both the pre-scrubber and post-scrubber testing. Note during post-scrubber testing the exhaust temperature was near sea water temperature and required heating to get the sample to the same conditions of the pre-scrubber and CFR 1065 conditions. Heating was implemented using heated dilution air, a heated sample line, and a heated tunnel body. This system was used for both pre- and post-scrubber samples, where more heating was needed for the post-scrubber sample to achieve the same filter temperature. After sample conditioning, $PM_{2.5}$ mass was collected on a Teflon filter and weighed off-line daily with a Mettler Toledo ultra-precision balance (0.1 μg resolution) placed in a Heraeus climate chamber until consecutive measurements were within 3.5 μg.

$PM_{2.5}$ mass was fractionated into sulfate, organic carbon (OC), elemental carbon (EC) and black carbon (BC). Sulfate was removed from the Teflon filter by sonication with deionized water and a small amount of alcohol and subsequently analyzed using a Dionex ICS-3000 ion chromatography (IC) via modified EPA Method 4.2. A thermal/optical method analyzed the carbon aerosol deposited on a quartz filter collected in parallel with the Teflon filter according to the National Institute for Occupational Safety and Health (NIOSH) 5040 reference method. The analysis reported elemental carbon and organic carbon (EC/OC) fractions. Equivalent black carbon (eBC) was measured with an AVL Micro Soot Sensor (MSS) Model 483 based on the photoacoustic measurement principle and an AVL Smoke Meter (FSN) Model 415 SE filter paper method. The AVL MSS continuously monitored $PM_{2.5}$ concentrations and was used to confirm that $PM_{2.5}$ levels were stable before and during filter collection.

Exhaust gas flow rates were calculated using both the air pump method and the carbon balance method. Engine power output in kilowatts (kW), engine revolutions per minute (RPM), boost pressure (bar), and intake manifold temperature (°C) were recorded during the testing in order to calculate the engine exhaust flow via the air pump method. Fuel consumption by the engine was also measured enabling calculation of exhaust flow using the carbon balance method. For this study, the results are based on exhaust flow rates from the carbon balance method, although the results for both methods are similar.

3. Results and discussion

The following sections present the experimental results of the gaseous and particulate emissions for pre- and post-scrubber operation. For the post-scrubber results, the analysis considers the combined results from the main engine and main generators. As such, the scrubber capacity on the x-axis represent the percent of the full scrubber capacity based on the exhaust flow rate through the scrubber using the sum of the exhaust flow from both tested engines (i.e., main engine and main generator). For example, the 4% scrubber capacity represents the main generator at 50% load and the main engine turned off, while the 85% scrubber capacity represents the main engine at 92% maximum load and the main generator at 50% load for a combined 85% scrubber capacity percentage. This approach allows for an evaluation of the emission factors (EF) for the vessel as a whole. Note that the main generator, which feeds into the scrubber unit, was targeted to be operated at 50% load for all tests. However, the main generators showed a large variation in load over the course of testing and varied from 29% of the maximum continuous rating (MCR) at the port to 56% of MCR at sea cruising.

3.1. *NOx, CO, and CO_2 emissions*

Table 3 shows the NOx, CO, and CO_2 emissions, expressed in g/kW-hr, at different scrubber capacity points pre- and post-scrubber. NOx is a targeted pollutant from marine engines, especially when ships operated at berth. Post-scrubber results show both increases and decreases in NOx emissions for the combined exhaust of the main engine and main generator. Since the use of a scrubber is not expected to have a large impact on NOx emissions and will likely not cause an increase in NOx

Table 3
Pre- and post-scrubber NOx, CO, and CO_2 emissions, expressed in g/kW-hr, for the main generator at 4% engine load and the combined exhaust stream of the main engine and main generator at different loads.

Engine load	NOx		CO		CO_2	
	Pre	Post	Pre	Post	Pre	Post
85%	13.8 ± 0.1	14.4 ± 0.4	0.21 ± 0.02	0.24 ± 0.00	617.0 ± 2.0	620.5 ± 4.9
70%	16.9 ± 0.1	16.6 ± 0.2	0.22 ± 0.03	0.22 ± 0.02	592.7 ± 6.2	607.4 ± 9.8
48%	15.7 ± 0.9	16.9 ± 0.1	0.19 ± 0.01	0.22 ± 0.00	574.0 ± 31.3	621.3 ± 2.8
4%*	15.0 ± 0.2	8.6 ± 0.1	1.34 ± 0.05	0.63 ± 0.00	763.1 ± 0.1	694.4 ± 0.0

*Main generator only with main engine turned off.

emissions, the observed differences in NOx were probably due to the engine load variation for the main generator along the trip. For the combined main engine and main generator exhaust stream, pre-scrubber NOx emissions ranged from 13.8 to 16.9 g/kW-hr and post-scrubber NOx emissions from 14.4 to 16.9 g/kW-hr. In general, the Tier 0 engine NOx emissions are comparable to the certification values for a Tier 1 Category 3 marine engines and are consistent with values reported in previous studies of Tier 0 and Tier 1 vessels [20,35]. NOx emissions did not follow a clear pattern with engine load. The intermediate 70% scrubber capacity showed the highest pre-scrubber NOx, with the maximum scrubber capacity showing the lowest pre-scrubber NOx. Our results agree with previous studies reporting lower NOx emissions with higher loads [10,17,36], but are in contrast with other studies showing higher NOx emissions with higher engine loads due to higher combustion temperatures that favor thermal NOx formation [7,13,35]. The lower pre- and post-scrubber NOx emissions at maximum load can be attributed to the reduced oxygen levels available in the combustion chamber to facilitate thermal NOx formation.

NOx emissions for the main generator at the lowest engine load condition and lowest scrubber capacity percent of maximum rating (representing at-berth operation with the main generator at 50% load) were slightly lower than those of the combined exhaust streams of the main engine and main generator, where the main engine was operating at intermediate loads. Elevated NOx emissions are expected for two-stroke SSD engines due to the longer expansion stroke and the more time available under high temperature conditions for NOx formation compared to medium speed 4-stroke engines [37]. Post-scrubber NOx emissions for the lowest scrubber capacity percent were statistically significantly lower than pre-scrubber emissions, resulting in a 42% scrubber efficiency. It is plausible that more NO was produced during the higher combustion temperature process of a 4-stroke engine, which was oxidized into NO_2. The latter was likely removed in the scrubber by absorption. This finding suggests that the use of a scrubber may lead to important NOx reductions while at berth. Post-scrubber NOx emissions are similar to but slightly lower than those recently reported by McCaffery et al. [10] when they utilized an ultra-low sulfur HFO in a medium speed 4-stroke auxiliary engine and found emissions that were below the Tier 2 NOx certification values (9.8 g/kW-hr) for auxiliary engines.

Pre- and post-scrubber CO emissions were relatively constant as a function of the percent of scrubber capacity for the combined exhaust stream of the main engine and main generator (Table 3). CO emissions levels are comparable or lower than those reported in previous studies of vessels with low speed two-stroke engines [7,8,10]. CO emissions did not show any statistically significant differences between measurements pre- and post-scrubber for the combined exhaust stream of the main engine and main generator. For the main generator, which is represented by the lowest scrubber capacity point, CO emissions levels were significantly higher than the CO levels observed when the ship was operated under cruising at sea conditions. Low speed two-stroke engines generally produce lower CO emissions than medium speed engines because of enhanced oxidation of the combustion products during the longer expansion stroke. The use of a scrubber for the main generator resulted in a 53% reduction in CO emissions at a statistically significant level.

CO_2 emissions dominated the gaseous emissions and exhibited a relatively flat trend with the percent of scrubber capacity for the combined exhaust stream of the main engine and main generator (Table 3). This finding is in contrast with previous studies reporting a typical declining trend of CO_2 emissions with increasing engine load [7,10,16,36]. It should be noted CO_2 emissions over the scrubber trended higher, but this phenomenon was likely related to engine load differences rather than a catalyst effect. It is worth mentioning that CO_2 emissions showed good repeatability at each engine load, indicating good consistency in the emissions measurements. The main generator produced higher CO_2 emissions compared to the combined exhaust of the main engine and main generator due to the lower combustion efficiency at medium loads for smaller displacement 4-stroke engines relative to two-stroke engines.

3.2. SO_2 emissions and scrubber efficiency

Pre- and post-scrubber SO_2 emissions are shown in Fig. 2. SO_2 emissions are highly dependent on fuel sulfur content. This study showed somewhat lower pre-scrubber SO_2 emissions than previous in-use studies tested high sulfur HFOs in two-stroke engines [7,9,14,20,32]. Pre-scrubber SO_2 emissions exhibited reductions with increasing engine load due to the better combustion efficiency at loads typical of cruising conditions compared to at berth operation. Post-scrubber SO_2 emissions showed dramatic reductions at all scrubber capacity points, resulting in scrubber efficiencies between 96.7% and 98.4%. Results reported here are in line with previous studies reporting similar SO_2 reduction efficiencies with wet scrubbers [30,33]. Compared to a recent study by McCaffery et al. [10], the post-scrubber SO_2 emissions reported here, which ranged from 0.10 to 0.14 g/kW-hr, were about three times higher than the SO_2 emissions obtained with an ultra-low sulfur HFO (sulfur content of 0.038%) without a scrubber, suggesting that developments in marine fuels quality and refining will likely provide greater reductions in SO_2 emissions than utilizing a scrubber.

3.3. $PM_{2.5}$ emissions and PM composition

Fig. 3 shows the $PM_{2.5}$ emissions and PM composition for pre- and post-scrubber measurements at all scrubber capacity points. Pre-scrubber $PM_{2.5}$ emissions ranged from 0.9 g/kW-hr to 1.46 g/kWh-hr, while the post-scrubber $PM_{2.5}$ ranged from 0.56 g/kW-hr to 1.24 g/kW-hr. Previous studies have shown similar or lower levels of $PM_{2.5}$ emissions from two-stroke marine engines operated with high sulfur HFO [7,9,14,35,36]. It should be noted that additional experiments performed with the scrubber in open loop vs. closed lope mode at 85% scrubber capacity showed no statistically significant differences in $PM_{2.5}$ emissions (1.22 vs. 1.25 g/kW-hr), indicating that $PM_{2.5}$ emissions were similar and were not affected by the scrubber operating modes. Overall, pre-scrubber $PM_{2.5}$ emissions did not show a consistent trend with scrubber capacity, whereas post-scrubber $PM_{2.5}$ trended higher with increasing scrubber capacity percentage. For the combined exhaust stream of the main engine and main generator, $PM_{2.5}$ emissions showed reductions of 37% and 16.3% over the scrubber at the 4% and 70% scrubber capacity points, respectively, while no statistically significant changes in $PM_{2.5}$ emissions were seen at the 48% and 85% scrubber capacity points. For the main generator at low load conditions, $PM_{2.5}$ emissions were found to be lower than those of the combined exhaust of the main engine and main generator, but scrubber efficiency was greater for the main generator at 37%. The overall ISO weighted reduction in $PM_{2.5}$ emissions over the scrubber was about 10%. The observed

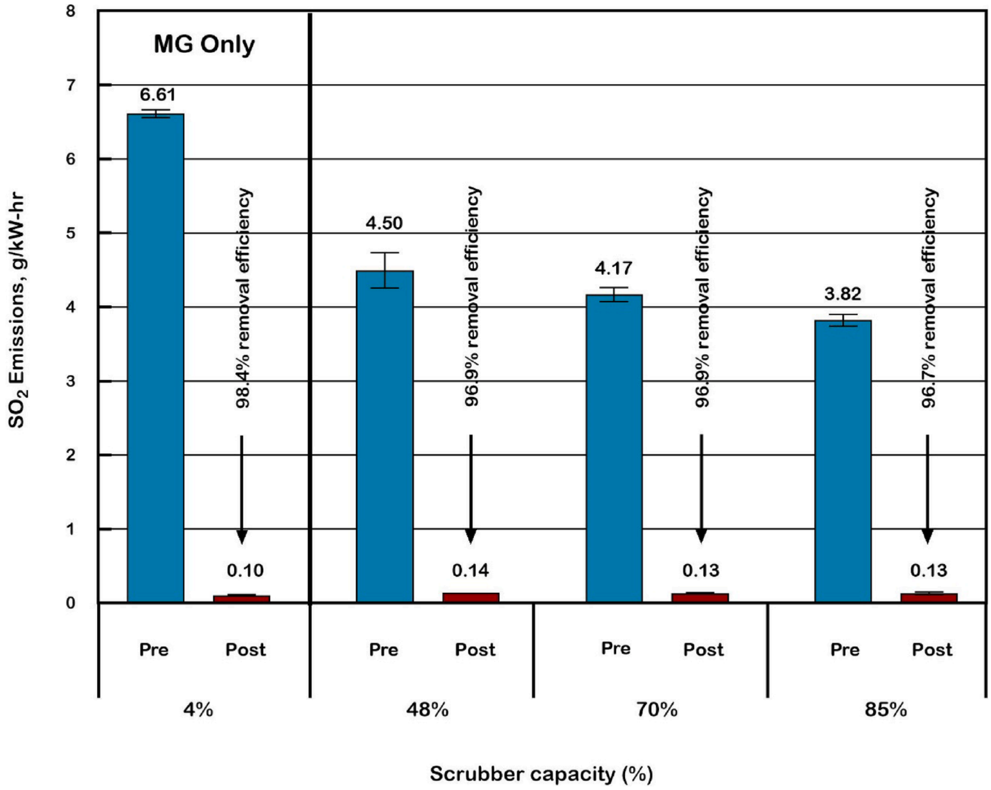


Fig. 2. Pre- and post-scrubber SO_2 emissions for the main generator at 4% engine load and the combined exhaust stream of the main engine and main generator at different loads.

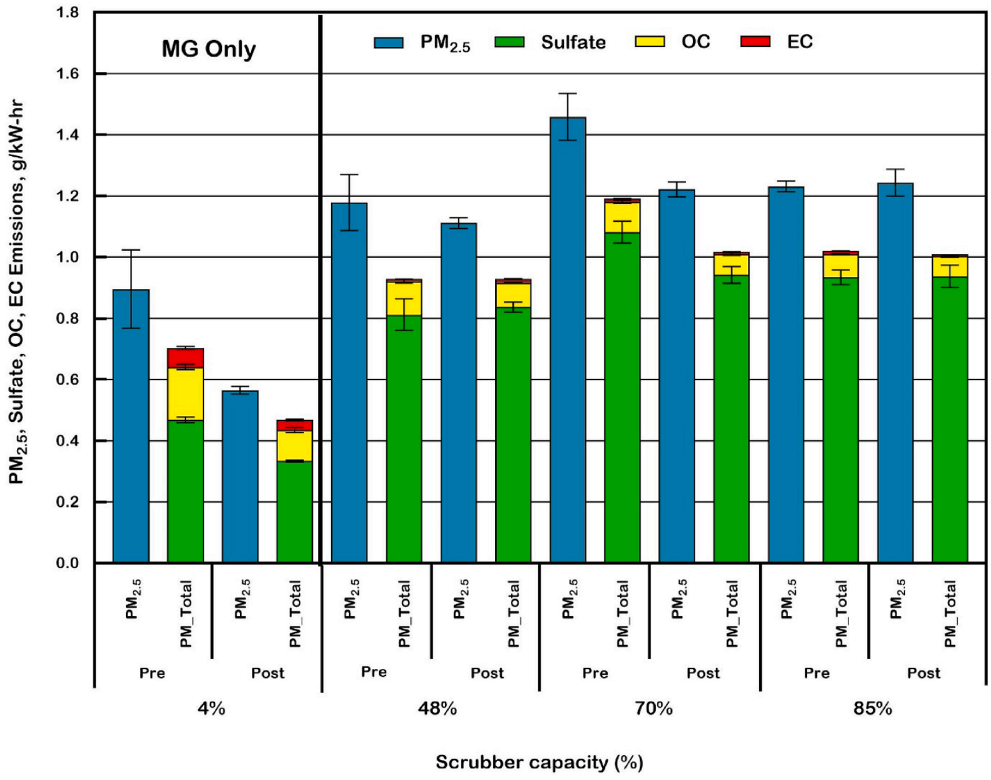


Fig. 3. Pre- and post-scrubber $PM_{2.5}$ mass emissions and total $PM_{2.5}$ composition including sulfate, OC, and EC fractions for the main generator at 4% engine load and the combined exhaust stream of the main engine and main generator at different loads.

reductions under the present test conditions were substantially lower than those reported in previous studies employed scrubbers [30–33]. For example, Fridell and Salo [33] demonstrated a 75% reduction in total PM emissions when they tested a high sulfur HFO on-board a two-stroke marine engine.

For the combined exhaust stream of the main engine and main generator at all scrubber capacity points, both pre- and post-scrubber $PM_{2.5}$ mass was predominantly comprised of sulfate (66.5%–93%), with smaller contributions of OC (6.5%–24.5%) and EC (0.6%–9%) fractions. For the main generator, sulfate (71.3%) was also the main component of $PM_{2.5}$ followed by OC (21.7%) and EC (7%). These results are consistent with previous studies that utilized high sulfur HFO [9,14], but differ from studies using very low sulfur HFO, where sulfate was a minor fraction of $PM_{2.5}$ and OC dominated the $PM_{2.5}$ composition [10,32]. Engine load did not show any obvious influence on $PM_{2.5}$ composition, except for the relatively higher OC and EC fractions for the main generator at the lowest load point, which can be ascribed to the incomplete combustion of heavy hydrocarbon components of the HFO and lubricant oil, generating more OC and EC emissions.

It should be noted that the low $PM_{2.5}$ removal efficiencies downstream the scrubber was primarily due to the small differences in sulfate for pre- and post-scrubber $PM_{2.5}$. Similar findings were reported in a different study, which utilized high sulfur HFO in a medium speed 4-stroke engine with and without a scrubber [31]. For the main generator over the scrubber's lowest capacity measured (4%), sulfate removal efficiency was close to 30%. OC removal efficiency over the scrubber was approximately 27% and 31% for scrubber capacity points at 48% and 70%, respectively, with lower OC removal efficiency of 17% at maximum scrubber capacity. The highest OC removal efficiency (~41%) was seen for the main generator. Overall, these results differ from a previous study that reported OC removal efficiencies captured by an open loop wet scrubber on the order of 70% [33]. As previously discussed, EC represented only ~ 1% of the total $PM_{2.5}$ mass for the combined exhaust stream of the main engine and main generator, resulting in less consistent removal efficiencies over the scrubber likely due to challenges measuring the low EC levels.

The very low removal efficiencies in $PM_{2.5}$ emissions by the scrubber are not entirely clear and depends on engine technology, operating conditions, fuel composition, sampling methodology, and scrubber design. Our results indicated that the temperature before the scrubber unit was sufficiently high and the humidity levels sufficiently low to ensure both the SO_2 and SO_3 will remain in the gas-phase when traveling in the exhaust. When both SO_2 and SO_3 entered the scrubber unit, the exhaust is rapidly cooled and the humidity increases significantly due to the exposure of sea water droplets. Under these conditions, the SO_2 is absorbed by the sea water droplets, which are subsequently discharged from the system. We theorize that SO_3 was more likely to transition from the gas- to particle-phase forming sulfuric acid (H_2SO_4) particles, which would not be absorbed by the droplets in the scrubber system [38]. These observations are in line with previous experimental and modelling studies that have shown that under conditions with rapid cooling, and excessive moisture and low dilution in the exhaust, similar to the conditions experienced in this study, there is a greater tendency for the formation of sulfuric acid particles [25,38,39]. The removal of these nuclei-sized sulfuric acid particles is dependent on Brownian diffusion. It is assumed that these particles are embedded in the scrubber fluid traveling around the sea water droplet, but not close enough to the droplet surface to diffuse and be captured.

Sampling methodology, even when following the ISO 8178 protocol can have a significant impact on PM emissions [37]. Especially in a scrubber environment, $PM_{2.5}$ measurements can be further complicated due to the formation of condensable particles, such as the gas-phase SO_3 into particle-phase hydrated sulfate ($H_2SO_4 \times 6.656\ H_2O$) and the partitioning of semivolatile organic compounds to the particle-phase. Studies have shown that sampling approach will affect PM emissions and their properties when the exhaust contains both solid and

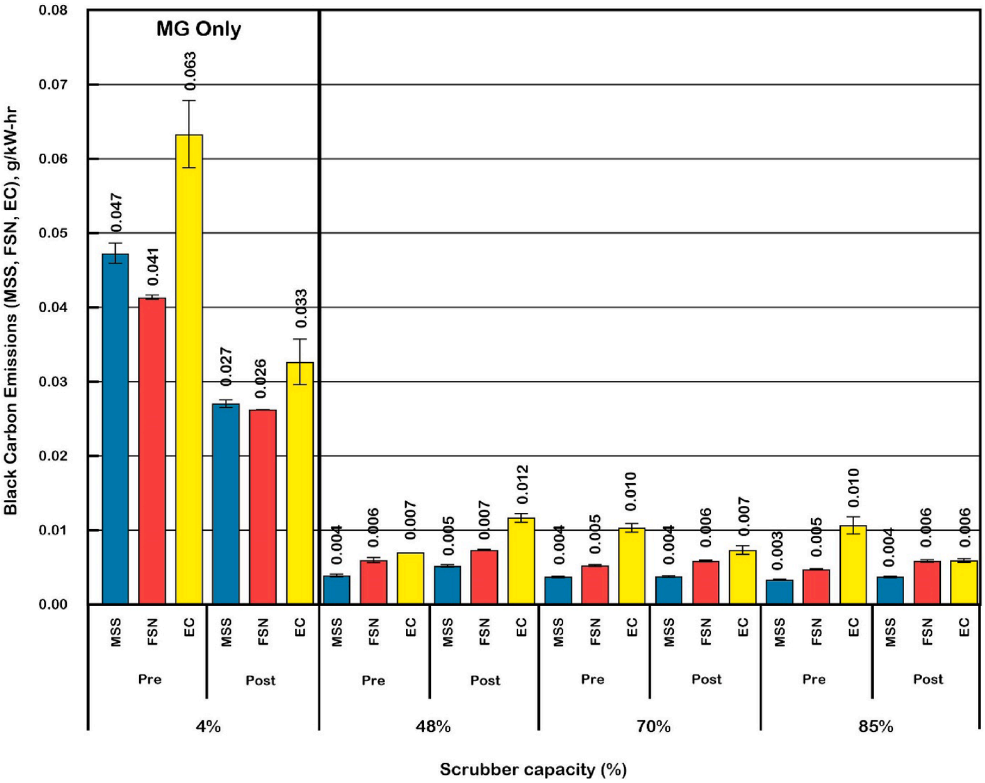


Fig. 4. Pre- and post-scrubber black carbon emissions measured with different methods for the main generator at 4% engine load and the combined exhaust stream of the main engine and main generator at different loads.

condensable PM [38]. The present work collected $PM_{2.5}$ on a filter using a dilution ratio of 6:1 to 20:1 and dilution air at 47 °C. In a different study by Fridell and Salo [33], a two-stage dilution unit was used with the first dilution being ~ 10:1 with the dilution air heated to 250 °C. Their second dilution increased the overall dilution from 64 to 106. Differences in sampling conditions can lead to differences in the penetration of condensable PM mass at the filter face and the overall measured $PM_{2.5}$ mass. Both approaches will capture the solid $PM_{2.5}$ mass, but an approach with a lower dilution ratio and collection temperature will capture more of the condensable $PM_{2.5}$ mass. We therefore theorize that the higher total PM removal over the scrubber reported by Fridell and Salo [33] was a result of some of the condensable mass being lost by using high dilution ratios and dilution air heated up to 250 °C, where the sulfuric acid particles and organic PM transitioned back to the gas-phase and penetrated the filter.

3.4. Black carbon emissions and scrubber efficiency

Pre- and post-scrubber black carbon emissions measured with three different instruments, each having a different measuring principle, are shown in Fig. 4. For the combined exhaust stream of the main engine and main generator, pre- and post-scrubber black carbon emissions ranged from 0.003 g/kW-hr to 0.009 g/kW-hr, while black carbon emissions ranged up to 0.063 g/kW-hr for the main generator. The FSN black carbon values were systematically higher than those obtained with the MSS, consistent to the results from Jiang et al. [40] when they tested a small two-stroke marine engine on marine gasoils and HFO with different sulfur contents. The EC results from the thermal optical method were higher than both the FSN and MSS measurements. Since sulfate dominated $PM_{2.5}$ composition, along with organic carbon (over 99.5%), high levels of sulfur species could potentially facilitate pyrolysis of OC to black carbon during the earlier heating stages of the NIOSH thermal optical method. This phenomenon could affect the EC-OC split point and lead to higher EC readings. It has been previously suggested that metals and metal oxides in HFO can enhance the oxidation of soot during combustion, which may also affect the NIOSH EC/OC method [41]. In addition, some metals could contribute more to the charring of the oxidized carbon species, especially when the fraction of EC on the filter is considerably less than OC [42].

For the combined exhaust stream of the main engine and main generator, there was a slight trend toward lower black carbon emissions measured with the FSN and MSS with increasing engine load, which is in line with previous studies [10,14,16,17]. The elevated black carbon emissions seen for the main generator, were likely due to the shorter residence time during combustion for soot to oxidize in localized fuel-rich areas compared to the low speed two-stroke main engine. The black carbon removal efficiencies over the scrubber varied between the methods and engine loads. The ISO weighted removal efficiencies were 39%, 35.6%, and 20%, respectively, for EC, MSS, and FSN methods, with much of the removal efficiency attributed to the lowest scrubber capacity. While the removal efficiencies for the combined main engine and main generators were not consistent with scrubber capacity, the main generator showed increased removal rates at 48.5%, 43%, and 36.6%, respectively, for EC, MSS, and FSN methods, also indicating greater removal efficiencies for the 4-stroke engine.

4. Conclusions

In this study, gaseous and particulate emissions were measured onboard a D7 Class container vessel while operating at sea and at berth using high sulfur HFO. Emissions were measured at sea at different engine loads for the main propulsion engine and main generator with and without the use of a hybrid wet scrubber system, and at berth for the main generator with and without the use of a scrubber. Results showed very low or no removal efficiencies for NOx, CO, and CO_2 emissions. The results from our measurements on wet scrubbers showed significant removal efficiencies in SO_2 emissions (>97%) across all engine loads, consistent with previous studies. The SO_2/CO_2 (% v/v) ratio, which is required for monitoring scrubber efficiency, was in the range of 0.19 to 0.64, and met the 2015 IMO Guidelines for EGCS of being less than 4.3, which corresponds to the sulfur equivalent of using a 0.1% sulfur fuel. Using this approach only considers the sulfur in the gas phase and not the sulfur in the particle phase. As such, the validation method is not accounting for all the sulfur species and may be slightly underestimating the scrubber performance as it relates to the fuel sulfur rule.

Although this work presents results for a single scrubber design and does not reflect the entire fleet of ships installed with scrubbers, we suggest that the use of scrubbers may not provide the desired reductions in $PM_{2.5}$ and black carbon emissions to achieve levels similar to those of ultra-low sulfur HFO combustion. The ISO weighted reduction in $PM_{2.5}$ emissions over the scrubber was 10% across all engine loads, which is significantly lower than the removal efficiencies reported in other studies. The absence of IMO standards for $PM_{2.5}$ emissions or EGCS sulfate emissions and the fact that sampling methodology likely affects significantly the measured PM, suggests the need for a separate $PM_{2.5}$ emissions standard at the exhaust upstream and downstream the scrubber system.

CRediT authorship contribution statement

Jiacheng Yang: Formal analysis, Investigation, Methodology. **Tianbo Tang:** Formal analysis, Validation, Investigation. **Yu Jiang:** Formal analysis, Investigation. **Georgios Karavalakis:** Writing - review & editing, Data curation. **Thomas D. Durbin:** Writing - review & editing. **J. Wayne Miller:** Writing - review & editing, Supervision. **David R. Cocker:** Data curation. **Kent C. Johnson:** Resources, Data curation, Supervision, Project administration.

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.

Acknowledgements

This work was supported by International Council on Clean Transportation (ICCT). The authors thank Mr. Edward O'Neil and Mr. Mark Villela of the University of California, Riverside for their contribution in conducting this research program. We also thank Dr. Kevin Thomson and Dr. Stéphanie Gagné from National Research Council (NRC) Canada and Dr. Tak Chan from Environmental and Climate Change (ECC) Canada for their contribution and guidance on the black carbon measurement.

References

[1] Eyring V, Isaksen ISA, Berntsen T, Collins WJ, Corbett JJ, Endresen O, et al. Transport impacts on atmosphere and climate: shipping. Atmos Environ 2010;44(37):4735–71.

[2] UNCTAD, Review of Maritime Transport 2017.

[3] Corbett James J, Winebrake James J, Green Erin H, Kasibhatla Prasad, Eyring Veronika, Lauer Axel. Mortality from ship emissions: a global assessment. Environ Sci Technol 2007;41(24):8512–8.

[4] Toscano, D. Murena, F. Atmospheric ship emissions in ports: A review. Correlation with data of ship traffic. Atmospheric Environment: X 2019;4:100050.

[5] Cames, M., Graichen, J., Siemons, A., Cook, V. Emission reduction targets for international aviation and shipping. European Parliament, Directorate General for Internal Policies, Policy Department A: Economic and Scientific Policy, November 2015. Retrieved from http://www.europarl.europa.eu/RegData/etudes/STUD/2015/569964/IPOL_STU(2015)569964_EN.pdf.

[6] Smith, T. W. P., Jalkanen, J. P., Anderson, B. A., Corbett, J. J., Faber, J.; Hanayama, S., O'Keeffe, E.; Parker, S., Johansson, L., Aldous, L., Raucci, C., Traut, M., Ettinger, S., Nelissen, D., Lee, D. S., Ng, S., Agrawal, A., Winebrake, J. J., Hoen, M., Chesworth, S., Pandey, A. Third IMO Greenhouse Gas Study 2014. International Maritime Organization (IMO) London, UK, April 2015.

[7] Chu-Van Thuy, Ristovski Zoran, Pourkhesalian Ali Mohammad, Rainey Thomas, Garaniya Vikram, Abbassi Rouzbeh, et al. On-board measurements of particle and gaseous emissions from a large cargo vessel at different operating conditions. Environ Pollut 2018;237:832–41.

[8] Chu-Van Thuy, Ristovski Zoran, Pourkhesalian Ali Mohammad, Rainey Thomas, Garaniya Vikram, Abbassi Rouzbeh, et al. A comparison of particulate matter and gaseous emission factors from two large cargo vessels during manoeuvring conditions. Energy Rep 2019;5:1390–8.

[9] Agrawal Harshit, Welch William A, Wayne Miller J, Cocker David R. Emission measurements from a crude oil tanker at sea. Environ Sci Technol 2008;42(19):7098–103.

[10] McCaffery Cavan, Zhu Hanwei, Karavalakis Georgios, Durbin Thomas D, Wayne Miller J, Johnson Kent C. Sources of air pollutants from a Tier 2 ocean-going container vessel: main engine, auxiliary engine, and auxiliary boiler. Atmos Environ 2021;245:118023. https://doi.org/10.1016/j.atmosenv.2020.118023.

[11] Pérez Noemí, Pey Jorge, Reche Cristina, Cortés Joaquim, Alastuey Andrés, Querol Xavier. Impact of harbour emissions on ambient PM10 and PM2.5 in Barcelona (Spain): evidences of secondary aerosol formation within the urban area. Sci Total Environ 2016;571:237–50.

[12] Tang L, Ramacher MOP, Moldanova J, Matthias V, Karl M, Johansson L, et al. The impact of ship emissions on air quality and human health in the Gothenburg area – Part 1: 2012 emissions. Atmos Chem Phys 2020;20:7509–30.

[13] Winnes H, Fridell E. Particle emissions from ships: dependence on fuel type. J Air Waste Manage Assoc 2009;59:1391–8.

[14] Yusuf Khan M, Giordano Michael, Gutierrez James, Welch William A, Asa-Awuku A, Wayne Miller J, et al. Benefits of two mitigation strategies for container vessels: cleaner engines and cleaner fuels. Environ Sci Technol 2012;46(9):5049–56.

[15] Cordtz Rasmus, Schramm Jesper, Andreasen Anders, Eskildsen Svend S, Mayer Stefan. Modeling the distribution of sulfur compounds in a large two stroke diesel engine. Energy Fuels 2013;27(3):1652–60.

[16] Moldanova J, Fridell E, Winnes H, Holmin-Fridell S, Boman J, Jedynska A, et al. Physical and chemical characterization of PM emissions from two ships operating in European emission control areas. Atmos Meas Technol 2013;6:3577–96.

[17] Zetterdahl Maria, Moldanová Jana, Pei Xiangyu, Pathak Ravi Kant, Demirdjian Benjamin. Impact of the 0.1% fuel sulfur content limit in SECA on particle and gaseous emissions from marine vessels. Atmos Environ 2016;145:338–45.

[18] Winnes H, Moldanova J, Anderson M, Fridell E. On-board measurements of particle emissions from marine engines using fuels with different sulphur content. Proc Inst Mech Eng Part M J Marit Environ 2014;230:45–54.

[19] Gysel Nicholas R, Welch William A, Johnson Kent, Miller Wayne, Cocker David R. Detailed analysis of criteria and particle emissions from a very large crude carrier using a novel ECA fuel. Environ Sci Technol 2017;51(3):1868–75.

[20] Agrawal H, Welch WA, Henningsen S, Miller JW, Cocker III DR. Emissions from main propulsion engine on container ship at sea. J Geophys Res 2010;115:D23205.

[21] Celo Valbona, Dabek-Zlotorzynska Ewa, McCurdy Mark. Chemical characterization of exhaust emissions from selected Canadian marine vessels: The case of trace metals and lanthanoids. Environ Sci Technol 2015;49(8):5220–6.

[22] Turner, D.R., Hassellov, I.-M., Ytreberg, E., Rutgersson, A. Shipping and the environment: Smokestack emissions, scrubbers and unregulated oceanic consequences. Elem Sci Anth 2017; 5:45.

[23] Lack DA, Corbett JJ. Black carbon from ships: a review of the effects of ship speed, fuel quality, and exhaust gas scrubbing. Atmos Chem Phys 2012;12:3985–4000.

[24] Ushakov Sergey, Stenersen Dag, Einang Per Magne, Ask Tor Øyvind. Meeting future emission regulation at sea by combining low-pressure EGR and seawater scrubbing. J Mar Sci Technol 2020;25(2):482–97.

[25] Andreasen Anders, Mayer Stefan. Use of seawater scrubbing for SO2 removal from marine engine exhaust gas. Energy Fuels 2007;21(6):3274–9.

[26] Brynolf S, Magnusson M, Fridell E, Andersson K. Compliance possibilities for the future ECA regulations through the use of abatement technologies or change of fuels. Transport Res D Transport Environ 2014;28:6–18.

[27] Endres S, Maes F, Hopkins F, Houghton K, Martensson EM, Oeffner J, et al. A new perspective at the ship-air-sea-interface: the environmental impacts of exhaust gas scrubber discharge. Front Mar Sci 2018;5:139.

[28] Tran TA. Research of the scrubber systems to clean marine diesel engine exhaust gases on ships. J Marine Sci Res Dev 2017;7:243.

[29] Ni Peiyong, Wang Xiangli, Li Hu. A review on regulations, current status, effects and reduction strategies of emissions for marine diesel engines. Fuel 2020;279:118477. https://doi.org/10.1016/j.fuel.2020.118477.

[30] Zhou J, Zhou S, Zhu Y. Characterization of article and gaseous emissions from marine diesel engines with different fuels and impact of after-treatment technology. Energies 2017;10:11110.

[31] Lehtoranta Kati, Aakko-Saksa Päivi, Murtonen Timo, Vesala Hannu, Ntziachristos Leonidas, Rönkkö Topi, et al. Particulate mass and non-volatile particle number emissions from marine engines using low-sulfur fuels, natural gas, or scrubbers. Environ Sci Technol 2019;53(6):3315–22.

[32] Winnes H, Fridell E, Moldanova J. Effects of marine exhaust gas scrubbers on gas and particle emissions. J Mar Sci Eng 2020;8:299.

[33] Fridell Erik, Salo Kent. Measurements of abatement of particles and exhaust gases in a marine gas scrubber. Proc IMechE Part M: J Eng Marit Environ 2016;230(1):154–62.

[34] Caiazzo Giuseppe, Langella Giuseppe, Miccio Francesco, Scala Fabrizio. An experimental investigation on sea-water SO2 scrubbing for marine application. Environ Prog Sustain Energy 2013;32(4):1179–86.

[35] Agrawal Harshit, Malloy Quentin GJ, Welch William A, Wayne Miller J, Cocker David R. In-use gaseous and particulate matter emissions from a modern ocean going container vessel. Atmos Environ 2008;42(21):5504–10.

[36] Huang Cheng, Hu Qingyao, Wang Hanyu, Qiao Liping, Jing Sheng'ao, Wang Hongli, et al. Emission factors of particulate and gaseous compounds from a large cargo vessel operated under real-world conditions. Environ Pollut 2018;242:667–74.

[37] Ntziachristos L, Saukko E, Lehtoranta K, Rönkkö T, Timonen H, Simonen P, et al. Particle emissions characterization from a medium-speed marine diesel engine with two fuels at different sampling conditions. Fuel 2016;186:456–65.

[38] Lemmetty M, Pirjola L, Mäkelä JM, Rönkkö T, Keskinen J. Computation of maximum rate of water-sulphuric acid nucleation in diesel exhaust. J Aerosol Sci 2006;37(11):1596–604.

[39] Schneider J, Hock N, Weimer S, Borrmann S, Kirchner U, Vogt R, et al. Nucleation particles in diesel exhaust: Composition inferred from in situ mass spectrometric analysis. Environ Sci Technol 2005;39:6153–61.

[40] Jiang Yu, Yang Jiacheng, Gagné Stéphanie, Chan Tak W, Thomson Kevin, Fofie Emmanuel, et al. Sources of variance in BC mass measurements from a small marine engine: Influence of the instruments, fuels and loads. Atmos Environ 2018;182:128–37.

[41] Sippula O, Stengel B, Sklorz M, Streibel T, Rabe R, Orasche J, et al. Particle emissions from a marine engine: Chemical composition and aromatic emission profiles under various operating conditions. Environ Sci Technol 2014;48(19):11721–9.

[42] Panteliadis P, Hafkenscheid T, Cary B, Diapouli E, Fischer A, Favez O, et al. ECOC comparison exercise with identical thermal protocols after temperature offset correction – instrument diagnostics by in-depth evaluation of operational parameters. Atmos Meas Technol 2015;8:779–92.