



Ship emissions in the future - review

Authors: Päivi Aakko-Saksa, Kati Lehtoranta

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Summary <p>This review covers the ship exhaust emissions already regulated (NO_x and SO_x), those anticipated to be regulated in the future (PM, PN, BC, methane) and some less common emission species (formaldehyde, NO₂, N₂O, NH₃). Furthermore, technologies to reduce emissions are discussed.</p> <p>LNG powered ships have shown reduction of SO_x and PM emissions of almost 100% and NO_x emissions about 90% compared to marine fuel oils. Methanol as marine fuel has slightly lower emission reduction potential than LNG. Exhaust treatment with SO_x scrubber removes SO_x emissions almost completely, while SCR is efficient for reduction of NO_x. SO_x scrubber, SCR and DOC indicated potential to remove also e.g. PM emission to some extent. Combination of distillate fuel, SCR and particulate filter could reduce almost 100% of SO_x and PM emissions, and more than 90% of NO_x emissions. However, particulate filters are not in commercial use for marine diesel engines using marine fuels, yet.</p> <p>When approaching climate-neutral shipping, renewable fuels (methane, methanol, distillate-type, hydrogen of renewable origin) and batteries are potential options. LNG has also GHG mitigation potential, however, compensated to some extent by methane emissions.</p> <p>There are several technologies capable to meet tightening emission regulations set for the ship exhaust emissions, although many technologies have their limitations.</p>		
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Written by	Reviewed by	Accepted by
Päivi Aakko-Saksa Principal Research Scientist	Zou Guangrong Senior Scientist	Hyrynen Johannes Vice President
VTT's contact address		
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Preface

The emissions from ships can be a significant source of air pollution in coastal areas and port cities and can have negative impact on human health and climate. Therefore, the IMO has implemented regulations to reduce emissions from ships. So far, these regulations cover emissions of sulphur oxides and nitrogen oxides. However, several other emission components in the ship exhaust are harmful, and new emission regulations are anticipated in the near future.

This report is a part of Business Finland funded INTENS project, Task 3.3.1 “Ship emissions in the future”. In this task, a short review on the ship emissions includes introduction to current emission legislation and results of various emission species from marine engines. Sulphur oxide and nitrogen oxide emissions are presented, and also currently unregulated particulate matter and particle number emissions amongst some other emission species. This review also presents some possible technology pathways to decrease emissions. Development of these technologies can be considered when preparing for the future ship emission regulations. This report aims to produce valuable information for the work where the minimized emissions are one basic criteria.

Espoo, 16 April 2019

Authors

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1. Introduction

The diesel fuel is a mixture of several types of hydrocarbons, and small quantities of organic compounds of sulphur, nitrogen and oxygen. In diesel engines, the fuel is combusted according to the following simplified reaction (scheme 1):



However, the combustion process in diesel engine is not perfect and products of incomplete combustion can be found in the exhaust gas. These products of incomplete combustion include unburned hydrocarbons (HC), carbon monoxide (CO) and particulate matter (PM). In the high temperature in chambers of the diesel engine, also the nitrogen in the air may react with the oxygen to form nitrogen oxides (NO_x). Diesel fuels contain also some amounts of chemically bound sulphur. Depending on the fuel sulphur level, some amount of sulphur oxides can be found in the exhaust gas. These emissions can have effects on air quality, human health and climate.

The International Maritime Organization (IMO) regulations consider emissions of NO_x and SO_x, globally. However, there are also other regulations set e.g. by EU, USA and China. In this review, these regulations are shortly discussed.

The focus in this work is on the ship emissions, already regulated, and the ones most possibly to be regulated in the near future. These include, in addition to NO_x and SO_x, e.g. the hydrocarbon, particulate matter and some other emissions. Furthermore, the focus is on emissions to air and on technologies to reduce these emissions. The possible emissions to water are not included in this study.

In this review of ship emissions, carbon dioxide (CO₂) is not in focus. However, greenhouse gas (GHG) strategy of the IMO and related projections are shortly discussed, related to ambitious target of the IMO to cut shipping sector's CO₂ emissions by 50% by 2050. Engine-out CO₂ emission is actually a product of the desired combustion reaction (1), but also a greenhouse gas and thus should be minimized.

2. Current legislation

2.1 IMO - Global, ECAs

The International Maritime Organization of the United Nations has been formed to promote maritime safety. The IMO ship pollution rules are in the MARPOL Annex VI titled “Regulations for the Prevention of Air Pollution from Ships”.

The IMO ship pollution rules limit the NO_x and SO_x emissions from ship exhaust (Fig. 1). The PM is expected to decrease indirectly through the SO_x limitations (by reduction of sulfate particle emissions), but at the moment, no direct global PM limitations exist (PM is limited in EU and USA). Global limits are set for NO_x and SO_x , and additionally, stricter limits in special emission control areas (ECA). At the moment the sulphur content of fuel is limited to 3.5% globally, and to 0.1% in SO_x emission control areas (SECA). Further sulphur reductions will be implemented globally in 2020 reaching 0.5% limitation. The NO_x limits are set for engines depending on the engine maximum operating speed. Tier I and II NO_x limits are global, while stricter Tier III limits are applicable for ships constructed after 2016 in NO_x emission control areas (NECA).

The IMO is evaluating the needs for regional and global control of black carbon (BC), which is one of the constituents of PM. The SO_x limits reduce PM associated sulphates and organics that are cooling species, while BC remains in PM thus increasing climate warming burden of shipping [1].

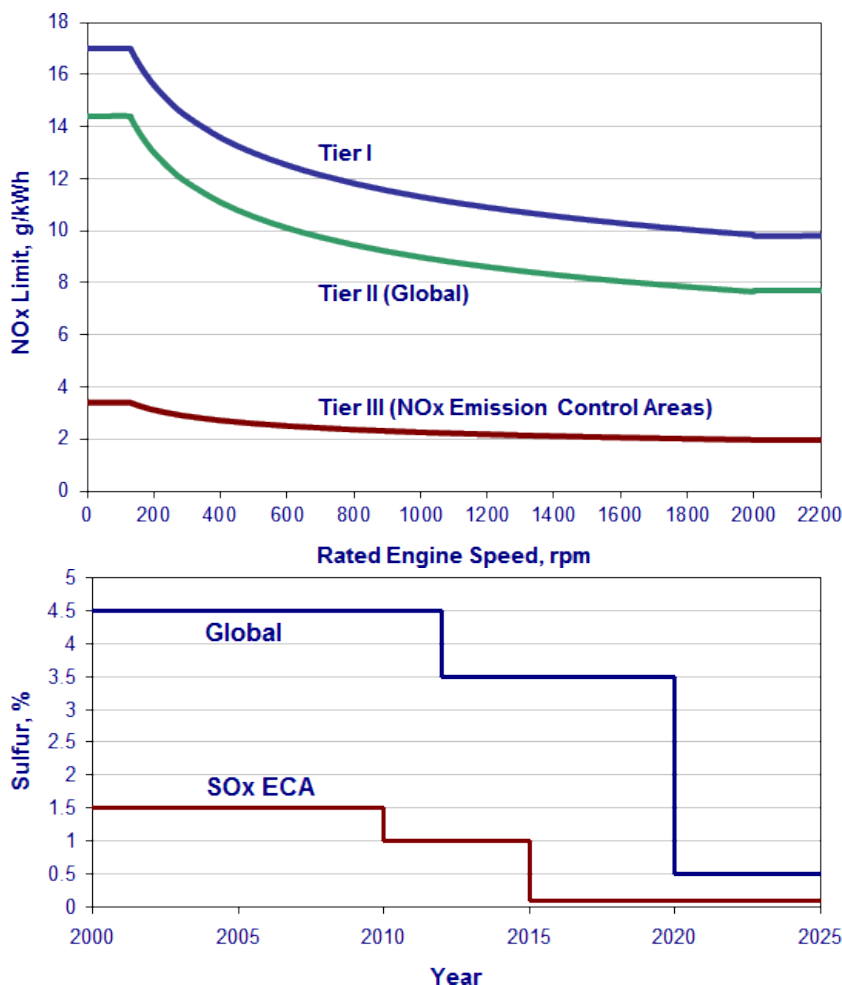


Figure 1. NO_x and SO_x limits by the IMO [2].

2.2 EU inland waterway vessels

European emission standards for engines used in new non-road mobile machinery (NRMM) have been structured as Stage I...V standards. Stage III A standards introduced emission limits for engines used in inland waterway vessels (Table 1), and these limits have significantly tightened under the Stage V regulation (Table 2).

New emission component will be limited for NRMM including inland waterway vessels in 2020, namely particle number emissions (PN). For light-duty vehicles, PN limit was introduced already in 2009 (UNECE Regulation 83), and later on for heavy-duty engines. The PM regulation covers only number of solid, non-volatile particles in size class above 23 nm, as sample precondition unit removes volatile particles. Thus, emission limits for inland waterway vessels include CO, HC, NO_x, PM and the Stage V regulation, applicable from 2020 on, has the requirement of PN_{>23nm} remaining below 10¹² kWh⁻¹ over a testing procedure involving several steady-state modes and weighing factors (based on ISO 8178 test cycles).

Table 1. Stage III A emission standards for engines in inland waterway vessels [2].

Category	Displacement (D) dm ³ per cylinder	Date	CO	HC+NO _x	PM
			g/kWh		
V1:1	D ≤ 0.9, P > 37 kW	2007	5.0	7.5	0.40
V1:2	0.9 < D ≤ 1.2		5.0	7.2	0.30
V1:3	1.2 < D ≤ 2.5		5.0	7.2	0.20
V1:4	2.5 < D ≤ 5	2009	5.0	7.2	0.20
V2:1	5 < D ≤ 15		5.0	7.8	0.27
V2:2	15 < D ≤ 20, P ≤ 3300 kW		5.0	8.7	0.50
V2:3	15 < D ≤ 20, P > 3300 kW		5.0	9.8	0.50
V2:4	20 < D ≤ 25		5.0	9.8	0.50
V2:5	25 < D ≤ 30		5.0	11.0	0.50

Table 2. Stage V emission standards for engines in inland waterway vessels (IWP & IWA) [2].

Category	Net Power kW	Date	CO	g/kWh			PN 1/kWh
				HC ^a	NO _x	PM	
IWP/IWA-v/c-1	19 ≤ P < 75	2019	5.00	4.70 ^p		0.30	-
IWP/IWA-v/c-2	75 ≤ P < 130	2019	5.00	5.40 ^p		0.14	-
IWP/IWA-v/c-3	130 ≤ P < 300	2019	3.50	1.00	2.10	0.10	-
IWP/IWA-v/c-4	P ≥ 300	2020	3.50	0.19	1.80	0.015	1×10 ¹²

^a A = 6.00 for gas engines

^b HC + NO_x

2.3 United States: Marine diesel engines

In the emission regulations in the US, marine engines are divided into three categories based on displacement per cylinder (Table 3). Categories 1 and 2 are further divided into subcategories.

Emission standards for category 1 and 2 engines are based on the land-based standard for non-road and locomotive engines. These engines are typically used in e.g. tugboats, supply

vessels, fishing vessels and as stand-alone generators for auxiliary electrical power on many types of vessels. Category 3 marine engines are typically used on ocean-going vessels such as container ships, oil tankers and cruise ships.

Table 3. Marine engine categories [2].

Category	Displacement per cylinder (D)		Basic engine technology
	Tier 1-2	Tier 3-4	
1	$D < 5 \text{ dm}^3 \dagger$	$D < 7 \text{ dm}^3$	Land-based non-road diesel
2	$5 \text{ dm}^3 \leq D < 30 \text{ dm}^3$	$7 \text{ dm}^3 \leq D < 30 \text{ dm}^3$	Locomotive engine
3	$D \geq 30 \text{ dm}^3$		Unique marine engine design

† And power $\geq 37 \text{ kW}$

For category 3, the US Environmental Protection Agency (EPA) has adopted Tier 1, Tier 2 and Tier 3 NO_x standards equivalent to the international IMO MARPOL Annex VI Tier I-III standards. Additionally, the EPA Tier 2-3 include a HC emission standard (2.0 g/kWh) and a CO standard (5.0 g/kWh) from new category 3 engines. No emission standard was adopted for PM, but manufacturers are required to measure and report PM emissions.

The strictest regulation is Tier 4 (see Table 4). In addition, CO emission standards apply for all category 1 and 2 engines starting with the applicable Tier 3 model year:

- i. 8.0 g/kWh for engines $< 8 \text{ kW}$,
- ii. 6.6 g/kWh for engines $\geq 8 \text{ kW}$ and $< 19 \text{ kW}$,
- iii. 5.5 g/kWh for engines $\geq 19 \text{ kW}$ and $< 37 \text{ kW}$,
- iv. 5.0 g/kWh for engines $\geq 37 \text{ kW}$.

Table 4. Tier 4 Standards for Marine Diesel Category 1/2 Engines.

Power (P) kW	NO_x g/kWh	HC g/kWh	PM g/kWh	Date
$P \geq 3700$	1.8	0.19	0.12 ^a	2014 ^c
	1.8	0.19	0.06	2016 ^{b,c}
$2000 \leq P < 3700$	1.8	0.19	0.04	2014 ^{c,d}
$1400 \leq P < 2000$	1.8	0.19	0.04	2016 ^c
$600 \leq P < 1400$	1.8	0.19	0.04	2017 ^d

^a 0.25 g/kWh for engines with 15-30 $\text{dm}^3/\text{cylinder}$ displacement.

^b Optional compliance start dates can be used within these model years.

^c Option for Cat. 2: Tier 3 PM/ NO_x +HC at 0.14/7.8 g/kWh in 2012, and Tier 4 in 2015.

^d The Tier 3 PM standards continue to apply for these engines in model years 2014 and 2015 only.

Category 1 and 2 engines are tested on various ISO 8178 test cycles (see. e.g. [2]).

2.4 Canada: Marine Engines

Transport Canada has authority to regulate emissions from marine propulsion engines larger than 37 kW. Current emission standards from ships are under the authority of Transport Canada. The Air Pollution Regulations of the Canada Shipping Act regulates the density of black smoke from ships in Canadian waters and within 1 mile of land.

2.5 China: Marine Engines

China's legislation to reduce pollutant emissions from marine engines includes several regulatory initiatives. China I and II emission standards (Tables 5 and 6) are for Category I

and Category II marine engines (based on US marine standards). These include also a methane emission limit for natural gas engines.

Table 5. China I marine engine emission standards.

Cat.	Displ. (SV) dm ³ per cylinder	Power (P) kW	CO g/kWh	HC+NOx g/kWh	CH ₄ ¹ g/kWh	PM g/kWh	Date
1	SV < 0.9	P ≥ 37	5.0	7.5	1.5	0.40	2018.7
	0.9 ≤ SV < 1.2		5.0	7.2	1.5	0.30	
	1.2 ≤ SV < 5		5.0	7.2	1.5	0.20	
2	5.0 ≤ SV < 15		5.0	7.8	1.5	0.27	2018.7
	15 ≤ SV < 20	P < 3300	5.0	8.7	1.6	0.50	
		P ≥ 3300	5.0	9.8	1.8	0.50	
	20 ≤ SV < 25		5.0	9.8	1.8	0.50	
	25 ≤ SV < 30		5.0	11.0	2.0	0.50	

¹ Applicable to natural gas (including dual fuel) engines only.

Table 6. China II marine engine emission standards.

Cat.	Displ. (SV) dm ³ per cylinder	Power (P) kW	CO g/kWh	HC+NOx g/kWh	CH ₄ ¹ g/kWh	PM g/kWh	Date
1	SV < 0.9	P ≥ 37	5.0	5.8	1.0	0.3	2021.07
	0.9 ≤ SV < 1.2		5.0	5.8	1.0	0.14	
	1.2 ≤ SV < 5		5.0	5.8	1.0	0.12	
2	5 ≤ SV < 15	P < 2000	5.0	6.2	1.2	0.14	2021.07
		2000 ≤ P < 3700	5.0	7.8	1.5	0.14	
		P ≥ 3700	5.0	7.8	1.5	0.27	
	15 ≤ SV < 20	P < 2000	5.0	7.0	1.5	0.34	
		2000 ≤ P < 3300	5.0	8.7	1.6	0.50	
		P ≥ 3300	5.0	9.8	1.8	0.50	
	20 ≤ SV < 25	P < 2000	5.0	9.8	1.8	0.27	
		P ≥ 2000	5.0	9.8	1.8	0.50	
	25 ≤ SV < 30	P < 2000	5.0	11.0	2.0	0.27	
P ≥ 2000		5.0	11.0	2.0	0.50		

¹ Applicable to natural gas (including dual fuel) engines only.

China has ratified MARPOL Annex VI and thus the IMO NO_x standards apply to Chinese flagged oceangoing vessels and foreign-flagged vessels operating within Chinese waters. Additionally, Domestic Emission Control Areas (DECA) “Low sulphur fuel requirements for ocean-going vessels operating and berthing within three coastal areas” was adopted in 2015 [2]. From 1 January 2018, ships berthing at any ports within the DECAs are required to use fuel oils with sulphur content ≤ 0.5%, except for the first hour after arrival and the last hour prior to departure. Further, from 1 January 2019, ships entering the DECAs are required to use fuel oil with sulphur content ≤ 0.5%.

3. GHG strategy, projections and mitigation

Strategy and projections

The IMO has ambitious greenhouse gas strategies to mitigate shipping's GHG emissions (initial strategy by 2018 and a revision in 2023). This strategy defines GHG mitigation targets in maritime transport, guiding principles and candidate measures to reach targets. Regulation on mandatory energy efficiency standards in shipping were introduced in 2013 [3].

DNV GL [4] projects modest increase in energy consumption in maritime sector to only 13 EJ (310 Mtoe) in 2050 compared with 12 EJ in 2015 regardless of increasing output in maritime sector (from 85×10^{12} to 107.8×10^{12} tonne-km). Additionally, DNV GL anticipates that global energy consumption smoothen instead of continuously increasing due to e.g. the transition to higher energy efficiency (Fig. 2). More conservative scenarios, e.g. by the International Energy Agency (IEA) ¹, still project substantial increase in energy demand in the future [5].

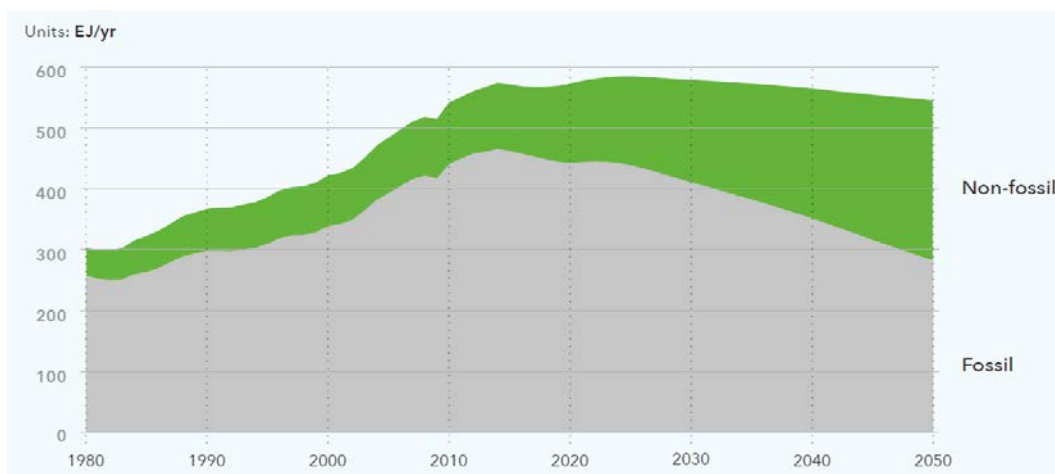


Figure 2. Projection of world primary energy supply by source [4].

In maritime trade, decline of trade of fossil fuels (coal, oil and gas) is anticipated, although compensated to some extent by trade related to biofuels. Trade of fossil fuels is substantial, representing for example 41% of maritime trade in 2016. More regionalised trade system and increased circular economy would reduce long-distance maritime trade, and intra-regional trade has already increased in Asia. Global demand for transport flows could reduce along with alternative maritime routes and modal shift to rail cargo transport. [3], [6]. Additionally, also other solutions are needed for major decarbonisation of shipping, such as technological solution (materials, design, less friction, waste heat recovery), operational solutions (route and harbour entrance optimisation, lower speeds, ship size, ship-port interface including onshore power supply) and alternative fuels (renewable fuels, hydrogen, ammonia, electric ships, wind assistance). [3].

ETP 2017 [6] projected that GHG reductions of 70% by 2060 relative to 2015 are needed in shipping in the beyond 2°C scenario (B2DS) despite of increase in maritime freight activity to 349×10^{12} tkm. To achieve this, energy intensity per ship kilometre would be nearly halved mostly by new ship designs and retrofitting (including wind assistance), and *half of the marine fuel mix could be switched to advanced biofuels*. ETP 2017 [6] projects that average ship size and utilisation rates continues increasing, and auxiliary systems and wind assistance will be used. In recent years, the average size of ships has increased, e.g. in the

¹ For example, the New Policies Scenario of IEA [5] projects higher global primary energy demand by 2040 (17 584 Mtoe, 736 EJ) than DNV GL (see Fig. 2).

global container fleet 18.2% annually from 2010 to 2015. Additionally, the average speed of the global fleet is projected to reduce.

One of the possible pathways to achieve 80% reduction in the carbon emissions from shipping by 2035 considered by Kirsten et al. [3] in Fig. 3 projects that the share of biofuels would be 22% and share of LNG 5% of marine fuels. Hydrogen would have the strongest uptake after 2025 via a low-carbon fuel standard or carbon pricing. However, GHG savings achievable with alternative fuels depend on their well-to-tank emissions. [3].

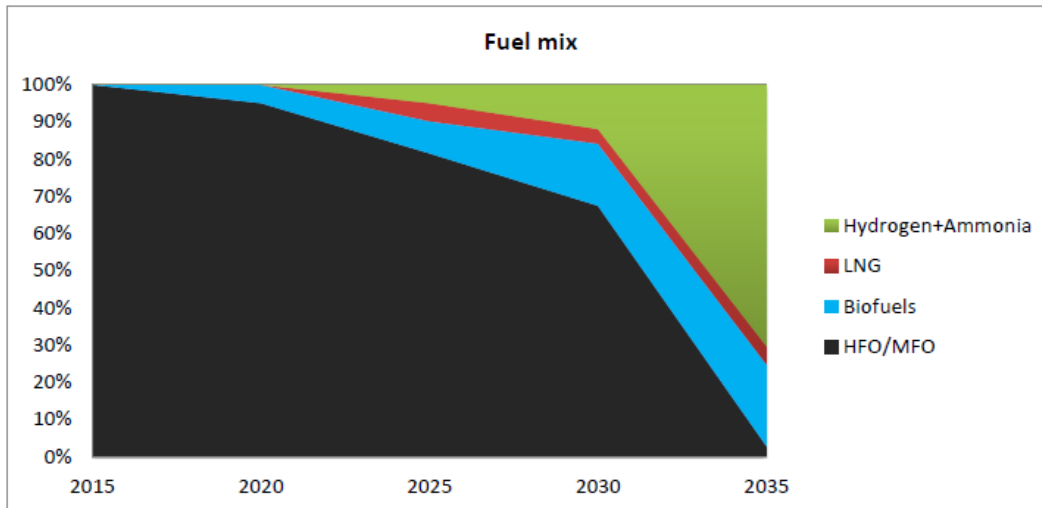


Figure 3. Fuel mix evolution between 2015-2035 for 80% carbon factor reduction [3].

GHG mitigation by fuels

Substantial GHG mitigation by fuels is possible only when their well-to-tank emissions are low. Consequently, GHG emissions are high for hydrogen produced from natural gas, and for batteries using electricity of fossil origin. Engine-out CO₂ emissions for different fossil fuels depend on carbon content of fuel and combustion efficiency of an engine (scheme 1 in introduction). For marine diesel engines using HFO, fuel-dependent CO₂ emissions are approximately 3114 g/kg fuel [7], while LNG has lower carbon content of fuel, and thus also lower engine-out CO₂ emissions. LNG has up to 30% CO₂ mitigation potential compared to HFO, although both fuels are of fossil origin. Unburnt methane emission compensates to some extent the GHG mitigation potential of LNG use. For example, if LNG had 800 g/kg fuel lower CO₂ emissions than HFO, this would be compensated by methane emission of approximately 29 g/kg fuel (5.8 g/kWh)². Thus control of methane slip is important to maintain LNG attractiveness for longer term [3]. ETP 2017 [6] does not include LNG in the B2DS, because of its GHG abatement potential is limited, for example shifting 50% of the international shipping fleet to LNG would reduce GHG emissions only by approximately 10%. Costs for LNG bunkering facilities gas delivery and liquefaction are also substantial. Fossil methanol is produced today from natural gas and thus its potential to reduce GHG emissions is lower than that for LNG.

Renewable and circular fuels could be used to meet the GHG targets of maritime transport. For efficient GHG mitigation, upstream GHG emissions of fuels are crucial (well-to-tank emissions), and thus renewable, sustainable raw materials are needed for producing fuels. Biofuels are able to reduce CO₂ emissions substantially depending on their production details. Renewable Energy Directive (RED, Directive 2009/28/EC) updated by RED2

² Calculation by authors. Based on a global warming potential of 28 times higher for methane than for CO₂ over a period of 100 years.

(Directive 2018/2001) defines that the GHG emission savings shall be at least 60% for biofuels and biogas consumed in the transport sector until 31.12.2020, and at least 65% starting from 1.1.2021 to be accounted for the purposes of Directive [8].

Availability of renewable fuels may be limited in short term, although their production from non-food biomass and waste are progressing. [3]. ETP 2017 [6] projects that advanced biofuels (e.g. biodiesel, biomethane, biomethanol) will be the main alternative to fossil fuels in shipping. In the B2DS, 5 EJ of advanced biofuels is assumed to account for nearly half of the total final energy demand in international shipping in 2060. Also ICCT [9] estimated 5 EJ per year of biofuels for maritime sector in 2050³. This would mean substantial increase in global biofuel production, which was only 3.3 EJ (78 Mtoe) in 2016 for all transport sectors [5].

ETP 2017 [6] projects that renewable hydrogen in the international shipping will be used, either as hydrogen or in form of electro-fuels (power-to-X, P2X, PtX). GHG balances of electro-fuels depend on their production details, particularly on origin of hydrogen used. Prerequisite for low GHG emissions for hydrogen is its carbon-free production instead of fossil methane reforming used today. According to Koponen and Hannula [10], 70% emission savings compared to fossil fuels can be achieved with biofuels enhanced by hydrogen (from electrolysis of water) when the carbon intensity of electricity remains under 84–110 gCO₂/kWh. Low-carbon electricity is anticipated, e.g. IEA [11] estimates that the global emissions of electricity production should decrease below 100 gCO₂/kWh by 2040 to achieve the two degree target. In Finland, emission factor of electricity production was on average 129 gCO_{2eqv}/kWh in 2017⁴. Costs of producing electro-fuels have been studied by e.g. Hannula and Reiner and Brynolf et al. [12], [13]. The cost of electrolytic renewable hydrogen is dominated by the renewable electricity price. Hannula⁵ has estimated that the production costs of e-methane could be 1.5-2.5 times higher than those of hydrogen, while e-methanol would be slightly more costly, and e-diesel (Fischer-Tropsch) more expensive than e-methane (appr. 1.4 x e-methane costs) due to higher capital investment and lower efficiency. When considering additional storage and distribution costs, differences in costs between liquid and gaseous fuels narrows. Whether to use e-hydrogen directly or after conversion to electro-fuel is governed by the type of end-use. [12].

Authors here note that volatile projections for energy consumption in maritime sector lead to variable shares of decarbonising technologies of energy consumed. For example, biofuel quantity of 5 EJ on market could lead to for example 10% or 40% share of biofuels of energy consumption in maritime sector by 2050 depending on assumptions made. Operational and compatibility issues need consideration particularly if blending ratios of biofuels with conventional fuels are high. Authors also note that electro-fuels are not included in the current marine fuel projections albeit their role might become substantial.

See basics of renewable fuels in Chapter 4.

³ Availability of low-carbon biomass is estimated as 50-60 EJ in 2050 for heat and power, transport sector and chemical production. Of this, 10 EJ is reserved for plastics (half of plastics) and some 35 EJ for transport. When reserving a part for aviation, and with optimistic scenarios for vehicle electrification in road transport, 5 EJ could be available for marine sector.

⁴ <https://www.energiavirasto.fi/sahkontuotannon-paastokerroin>, accessed in March 2019.

⁵ Costs of e-fuels estimated by Ilkka Hannula, VTT. Discussions in 2018/2019.

4. Fuels

4.1 Demand of marine fuels

In 2015, global marine fuel consumption was 266.3 Mt, which represents approximately 10% of transport fuels consumption (Table 7). Large ships, such as container ships, bulk carriers and oil tankers mainly having slow speed diesel (SSD) 2-stroke engines, consume over 70% of marine fuels, mainly residual fuel (HFO). 19% of marine fuels consumed globally are distillates used mostly in medium speed diesel (MSD) 4-stroke engines. Fishing vessels consume approximately 2% of marine fuels. LNG represented 2.4% of global marine fuels in 2015. [14].

In the geographic Arctic, 5.4 Mt of marine fuels are consumed annually, and about 42% of these are residual fuels [15]. In the Arctic defined by the Polar Code marine fuel consumption is only about 0.44 Mt annually, because Scandinavia is excluded. However, emissions formed in Scandinavia can potentially reach Arctic.

As regards the evaluation of emissions based on fuel consumption data, the most significant marine emitters seem to be container ships and oil tankers (SSD 2-stroke) globally, while in the Arctic all shipping sectors are important. In the geographic Arctic, a high share of fuel is used in smaller vessels having high speed diesel (HSD) engines (e.g. fishing ships).

Table 7. Fuel consumption by main engine type in 2015 [14].

	SSD, e.g. container ships, oil tankers (Mt)	MSD, e.g. ferries, cruisers, RoRo, RoPax, passenger (Mt)	HSD, mainly small, e.g. fishing vessels (Mt)	Total (Mt)
Global ^a	Res. 180.5*, 2.3** Dist. 12.2*, 0.4** LNG 0.03 <i>tot. 192.7*, 2.8**</i>	Res. 26.2**, 0.26* Dist. 20.7**, 0.5* LNG 2.3 <i>tot. 48.9**, 0.7*</i>	Res. 0.5**, 0.01* Dist. 13.7**, 1* LNG 0 <i>tot. 14.1**, 1*</i>	Res. 210.3 Dist. 49.5 LNG 6.5 <i>tot. 266.3^a</i>
The Arctic (geographically) ^b	Res. 1.63 Dist. 0.08 <i>tot. 1.72</i>	Res. 0.63 Dist. 0.63 <i>tot. 1.26</i>	Res. 0 Dist. 2.43 <i>tot. 2.43</i>	Res. 2.26 Dist. 3.14 <i>tot. 5.40</i>
The Arctic (Polar code) ^c	0.202	0.045	0.114 (other 0.075)	0.44
Note	Mainly residual fuels	About 50% distillates	Mostly distillates	

SSD = Slow speed diesel MSD = Medium speed diesel HSD = High speed diesel *2-stroke **4-stroke

Res. = Residual fuels, Dist. = Distillate fuels

^a Global fuel consumption in 2015 (Comer et al. 2017). Additionally, steam/gas turbine: residual fuel 0.21/0.6 Mt, distillates 0.2/0.75 Mt and LNG 4.1/0.02 Mt.

^b Arctic fuel consumption by main engine type in 2016 (based on Winther et al. [16]).

^c [17]

4.2 HFO, MDO, MGO, hybrid fuels

At the moment, the sulphur content of marine fuels is limited to 3.5% globally. Further global sulphur reduction will be implemented in 2020 reaching 0.5% limitation. This is expected to have a huge impact on the demand for residual heavy fuel oils, which at the moment are the main fuels used for global shipping. Refining industry's challenge is to produce low-sulphur fuel in sufficient quantity and quality (and at the right price) in 2020. In SO_x emission control areas, the sulphur content of fuel is already limited to 0.1 %.

HFO is residual fuel representing the worst quality of marine fuels today as it may contain substantial amounts of harmful substances, such as sulphur, heavy metals (e.g. V and Ni in ash components), and asphaltenes associated with polyaromatic hydrocarbons (PAHs).

Marine distillate fuels are cleaner than residual fuels, but still worse than road diesel in many regions, for example in Europe sulphur content of road diesel is below 0.001%.

International standard ISO 8217 specifies properties of several residual and distillate marine fuels (examples in Table 8). Of distillate fuels, DMA (also called marine gas oil, MGO), is free from residual fuel, while DMB (also called marine diesel oil, MDO), may have traces of residual fuel. ISO 8217 specifies properties of, for example, the following marine fuel classes:

- Residual fuels (e.g. RMA, RMB) are classified by their viscosities (e.g., 10, 30, 80, 180, 380, 700).
- DMA is a general marine distillate that must be free from traces of residual fuel. DMA is primarily used in Category 1 marine engines (< 5 litres per cylinder).
- DMB may have traces of residual fuel. DMB is typically used for Category 2 (5-30 litres per cylinder) and Category 3 (≥ 30 litres per cylinder) engines.

In addition, hybrid fuels may be utilized in ships. Hybrid fuels may have low sulphur content, e.g. below 0.10% (m/m), even if other fuel properties resembled those of the residual fuels [18].

Marine distillate fuels have different fuel properties than residual fuels, and switching these fuels is not always straightforward. When proper engine and emission performance is desired, marine diesel engines designed for residual fuel use may need adjustments for distillate fuel use, or even retrofitting (e.g. injectors). This applies particularly to old engines, whereas modest (or no) additional engine optimization may be needed for modern marine diesel engines when changing from residual to distillate fuels. Blending of different residual fuels with each other, and particularly with distillate or biofuels, may be challenging due to for example separation of asphaltenes from residual fuel leading to sludge. Practically, compatibility testing for fuel blending is a common procedure, however, traditional testing methods may not be applicable for new blending needs.

Table 8. Selected fuel properties in fuel standards for some residual and distillate marine fuel classes and road diesel fuel^a.

	RMG 380 ISO 8217:2010	DMA (MGO) ISO 8217:2017	DMB (MDO) ISO 8217:2017	Road diesel^a EN 590:2013/2017, ASTM D 975
Kinematic viscosity, mm ² /cm	max. 380 (50 °C)	2-6 (40 °C)	2-11 (40 °C)	2-4
Cetane index, min		40	35	46
Sulphur, max., %(m/m)	statutory	1.0 ^c	1.5 ^c	0.001
Acid number, max., mg KOH/g	2.5	0.5	0.5	0.08 ^b
Carbon residue, max., %(m/m)	18	0.3	0.3	0.3 ^d
Pour point summer, max, °C	30	0	6	
Ash, max., %(m/m)	(0.15)	0.01	0.01	0.01

^a ISO 8217 (2017) defines DF grades that allow FAME up to 7%(V/V). ^b WWFC Category 4

^c Within SECA, in maximum 0.1%(m/m). In 2010 edition of ISO 8217, DMA 1.5 %(m/m) and DMB 2.0 %(m/m).

^d On 10% distillation residue.

4.3 Natural gas and methanol

Natural gas (NG) is mainly composed of methane. Liquefied natural gas (LNG) is natural gas that has been cooled down to -162 °C to enable liquid form, primarily to increase its energy density. Methane has higher hydrogen to carbon ratio compared to other marine fuels, and thus also lower engine-out CO₂ emissions per energy unit produced.

NG engines are used worldwide in energy production and vehicle applications as well as increasingly in ship applications. NG can be used with different types of engine technologies,

for example using commercially available dual fuel engine concept. For LNG use, investments in ships and harbour infrastructure are emerging. Additionally, safety measures and space for tanks are needed on board ships. Economic aspects related to the LNG as well as the growth of the LNG supply chain remains to be seen (Acciaro 2014 in [19]).

Methanol is liquid fuel produced from natural gas. Methanol is used as marine fuel for example in car ferry Stena Germanica in Sweden and in seven ocean-going ships [20]. In a dual-fuel engine, a pilot fuel ignites the methanol (5% diesel and 95% methanol). Diesel engines can be retrofitted for methanol use and newbuilds are also available. Minor modifications on harbour infrastructure and safety measures are needed for using marine methanol. Additionally, methanol is biodegradable. [3].

4.4 Biofuels and renewable fuels

Fossil fuels can be replaced by their renewable counterparts, many of which are chemically similar to fossil fuels, just produced from bio- or renewable sources (Table 9). Some ships are already running on biofuels. The company GoodFuels has pioneered the labelling of advanced biofuels as a waste or residue origin. ExxonMobil has planned to introduce algal biofuels by 2025, and Statoil has started to develop fuels from seaweed. Advanced biofuels or renewable fuels can be produced even from e.g. cellulosic or waste materials. Additionally, renewable hydrogen can be converted to synthetic fuels using CO₂ or nitrogen (called electro-fuels, e-fuels, power-to-X fuels, P2X, PtX, X-to-liquid XTL).

Table 9. Basic classification of alternative fuels for shipping.^a

Fossil form	Renewable counterpart	State
Methane, e.g. LNG	Biomethane (e.g. biogas-based LBG), renewable synthetic methane, e.g. bio-SNG, e-methane ^b	Gas
Fossil methanol	Renewable/bio-methanol, e-methanol ^b	Liquid
Liquid hydrocarbons <ul style="list-style-type: none"> • Residual fuels (HFO) • Distillates (MGO) • Gas-to-liquids (GTL) 	Paraffins, such as oils and fats hydrotreated (HVO), biomass-to-liquid (BTL), e-diesel ^b	Liquid
No	Vegetable oils and animal fats or their esters (FAME)	Liquid
No	Pyrolysis oil fuels based on plastics, lingo-cellulosic feedstock etc.	Liquid

^a Less common fuel options are e.g. hydrogen, batteries, dimethyl ether (DME) and ammonia.

^b Electro-fuel from renewable hydrogen and CO₂.

Traditional biofuels commonly mean fuels produced from oils and animal fats. For use in high-speed diesel engines, oils and fats are transesterified with methanol to fatty acid methyl ester (FAME), commonly called biodiesel, to achieve fuel properties compatible with those engines. For marine diesel engines, oils and fats are typically de-gummed and de-acidified, but not transesterified, and thus their properties are much worse than those of biodiesel. As biofuels are compatible with the existing marine engines, and fuel infrastructure, their adaptation is in principle straightforward. However, oils and fats in both untreated and esterified forms are associated with e.g. stability problems (only 6-month storage time for FAME for road transport use) and there is not much experience on the performance of their blends with marine fuels. ISO 8217 (2017) defines DF grades, which allow FAME up to 7%(V/V). The regular marine fuel grades (e.g. residual fuels, DMA and DMB) shall not contain FAME (the “de minimis” 0.5%). Some shipping companies use high blending ratios or even neat biofuels, however, in these cases engines compatible with biofuels in question are used.

Specific *low-quality biofuels* may also enter into the marine fuel market, for example bio-oils produced by pyrolysis of plastics or cellulosic feedstocks. Properties of these fuels vary drastically depending on the feedstock, production process and degree of upgrading. Experience of suitability of these fuels for marine engines or compatibility of their blending with marine fuels is lacking. [21], [22].

In road transport sector, *high quality paraffinic renewable fuels* have been used successfully as blends with diesel fuel or even as such [23]. Paraffinic fuels can be produced by a) hydrotreatment of oils and fats, b) gasification of biomass and Fischer-Tropsch liquefaction (BTL fuel), c) also hydrogen and CO₂ can be converted to paraffinic fuels (called electro-fuels, e-fuels, power-to-X fuels, P2X, PtX, X-to-liquid XTL). Despite of different production pathways, HVO, BTL and respective electro-fuels consisting of paraffins (alkanes) are chemically similar (and similar to fossil GTL), and they typically are of better quality than the traditional road diesel fuel (Paraffins in [24]). Liquid diesel-type renewable fuels are compatible with the existing marine engines and distillate fuels, and thus their adaptation is in principle straightforward. However, experience is limited of using paraffinic fuels in combination with challenging residual marine fuels, and compatibility problems may arise.

Gaseous LNG (fossil methane) can be replaced by (or blended with) renewable methane that can be produced using several pathways, a) from biogas⁶ by cleaning and upgrading (removal of CO₂ and impurities), b) from biomass through gasification and methanation c) from renewable hydrogen and CO₂ by synthesis to e-methane.

Renewable or synthetic methane can be converted to liquid methanol.

Some of these advanced renewable fuels are described in the box below.

Box - Synthetic low-carbon renewable fuels

- **Paraffinic, high-quality diesel-type fuels.** Compatible with diesel engines and fuel infrastructure. Chemically similar to fossil GTL fuel. Limited experience in blending with challenging marine fuels, however, commonly blended with diesel fuel for road transport sector.
 - *Hydrotreated "HVO" oils and fats*, produced from fatty acids and hydrogen.
 - *Renewable "BTL" diesel-type fuel*, produced from biomass.
 - *E-diesel*, produced from renewable hydrogen and CO₂.
- **Synthetic renewable methane.** Compatible with current marine engines for LNG use. Chemically similar to fossil natural gas.
 - *Biomethane*, produced from biogas.
 - *Renewable methane*, produced from biomass.
 - *E-methane*, produced from renewable hydrogen and CO₂.
- **Synthetic renewable methanol.** Marine engines for methanol use are commercial. Chemically similar to fossil methanol. Produced via methane (see production pathways above).

4.5 DME, ammonia and other power sources

Hydrogen, batteries, dimethyl ether (DME) and ammonia are not mature or commercial technologies for maritime use, although they are demonstrated in some applications.

Dimethyl ether (DME) is produced from methanol. DME is a gaseous fuel (similarly to LPG) and it requires special engines and fuel infrastructure. DME is compatible with the diesel cycle. DME is not used as a marine fuel today.

⁶ Biogas can be produced from many kinds of organic materials, e.g. wastewater sludge typically by anaerobic digestion.

Hydrogen (H₂) emits zero “tailpipe” emission when used in fuel cells, while NO_x emissions are formed when used in internal combustion engines (for GHG emissions, see Chapter 3). Hydrogen is used most efficiently in fuel cells. Conversion of hydrogen to electro-fuels (Chapter 4.4) enables its easy use in internal combustion engines (ICEs). Hydrogen blended in methane is called hythane fuel, which can be used in ICEs. Hydrogen is a gaseous fuel and its compression and liquefaction is expensive. Distribution infrastructure would be needed for using hydrogen in shipping.

Ammonia could be used in fuel cells or in modified ICEs, if safety issues are passed. Due to safety concerns, ammonia is converted to urea for use as a reducing agent in the exhaust gas treatment system (SCR), though these quantities are relative low. Ammonia is an invisible, toxic gas (NIOSH limit 25–30ppm long-term exposure, 300ppm immediately dangerous, 5000ppm fatal within minutes). To date, no ammonia powered ships are operational.

Fuel cells (FC) use hydrogen (stored as compressed, liquefied or in liquid organic hydrogen carriers), methane (e.g. LNG), methanol or ammonia. The FC technologies are e.g. the Proton Exchange Membrane fuel cell (PEMFC) and the Solid Oxide fuel cell (SOFC). The fuel efficiency is estimated at 50-60% for PEMFCs and 60% for SOFCs (85% with the use of heat recovery). PEMFC technology is sensitive to impurities in the hydrogen. SOFCs can pose a safety concern because of the high operating temperatures (800-1000 °C). FCs are still developing, expensive and space demanding, and thus considered for auxiliary engines, hybrid and low power machinery, with an estimated 2–20% CO₂ reduction potential. [3]. Solid oxide and molten carbonate fuel cells could be suitable for high-power marine propulsion, while PEM for low-power applications. Technology learning in other sectors than shipping will be determining for fuel cell deployment, although fuel cells using hydrogen and methanol have been demonstrated in shipping.

Electric/hybrid propulsion based on batteries, flywheels or super capacitors are relatively costly. Hybridisation of some ships may provide fuel savings of 10-40%. GHG emissions are low for all-electric ships on the condition that low-carbon electricity generation is used. Bloomberg New Energy Finance (2017) estimated that by 2030 lithium-ion battery pack prices would fall to \$73/kWh compared to \$273/kWh in 2016. [3].

Wind power uptake has been modest. The technologies with the highest maturity, kites and rotors, are considered most effective at slow speed (e.g. kites below 16 knots)⁷. Rotors are challenging for container ships due to interferences with cargo handling.

Solar energy can be applied with wind technology for auxiliary power demands. [3].

Nuclear propulsion for military and submarine purposes has been used since 1955, and it is still used for some icebreakers (primarily in Russia and military vessels, about 200 reactors). Nuclear power enables the vessel to run for long periods of time without the need to refuel. Challenges with nuclear include significant environmental and health risks (e.g. radioactive fuel and storage for spent fuel), training of staff, nuclear regulation, security, public perception, disposal, etc. Environmental consequences could be worse along inhabited coastlines than in power plants. A majority of countries would not allow nuclear vessels to enter their ports. In late 2017, China decided to invest in the development of two prototype molten salt nuclear reactors for their use in aircraft carriers, drones and military aircrafts. [3]. ETP 2017 [6] does not include nuclear in the B2DS scenario.

⁷ Norsepower, a Finnish start-up has installed its Rotor Sail Solutions on board some ships.

5. Methods for evaluation of emissions

Studies from different emission measurement programs are evaluated based on public reports and articles. Particularly, recent emission measurements carried out by Finnish research organisations give a comprehensive view on the emissions from modern marine engines using different fuels and exhaust treatment technologies [25][26][27][28].

In this report, only the results with engine loads higher than 50% are accounted for.

Specific Fuel Oil Consumption (SFOC) depends on engine and its characteristics. Additionally, fuel consumption varies along with engine load. Buhaug et al. [29] presented SFOC for different engines, however, they concluded that data was not sufficient to more detailed separation SFOC for different engine types than for engine ages and sizes (Table 10). Emissions per kg fuel can be converted to emissions per kWh by using SFOC. For this purpose, EF (g/kg fuel) is multiplied by SFOC (kg/kWh). In this report, SFOC of 200 g/kWh is used for conversions when needed.

Table 10. SFOC (g/kWh) used by Buhaug et al. [29].

Engine year	>15 MW SFOC (g/kWh)	5-15 MW SFOC (g/kWh)	<5 MW SFOC (g/kWh)
before 1983	205	215	225
1984-2000	185	195	205
2001-2007	175	185	195

6. SO_x emissions

6.1 SO_x formation and fuel sulphur content

Through combustion of sulphur present in fuel, SO_x emissions form. Consequently, SO_x emissions from marine diesel engines using different fuels vary substantially depending on fuel sulphur content: SO_x emissions decrease when sulphur content of fuel decreases (Fig. 4). Specifically, combustion of fuel sulphur leads to SO₂ formation and to a minor amount of SO₃. These sulphur oxides combined are called SO_x emissions; however, measurement instruments typically detect only SO₂ concentrations.

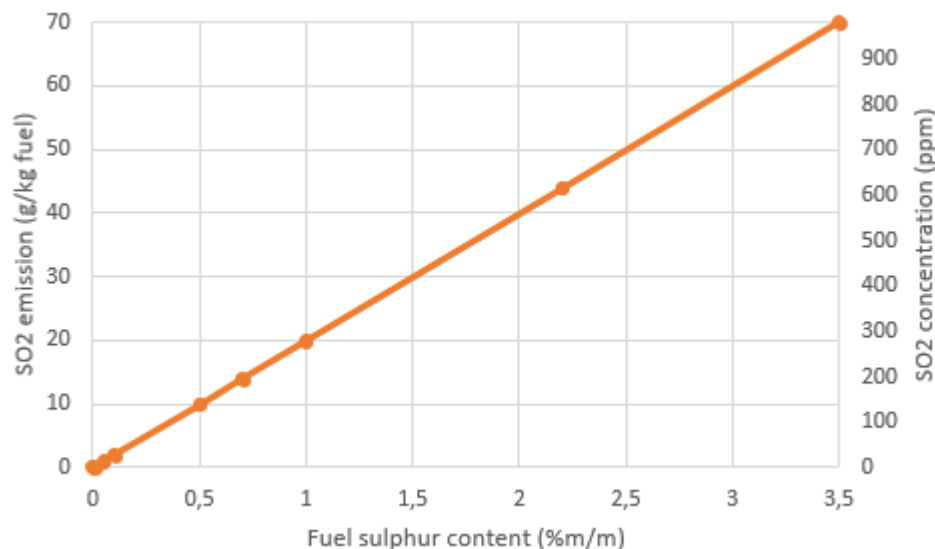


Figure 4. Theoretical SO₂ emission in the exhaust gas formed in the combustion of fuels having different sulphur contents.

Residual fuels are marine fuels having high sulphur contents, whereas lower sulphur contents are found from marine distillate fuels (e.g. DMA, DMB). Almost sulphur-free marine fuels are LNG or methanol, as well as most renewable fuels (See Chapter 4). Fuel with 3.5%(m/m) sulphur content leads to SO₂ emissions of 70 g/kg fuel, and fuel with 0.5%(m/m) sulphur content to SO₂ emissions of 10 g/kg fuel, respectively. Distillate fuels targeted to SECA regions having sulphur content below 0.1% results in SO₂ emissions below 2 g/kg fuel. For high-sulphur residual fuels and low-sulphur distillate fuels, several onboard measurement campaigns have confirmed variation in SO₂ emissions along with fuel sulphur content [27], [28], [30].

LNG and methanol contain only minor amount of sulphur, and thus SO₂ emissions from DF engines using these fuels are assumedly extremely low although pilot diesel could lead to some SO₂ emissions. However, published SO₂ emission results from these technologies were not available. For smaller alcohol diesel engine using methanol fuel (additised with ignition improver) showed SO₂ emissions below the detection limit.

6.2 SO_x scrubbers

When low SO_x emissions are desired, high-sulphur residual fuels can be used only when combined with exhaust gas treatment, namely SO_x scrubbers. Different types of SO_x scrubbers cover a fresh water (closed loop), seawater (open loop), a hybrid scrubber

(applicable to fresh and sea water) and a dry scrubber. Scrubbers have been used for years in power plants⁸, while they were introduced only recently in ship applications.

There is limited number of studies available presenting scrubbers' performance onboard. However, the following onboard studies covered several scrubber technologies:

- One of the recent studies was carried out on a modern cruise ship having a hybrid SO_x scrubber combined with a residual fuel having 0.65% sulphur content (reported by Timonen et al. [27]).
- Another recent study was carried out onboard a RoRo passenger (RoPax) ship equipped with an open loop SO_x scrubber (ECO-DeSO_x, Ecospray Technologies), and a diesel oxidation catalyst (DOC, Ecospray Technologies) using residual fuel at 1.9% sulphur content (reported by Teinilä et al. [28]).
- Emission results from a container ship (1987) retrofitted with SO_x scrubber (Alfa Laval PureSO_x, MY2015, "open loop" mode at sea and "closed loop" mode in port, fresh water/sodium hydroxide (NaOH) solution was reported by Johnson et al. [31]).
- The roll-on roll-off ship Ficaria Seaways and a SO_x scrubber system (Alfa Laval PureSO_x) having open and closed loop modes (only the open seawater mode was used during the measurements) was reported by Fridell and Salo [32].
- Emission results from ships were presented by Yang et al. [33]: 1) Container ship with Mitsui Man B&W 16.6 MW engine and Alfa-Laval scrubber 2) Cruise ship with Wärtsilä 4 x 12.6 MW engines without scrubber and 3) Ro-Ro Hyundai Man B&W 15.6 MW engine with Wärtsilä scrubber.

The emission results reported in the over-mentioned studies showed that SO_x scrubbers reduced the SO₂ emissions effectively to levels corresponding to <0.1% S in the fuel. Practically, SO₂ emissions measured were at negligible level after SO_x scrubber in several onboard measurement campaigns [27], [28], [31], since SO₂ emissions below 0.6 g/kg fuel after SO_x scrubber represents fuel sulphur content of below 0.03%(m/m). Consequently, SO_x scrubbers in measured in the evaluated studies showed lower SO_x emissions than those when using marine distillate fuel close to 0.1%(m/m) sulphur content.

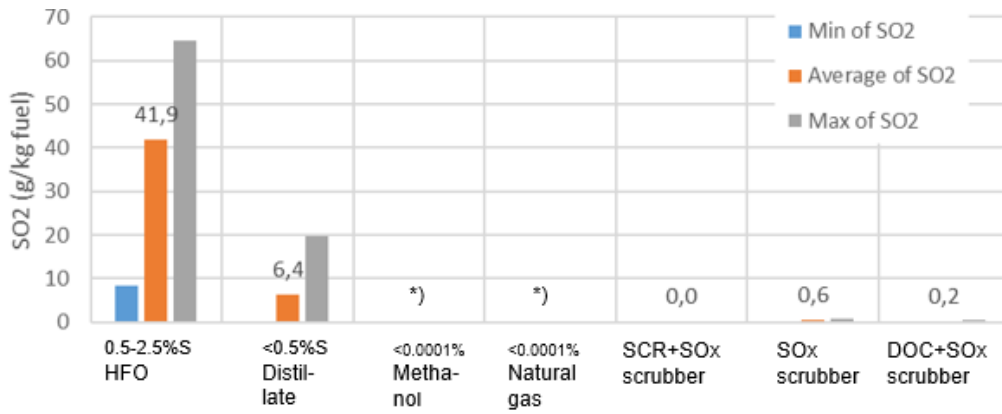
6.3 SO_x emission summary

The SO_x emission results from the studies evaluated are summarised in Fig. 5. Here engines having conventional and modern fuel injection systems are covered at engine loads higher than 50%.

Engine-out SO_x emissions are proportional to the sulphur content of fuel. For example, reducing marine fuel sulphur content from 3.5%(m/m) to 0.1%(m/m) decreases SO_x emissions approximately from 70 g/kg fuel to below 2 g/kg fuel. LNG and methanol contain only minor amounts of sulphur leading to extremely low SO_x emissions depending on pilot diesel in DF engines.

For SO_x scrubbers, extremely low SO_x emissions have been reported [27], [28], [31], corresponding to fuel sulphur content below 0.03%(m/m).

⁸ An older study by Oikawa et al. [120] did a performance test on an existing seawater flue gas desulfurization system employed at a 600-MW power plant (utilizing coal containing 0.62% sulphur) and showed excellent desulfurization efficiency, high reliability, as well as acceptable environmental impacts.



*) SO₂ emissions from use of methanol and natural gas are very low based on their low sulphur contents.

Figure 5. SO_x emissions from MSD and SSD marine engines at engine loads above 50% MCR. [25], [27], [28], [30], [31], [34]–[37] [38]–[40][41][42][43][44]. High variation in SO_x emissions for HFO and distillate fuels is due to their different sulphur contents (see Fig. 4).

7. NO_x emissions

7.1 NO_x formation and engine/combustion control

NO_x emissions are produced from the reaction of nitrogen (N₂) and oxygen (O₂) of intake air during the combustion process, especially at high temperatures. Composition of air is 78% N₂ and 21% O₂, whereas nitrogen contents of marine fuels are typically too low to form substantial NO_x emissions. In the combustion process, from the nitrogen of intake air, mainly NO is formed, apart from minor amount of NO₂. Measures to decrease NO_x emissions are related to engine design, combustion control, exhaust gas recirculation (EGR), exhaust gas treatment (e.g. SCR) or low-NO_x fuels.

Injection timing retard and charge air cooling reduce NO_x emissions. In both cases, the lower combustion pressure leads to lower peak combustion temperature and thus lower NO_x emissions. However, these lead to loss in fuel economy, and also PM emissions increase. This physical characteristic is known as the NO_x/PM trade-off. However, both NO_x and PM reduce when moving from conventional diesel technologies to advanced diesel engine technologies equipped with e.g. turbocharger and electronic engine control. [2].

Engine tuning to low PM emission combined with a NO_x reduction technology enables simultaneous abatement of NO_x and PM emissions together with maximum fuel economy. Such NO_x reduction technologies are EGR, which is an internal technology of an engine, and SCR, which is exhaust aftertreatment technology.

EGR reduces NO_x by mixing a part of the exhaust gas into the intake combustion air. Lower oxygen and higher water and CO₂ concentration in the intake air results in suppressed combustion temperatures and reduced NO_x formation. EGR tends to increase PM emission [45].

The potential of engine tuning to reduce emissions is proven for high-speed diesel engines, while respective studies are not publicly available for large marine engines ([2], accessed in 2018, [46]).

7.2 Selective catalytic reduction (SCR)

The SCR system utilizes a catalyst and ammonia to reduce NO_x emissions. Several chemical reactions can occur in the SCR system, with the dominant one involving nitrogen monoxide, ammonia, and oxygen reacting to produce nitrogen and water. Due to toxicity and handling problems associated with ammonia, water solution of urea is widely used as an ammonia source. The target is to have effective urea decomposition upstream from the SCR catalyst. Optimization of the urea feed is important since all ammonia inserted into the SCR catalyst should be effectively utilized for NO_x reduction and no ammonia should be found in the downstream of the catalyst.

SCR catalysts in ship applications are usually vanadium based since V₂O₅ catalyst has high activity and sulphur tolerance [47], [48]. SCR technology is compatible even with high-sulphur marine fuels as monolithic fixed beds have square holes, large enough to avoid clogging and poisoning. [19], [27], [28], [45].

Very good NO_x reductions (near 90%) for SCR systems are reported in several ship applications. Zheng et al. [49] reported a case study of SCR development to meet IMO Tier III requirements. They achieved an 80% NO_x reduction with vanadium based SCR. Jayaram et al. [50] reported NO_x reductions of 90-91% measured for SCR retrofit of auxiliary engines on ocean-going vessel. That SCR also used a vanadium catalyst and was tested using

heavy fuel oil as fuel at load modes 35%, 50% and 67% with exhaust temperature being 327-363°C. Winnes and Fridell [51] reported NO_x emission factors resulting to above 90% NO_x reduction for a ship operating at full speed at 75% load. Nuskowski et al. [52] reported results from two ferry engines fitted with SCR. The NO_x conversions were measured to be between 36% and 94%. The lower efficiency values were attributed to the urea injection strategy, which meant that no urea was injected before the catalyst temperature reached a 300°C threshold. They concluded that the SCR would provide greater NO_x reduction for vessels with longer trips or hotter exhaust temperatures. One performance study of SCR with heavy fuel oil with high sulphur level yielded NO_x reduction efficiencies from 75% to 99% with vanadium-based SCR catalysts at exhaust temperature of 340°C [53]. Further studies showed that the NO_x reduction efficiency varied with temperature, reaching the highest values near 90% at 340-400°C and the lowest values near 70% at the lowest test temperature of 260°C. By increasing the catalyst loading the NO_x efficiency was found to increase at low temperatures while at higher temperatures practically no differences were found in the NO_x efficiencies of the three differently loaded catalysts [47].

7.3 Fuel effect on NO_x emission

There are differences in combustion temperatures between fuels. For LNG and methanol, reduced NO_x emissions are achieved as a result of reduced peak temperatures in the engine chamber during combustion. This is evidenced for LNG DF marine engine for example in the onboard ship measurements reported by Anderson et al. [54].

Limited data for DF marine engine using methanol fuel indicates substantially lower NO_x emissions than those for marine diesel engine using residual or distillate fuels [55]. However, NO_x emissions for methanol DF seem to be higher than those for LNG DF or SCR equipped marine diesel engines.

As concerns paraffinic fuels (HVO, GTL, XTL), their use generally reduce NO_x emissions when compared to traditional diesel fuel based on experiences with road and non-road applications. This is opposite to FAME type biodiesel, which typically increases NO_x emissions when compared to traditional diesel fuel [24].

Water in fuel emulsions (WiFE) were developed to reduce NO_x emissions from heavy-duty on-road and off-road diesel engines, for example Lubrizol's PuriNOx contains approximately 20% water [45], [56]–[58]. Water is not soluble in diesel fuel, thus emulsifier additives are necessary to keep emulsion homogenous or direct injection of water can be used. Concerns over the use of WiFE include increased wear of the engine (contact with water) and the stability of diesel-water-additive emulsions [56].

7.4 NO_x emission summary

Several technologies reduce ship NO_x emissions efficiently compared with residual fuel use in marine diesel engines (Fig. 6). NO_x emissions from marine diesel engines using residual and distillate fuels vary from approximately 50 to 100 g/kg fuel at engine loads higher than 50% MCR in the absence of NO_x reduction technologies.

NO_x emissions from 2-stroke SSD engines are typically higher than those from 4-stroke MSD engines, which is reflected also as higher emission limits for 2-stroke SSD engines than for 4-stroke MSD engines (Chapter 2.1). Residual fuels are mainly used in 2-stroke SSD engines and distillate fuels in 4-stroke MSD engines. Thus, the differences in NO_x emissions between residual and distillate fuels are mainly due to differences between engines types and not due to differences between fuels. When measured in one engine, NO_x emissions were not substantially different between residual and distillate fuels for example in a study reported by Aakko-Saksa et al. [25].

Very low NO_x emissions are achieved when using LNG as a fuel, or when applying a SCR catalyst. In the study by Anderson et al. (e.g. [54], NO_x emissions were on average as low as approximately 6 g/kg fuel for LNG DF engine. The highest NO_x emissions for natural gas were observed in testbed measurements, which may be related to this specific engine [59].

Limited data with methanol fuelled marine engine showed substantial reduction in NO_x emissions compared to marine diesel engines. However, NO_x emissions were higher for methanol DF engine than for LNG DF or SCR equipped engines [55]. For special diesel engine using methanol fuel (additised with ignition improver), NO_x emission level was only 11 g/kg fuel ([60] not shown in Fig. 6).

SO_x scrubber may also show a small decrease in NO_x emissions, approximately 5-10%, probably due to transfer of nitrogen oxides into water. [27].

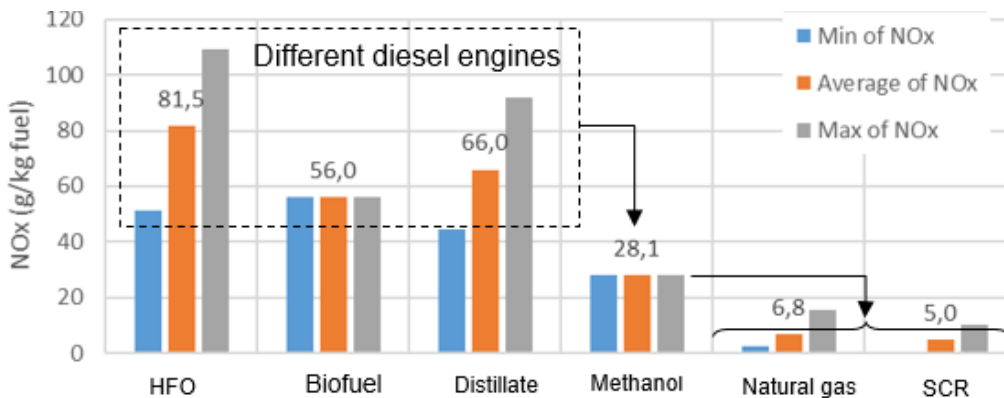


Figure 6. NO_x emissions from marine engines using different fuels and SCR exhaust gas treatment technology. MSD and SSD engines, engine loads above 50% MCR. [14], [25], [27], [28], [30], [31], [34], [35], [50], [51], [54], [55], [59], [61][38]–[40][41][42][43].

8. Particulate matter, particle number and black carbon emissions

8.1 General

The PM mass emission is formed through incomplete combustion of fuel (and lubricant). Not only PM mass emission is important, but also its composition and particle number (PN) emissions, especially number of ultrafine particles. Engine exhaust PM emission contains black carbon, brown carbon (BrC), organic carbon (OC), inorganic ions (sulphates, nitrates), polyaromatic hydrocarbons (PAHs), metals and particle bound water. Composition of PM emission depends on engine, fuel and exhaust treatment technologies applied.

Many chemical species (e.g. PAHs in PM) are harmful for human health and have been linked with heart and pulmonary diseases, and even with Alzheimer's disease [62]. This is an important aspect as ships mainly travel near densely inhabited coastal areas within 400 km of coastlines [63].

Particle emissions from ships induce adverse health and climate effects. As regards climate change, CO₂ is the strongest ship emission contributing to the global warming; and BC associated with PM is the second strongest contributor. BC emission is particularly significant to the Arctic climate through its deposition on ice and snow [1], [64]–[66]. Residence time of black carbon emission in the atmosphere is around 7.3 days, and thus the ship plumes influence at a distance from the source [67].

8.2 PM emissions

8.2.1 The effect of sampling on PM results

Measurements of particle emissions are challenging. Overall, definition of particle emission is not simple as the results (both mass and number based) depend on the measuring conditions, particularly on the dilution system. Aerosol changes during the cooling and dilution when the exhaust gas exits the tailpipe, and during diluted sampling in the PM emission measurements (see Fig. 8b for diluted and hot sampling). The particle emission results also depend on the instrument used for the measurement. Ntziachristos et al. [68], [69] points out that ruling PM emissions from marine engines will first require a more strict determination for sampling conditions than currently enforced by the ISO 8178 protocol, at minimum in terms of the dilution ratio range allowed.

Sulphur content of fuel has a particular role in ship PM emissions, since for the high-sulphur fuels the major component in ship PM emission is sulphate. Fuel sulphur is combusted almost completely to SO₂ (Fig. 4), but a few percent of fuel sulphur may be oxidised to SO₃, and further to SO₄ present in PM (Fig. 7a). Thus, PM associated SO₄ emissions correlate with sulphur content of fuel, although degree of conversion depends on many factors. Elevated air to fuel ratio and combustion temperature as well as presence of e.g. vanadium increase the conversion of SO₂ to SO₃. [70], [71].

For high-sulphur fuels, the effect of sampling procedures on the condensable constituent of exhaust gas (sulphuric acid, water and organic compounds) is substantial. Sulphates present in PM are in a form of sulphuric acid and e.g. metal sulphates. Sulphuric acid in the exhaust gas is sensitive towards changes in the PM sampling conditions, while metal sulphates are

rather persistent. Small changes in sampling conditions affect sulphuric acid related PM emission, and water bound in sulphuric acid further increase this effect⁹.

Condensing of sulphuric acid from exhaust gas can be avoided by using higher PM sampling temperature than the acid dewpoint temperature of the exhaust gas. In raw exhaust gas, sulphuric acid is in gaseous form, since exhaust temperatures are typically higher than respective dewpoint temperatures (blue line in Fig. 7b). Consequently, sulphuric acid is not assumedly present in PM emission when collected with “hot” sampling.

Sulphuric acid condenses in the PM emission in diluted sampling (ISO 8178) at sufficient fuel sulphur contents and at relatively low dilution ratios (Fig. 7b) [72]. Once sulphuric acid is condensed in PM (or nucleated), it will not evaporate easily as its boiling point is high (337 °C, decreased by Kelvin effect, increased by bound water). Appropriately low dilution ratios are needed to maintain collected PM mass sufficient for weighing. Furthermore, authors note that sulphuric acid precursor (SO₃) present in the exhaust gas is relevant in the atmospheric reactions, and thus non-condensing PM sampling conditions are not necessarily desirable. However, this issue needs further considerations.

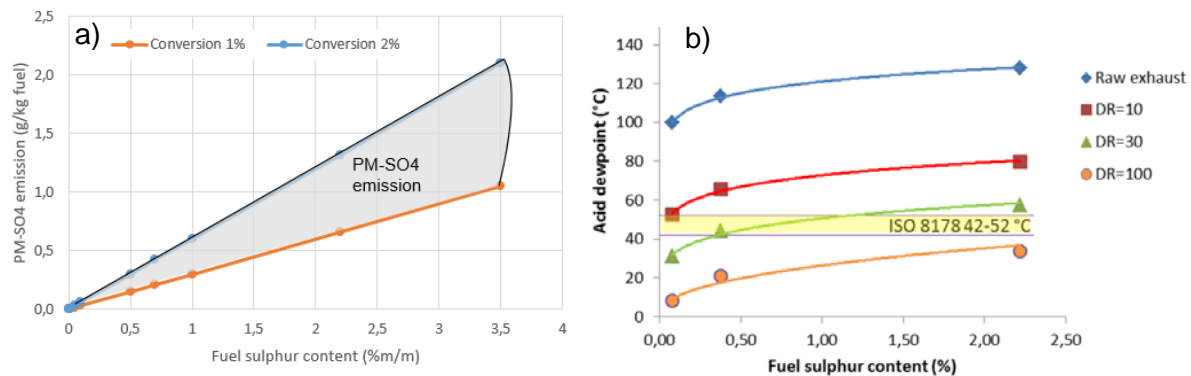


Figure 7. a) Content of sulphates in PM depends on sulphur content of fuel. Here conversions of 1% and 2% of fuel sulphur content to SO₄ in PM is assumed. b) Fuel sulphur content and dilution ratio in sampling affect condensing of sulphuric acid. [26].

8.2.2 PM emission and its composition (SO₄, OC, PAHs, metals)

Fuel characteristics, engine type and operating conditions contribute to the observed particle emission level (e.g. [73]). Amongst the studies evaluated here, PM emissions were the highest for marine engines using *high-sulphur residual fuels*, on average up to 7.5 g/kg fuel (Fig. 8a). PM emissions for high-sulphur fuels contained mainly sulphates, organic matter and metal oxides (ash) in PM (Fig. 9a). PM emission for high-sulphur fuel having sulphur content of 2.2% was more than twofold when diluted sampling was used instead of hot sampling, which is related to the phenomenon explained in section 8.2.1. Hydrated sulphuric acid and semivolatile organic compounds condense on particles from the gas phase during diluted sampling, whereas mainly persistent metal sulphates and heavy organic compounds are present in the exhaust PM emission collected using hot sampling. Similar comparison of PM emission for different fuels using hot and diluted sampling principles is shown also for 0.1%S and Bio30 fuels in Aakko-Saksa et al. [72].

For *distillate fuels*, which had low fuel sulphur contents, PM emissions were low, on average below 0.5 g/kg fuel. Also sulphate emissions were very low when using distillate fuels. As concerns *paraffinic fuels* (HVO, GTL, XTL) or *oxygenated FAME type biodiesel*, their use in high-speed diesel engines generally reduces PM and soot emissions when compared to traditional diesel (Fatty acid esters in [24]). Sulphur contents of these fuels are typically very

⁹ At 50% relative humidity, “combined water” is calculated as 1.32 x the amount of sulphuric acid (SAEJ1936).

low, and they don't contain much impurities. For *oxygenated biodiesel*, oxygen in fuel may enhance combustion of PM.

Extremely low PM emissions were observed for *LNG DF engines*, around 0.02 g/kWh (0.1 g/kg fuel) by Lehtoranta et al. [59] and Verbeek et al. [74].

Methanol use assumedly leads to low PM emissions; however, measured results are sparse. For smaller alcohol diesel engines using methanol fuel (additised with ignition improver), PM emission was 0.2 g/kg fuel [60], which is at the same level as PM emissions observed for low sulphur distillate fuels used in marine diesel engines.

SO_x scrubber, SCR and DOC may remove PM to some extent. Fig. 8b shows the results from two studies where PM emissions were measured before and after exhaust treatment technologies [27], [28].

SO_x scrubber has reduced PM emission in many studies, although not consistently. Reductions of PM emission over the *SO_x scrubbers* have been generally 17-45% depending on the engine and fuel, while in some studies PM emission has not reduced [33]. Exhaust gas is cold after *SO_x scrubber*, and the sampling conditions before and after scrubber may affect the observed PM emissions (e.g. different dilution systems).

SCR and DOC may remove a part of PM emissions by oxidising the organic fraction of PM, and possibly also sulphates and metal oxides in PM may be reduced [27], [28], [75], [76]. In one study [28], PM reduction over diesel oxidation catalyst was mainly due to reduced sulphate content of PM (Fig 8b, Fig 9a: 1.9%S E4 vs 1.9%S E4 DOC+scrubber).

Particulate filters, amongst others, potentially reduce PM emissions. These technologies are discussed in Chapter 8.5.

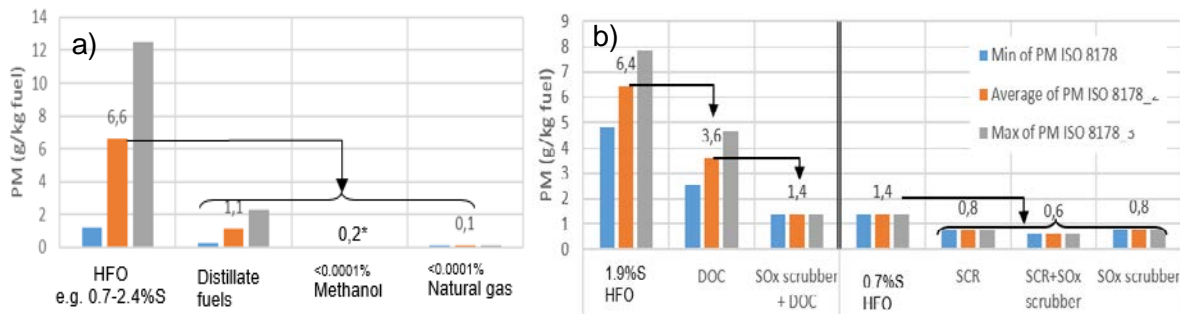


Figure 8. PM emissions from marine engines using a) different fuels and b) exhaust gas treatment: measured before and after DOC, SCR and SO_x scrubber, two ships. MSD and SSD engines equipped with modern fuel injection systems, engine loads above 50% MCR. [25], [27], [28], [30], [31], [35], [37]–[43], [50], [60], [77].

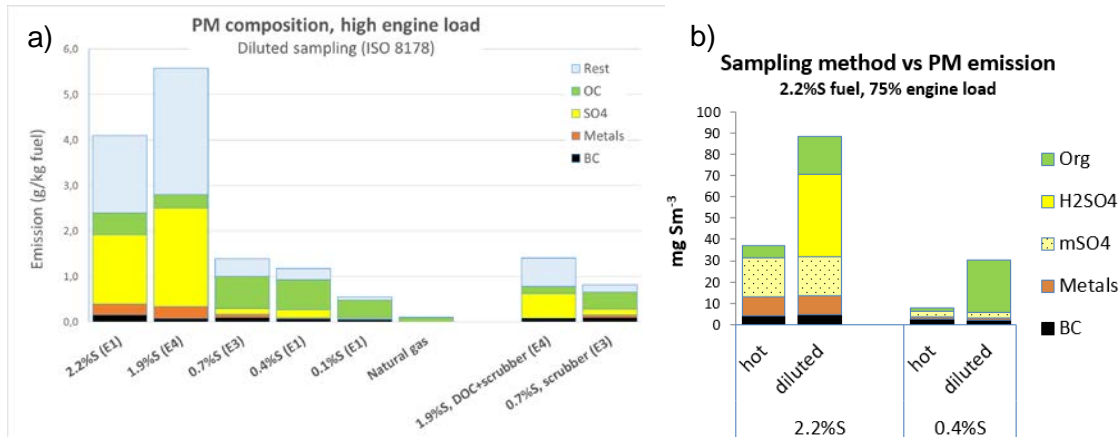


Figure 9. Composition of PM when using a) different fuels and exhaust gas treatment technologies, three engines E1, E3 and E4 b) different PM sampling methods. [25], [28], [37], [72], [78].

Besides sulphates and organic compounds, PM emission in exhaust gas from internal combustion engines may contain polyaromatic hydrocarbons with and without heteroatoms (N, S, O). These may originate from unburnt fossil fuel, and additionally they may form in incomplete combustion of fuel [79], [80]. Many PAHs have been identified as carcinogenic and mutagenic, for example, benzo(a)pyrene. Lists of priority PAHs are defined taking into account classifications by International Agency for Research on Cancer (IARC). Definitions include carcinogenic substances in Group 1, probably carcinogenic in Group 2A and possibly carcinogenic in Group 2B [81], [82]. The US EPA listed in 2007 mobile-source air toxics including seven priority PAHs, and European directive 2004/107/EC defined slightly different list of relevant PAHs. Sum of priority PAHs presented in this report include benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene).

Residual fuel use in marine diesel engine led clearly to the highest PAH emissions, while PAH emissions were modest or low for other combinations of fuels and exhaust gas treatment technologies (Fig. 10).

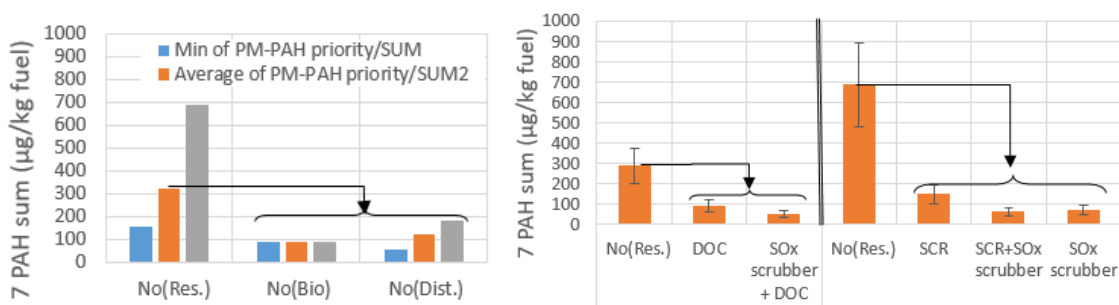


Figure 10. Sum of seven PAH emissions in PM emissions from marine engines using different fuels and exhaust gas treatment technologies. MSD and SSD engines at engine loads above 50% MCR. [25], [27], [28], [34], [78].

Heavy metals are accumulated in exhaust PM originating from fuel, engine oil or engine wear. Residual fuels may contain substantially V, Ni, Fe, Ca and Na, while Ca is the dominant metal in engine oil for large marine engines.

Only a few studies have reported metal emissions from marine engines. For an example, vanadium emissions are shown in Fig. 11. Substantial V and Ni emissions from marine diesel engines using residual fuel have been observed, while metal emissions have been low for

cleaner fuels and when using exhaust gas treatment technologies. DOC reduced efficiently heavy metals originating from residual fuel use. Residual fuel used in combination with SO_x scrubbers was relatively low in sulphur content, and so was metal content in fuel and exhaust.

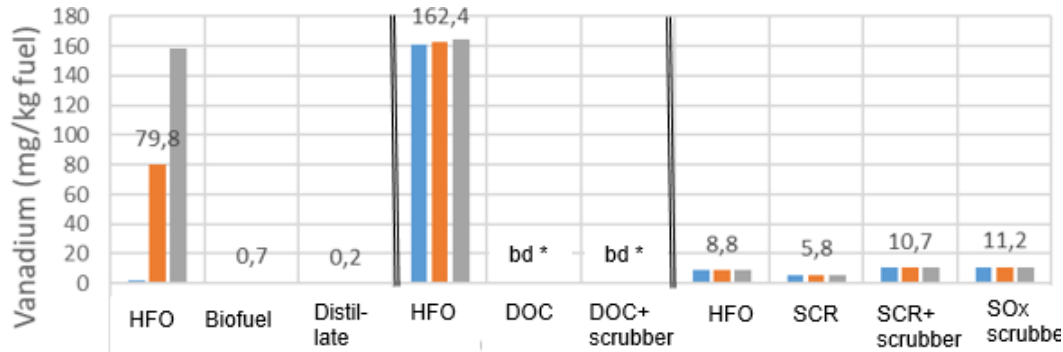


Figure 11. Vanadium emissions from marine engines using different fuels and exhaust gas treatment technologies. MSD and SSD engines at engine loads above 50% MCR. *bd = below detection limit. [25][78][27][28].

8.3 Black carbon emissions

Black carbon emission is a part of PM emission from marine diesel engines. BC emission form in the combustion of carbonaceous matter [83]. BC contains more than 80% of carbon in double bonded forms. Primary BC particles, 10–90 nm spherules, cluster together immediately after formation in a flame to form aggregates [84]. Particles containing BC, brown carbon¹⁰ and/or some metals typically have a dark colour and they absorb light, thus warming the climate. Instead, particles containing mostly organic carbon and/or inorganic ions (e.g. sulphates) typically scatter solar radiation and they are considered to cool the climate. ([1] and references in [27], [72]).

The IMO has agreed a definition for BC covering different properties according to Bond et al. [66]: “Black Carbon is a distinct type of carbonaceous material, formed only in flames during combustion of carbon-based fuels. It is distinguishable from other forms of carbon and carbon compounds contained in atmospheric aerosol because it has a unique combination of the following properties:

- It strongly absorbs visible light with a mass absorption cross section of at least $5 \text{ m}^2 \text{ g}^{-1}$ at a wavelength of 550 nm;
- It is refractory; that is, it retains its basic form at very high temperatures, with vaporization temperature near 4000 K;
- It is insoluble in water, in organic solvents including methanol and acetone, and in other components of atmospheric aerosol; and
- It exists as an aggregate of small carbon spherules”

BC reduction technologies

Evidence on the capability of *distillate fuels* to reduce BC emissions compared with residual fuels is not consistent. CIMAC [45] found very little evidence to support this claim, while Lack [85][86] found that moving from residual to distillate fuels would reduce BC emissions by an average of 33%, and also Aakko-Saksa [87] found respective reduction of BC emissions by

¹⁰ Brown carbon material is dark constituent of PM, which contains e.g. long-chain, polymeric, (poly)aromatic and refractory pyrolysed organic compounds.

on average 26%. However, variation between studies was substantial: some studies showed up to 50% reduction of BC emission when moving from residual to distillate fuel, while some studies showed even increased BC emission. An increase in BC emission for distillate fuel was reported e.g. by Moldanova et al. [88]. for the 6 MW engine. Aakko-Saksa et al. [25] found an increase in BC emission when moving from high-sulphur residual fuel to lower-sulphur (below 0.5%S) residual fuel for an old engine at low engine load. Such fuels may be increasingly present when the global sulphur limit of 0.5% will be in force in 2020. Similar indications have been reported also for high-speed diesel engine [31]. New engines could be less sensitive to fuel changes than old engines.

Synthetic, bio and renewable paraffinic diesel-type fuels (GTL, HVO, BTL, XTL) assumedly lead to the BC emissions close to those observed for fossil distillate fuels, or slightly lower. Results from only two emission studies on paraffinic fuels on marine diesel engines were found. Verbeek [89] reported of PM reduction from 16 to 60% and smoke reduction of 32% when comparing GTL with diesel (EN590) fuel for inland ships. Betha [90] reported of a plume study on a high-speed engine showing increased BC emissions with paraffinic HVO compared to ultra-low sulphur diesel, however, plume measurements may not be appropriate for comparing two hydrocarbon liquid fuels with each other. A number of studies on heavy-duty applications have proved lower soot emission for paraffinic fuels than for conventional diesel fuel [23], [91], [92].

The results of two studies showed that unesterified, oxygen-containing biofuels substantially reduced the BC emissions when compared to residual or distillate fuels. Petzold et al. (2011 in [19], found elementary carbon (EC)¹¹ emissions up to 30% lower for palm oil and animal fat than for distillate fuel (MGO), but higher for soybean and sunflower oils. For biofuels, also ash and sulphate emissions were low. FAME type biodiesel (ULSF, soybean blends B20, B50) reduced EC emissions in a marine diesel engine at 75% load (reduction of 20-42%) (Jayaram et al. 2011 in [19]). The effect of FAME type biodiesel on emissions from road and non-road applications have reduced PM and soot emissions [24].

The BC emission results for *LNG DF* engines are available from e.g. EUROMOT, Lehtoranta et al. [59] and Aurela et al. [93]. In the EUROMOT data, natural gas used as a main fuel in the DF engines resulted in low BC emissions in all engine size categories tested (below 0.007 g/kg fuel at high engine loads). Only in one case, higher BC emission was observed (0.083 g/kg fuel). Emission results from the use of *methanol* in marine diesel engines are sparse, particularly as concerns BC emissions. Theoretically, the oxygen containing methanol molecule containing only one carbon atom is clean-combusting. Stojcevski [94] reported reduced BC emissions when using methanol instead of distillate fuel as a main fuel in a DF engine. BC emissions reduced by 55-75% depending on the pilot fuel injection when compared with distillate fuel. When diesel fuel is the main fuel in LNG DF or methanol DF engines, BC emissions are similar to diesel engines.

Water in fuel emulsions are designed to reduce NO_x emissions; however, addition of water in fuel may also reduce BC emissions in engines equipped with conventional fuel injection at low engine loads, while the benefit may be modest in modern engines. WiFE may improve fuel droplet dispersion and mixing in the combustion chamber, although at high loads this effect can be offset by the increase in injection duration [45]. Modern fuel injection systems provide good fuel/air mixing over a very wide power range. [19]. In some sources, substantial ship BC reductions are reported when using WiFE [14], [85], however, along with energy loss (refs in [19]).

Metals can act as catalysing agents, called "fuel-borne catalysts" or "colloidal catalysts". Residual marine fuels often contain metals, e.g. V, Ni, Fe and Na, and particularly vanadium

¹¹ EC is refractory material of PM measured with thermal methods, while BC is optically determined.

may catalyse BC combustion [95]. Heavy metals are negative features in fuels as many of them are toxic and cause harmful health and environmental effects.

As a summary for fuels, Fig. 12a shows that BC emissions have been very low when using methane (natural gas), methanol or oxygen containing (fatty acid type) biofuel in the studies evaluated. Differences in BC emissions between residual and distillate fuels are generally lower than respective differences between different marine diesel engines, and thus studies considered for these liquid hydrocarbon fuels should be carried out in one engine. This kind of evaluation reported by Aakko-Saksa [87] concluded that BC reduction was on average 26% when moving from residual to distillate fuels, but large variation was found between different studies.

Exhaust treatment technologies (SO_x scrubbers, SCR, DOC) designed for other purposes than for reducing BC emissions were not particularly effective in reducing BC emissions in limited number of studies available (Fig. 12b). BC emissions are anticipated to reduce efficiently by using particulate filters and potentially also by ESP-type solutions. These technologies are discussed separately in Chapter 8.5 as they reduce generally PM related emissions, and not only BC emissions. These technologies are not commercial for ships, yet.

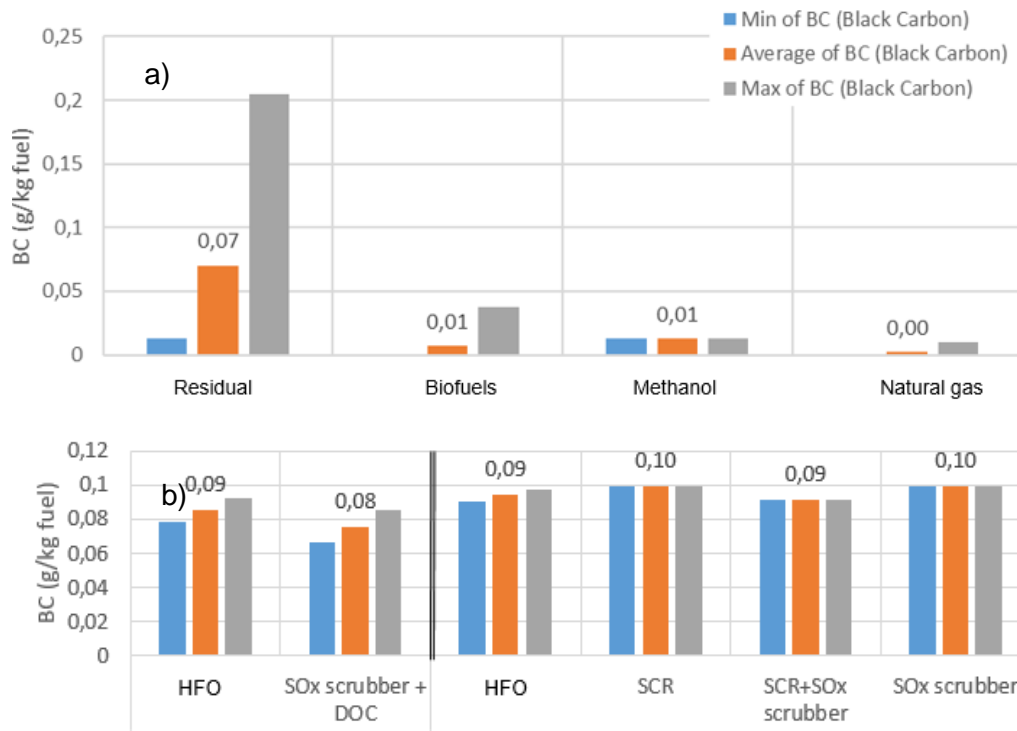


Figure 12. BC emissions from marine engines using a) different fuels and b) exhaust gas treatment by DOC, SCR and/or SO_x scrubber. MSD and SSD engines at engine loads above 50% MCR. [14], [25], [27], [28], [30], [31], [34], [37]–[40], [42], [44], [50], [55], [61], [69], [88], [96]–[104].

8.4 PN emissions

Studies on PN emissions from marine diesel engines are sparse. Furthermore, there are fundamental differences in the characteristics of PN emissions reported. Legislative PN limits refer to solid, non-volatile particle number emissions (PN_{solid}), while considerations of real-life PN emissions account also for volatile PN (PN_{total}). Measurement method selected for legislation was characterized by capability to achieve repeatable results.

Fig. 13 shows results of non-volatile PN_{solid} emissions from marine engines. When using residual fuel or distillate fuel in marine diesel engines with or without exhaust treatment technologies, PN_{solid} emissions were from 3×10^{14} 1/kg fuel to 7×10^{14} 1/kg fuel in other cases than in one study, in which an older engine had PN_{solid} emission of 1.6×10^{15} 1/kg fuel [37], [105]. Thus range of PN_{solid} emissions from marine diesel engines is quite large, from approximately 1×10^{14} 1/kg fuel to 2×10^{15} 1/kg fuel, modern engines potentially being in the lower part of range. Moving from residual to distillate fuels seems not to affect substantially the PN_{solid} emissions. Some studies on PN emissions from marine diesel engines using biofuels have been reported. Ushakov et al. [106] found an increased PN emission for paraffinic GTL fuel compared with distilled MGO fuel. Also for biodiesel, PN emission elevated as particles sizes reduced in a study by Jayaram et al. (2011 in [19]). Instead, the PN_{solid} emission reduced when moving from IFO to biofuels, while PN emission did not change in a study by Petzold et al. (2011 in [19]). Biofuels (soybean, sunflower, palm oil and animal fat) were studied in a 400 kW single cylinder engine in comparison with MGO (< 0.1% S) and IFO (2.17% S). Authors note that particularly as concern biofuels, number of studies are too sparse for conclusions on the effect of biofuels on particle number emissions from marine engines.

From the studies evaluated, one of the technologies showed very low PN_{solid} emissions, substantially lower than those from marine diesel engines, namely LNG DF engine using natural gas as a fuel. PN_{solid} emission for LNG DF was only 6.5×10^{12} 1/kg fuel in a study reported by Lehtoranta et al. [37].

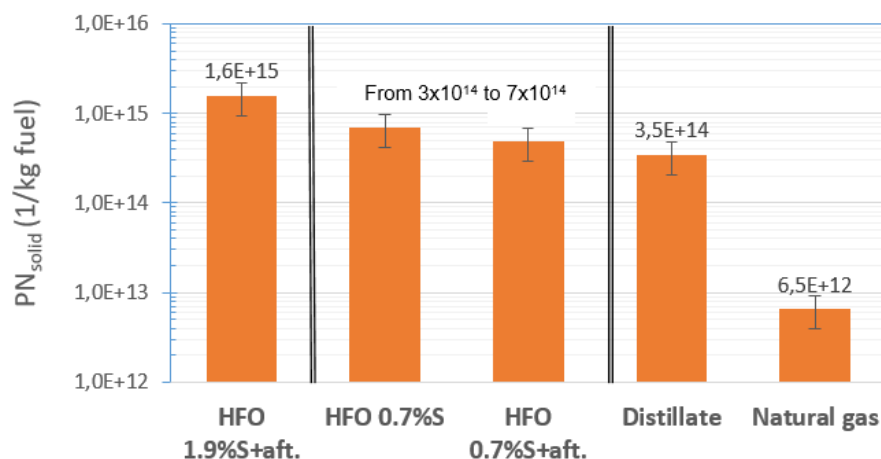


Figure 13. PN_{solid} emissions from marine engines using different fuels and exhaust gas treatment technologies. MSD and SSD engines equipped with modern fuel injection systems, engine loads above 50% MCR. [37], [105].

As mentioned, legislative PN limits refer to solid, non-volatile particle number emissions, and studies published so far mainly present results of PN_{solid} emissions. For assessing the health effects of exhaust from marine engines, total PN emissions besides PN_{solid} emission is significant. In the recent measurement campaigns [25][27][28] both volatile and non-volatile PN emissions were measured, however, the total PN results are not published, yet (manuscript in progress by Kuittinen et al.).

Hallquist et al. [76] studied particle number emissions onboard a ship, from one of the ship's four main MSD diesel engines equipped with SCR. Fuel was low-sulfur marine residual fuel. At engine load of 75%, emission factor for PN was 10.4×10^{16} 1/kg fuel, and about 50% of the PN were found to have a nonvolatile core at 250 °C. Thus total PN and non-volatile PN_{solid} emissions were higher than those presented in Fig. 13.

Some studies indicate higher particle numbers for MGO than for IFO (refs in [19], and some only minor differences. For example, Anderson et al. [107] reported that when using an IFO

fuel blend (0.12%S) in comparison with MDO in Volvo Penta D3-110 engine, no or only small differences appeared in particle numbers, but differences were seen in particle diameters larger than 50 nm.

For LNG, Anderson et al. [54] found low total PN emission, which is in-line with study reported by Lehtoranta et al. [37] showing low PN_{solid} emissions for natural gas fuelled engine.

8.5 Particulate reducing exhaust treatment technologies

Particulate filters

Diesel Particulate Filters (DPFs) are used for automotive diesel engines, and they efficiently reduce (more than 90%) emitted particles, provided that the fuel is sulphur-free diesel (below 0.001% sulphur content). Even then, filter clogging may be an issue. DPFs have small channels (micrometre range) where solid PM is collected and periodically removed (regenerated) [19]. In Europe, the solid particle number limits for diesel vehicles are met only with efficient closed, wall-flow DPFs, while “open type filters” do not remove particles sufficiently to meet particle number limits [2]. Automotive DPFs are not technically applicable when using marine fuels containing substantially sulphur, ash and other impurities. Automotive PM consists almost entirely of BC, which is combustible in passive soot regeneration of a filter (NO₂ assisted), or active regeneration (oxygen at appr. 600 °C). Marine PM contains, e.g. metal oxides and sulphates, which are not combustible and prevent the use of regeneration strategies from automotive applications. There are also other technical challenges related to e.g. exhaust gas temperature and back-pressure, reliability, durability and filter size [19], [45], [108].

Some DPF designs for marine diesel engines have been demonstrated. A ceramic filter manufactured by NGK (CERALEC system) is installed in auxiliary engines on 10 Pure Car Carriers to prevent new cars from fouling due to acid particulates during loading and unloading of cars at ports. [109], [110]. An early demonstration of DPF was conducted on a ferry by Mitsui O.S.K. in 2012, (ref in [19]). Køcks et al. [111] reported a demonstration with an integrated particle filter and SCR system (Dinex F-SCR) on an inland ferry using marine diesel with sulphur content below 0.1%. Another demonstrated technology is the ECO-Jet system developed by Haldor Topsoe A/S, a multi-catalytic soot filtration for marine applications [108].

Particulate filters are not yet in commercial use for marine diesel engines using marine fuels, or proven for long-term durability. Some of the key questions are how clean fuel is needed, and how regeneration performs? The sulphur limit of 0.5% for marine fuels in 2020 may improve the quality of fuels; however, this may not be sufficient for DPFs, e.g. due to possibly remaining residual components, ash and other impurities. Takahashi and Masuda [110] also pointed out concerns on engine exhaust back-pressure with filters, negative effect on engine performance, space needed, blowers, regeneration of filters, additional energy consumption, and storage and disposal of the collected particulates.

Electrostatic Precipitators (ESP) and bag filters

Electrostatic precipitators (ESP) and bag filters are used in some large land-based industrial plants, which however, cannot be applied directly to marine diesel engines. When compared to wet scrubbers, ESPs and bag filters are larger and more expensive, although waste gas flow rates and temperatures are lower and they do not form sludge that requires treatment. New ESP developments include Wet Electrostatic Scrubbers (WES), the Heterogeneous Condensation Scrubber (HCS) and the Bubble Towers (BT). However, these need a washwater treatment unit. WES increases particle charging by using sprayed droplets as diffused particles collectors in place of the ESP plates. [19]. New design of ESP system is

developed by Usui Co. for marine diesel engines [110][112]. For an “ESP+C” system, exhaust gas flow rate design is higher than traditional and back-pressure is low. Also Park [113] reported on ESP development. ESP-based systems may achieve high particulate reduction at low pressure drop, and operate on suitable exhaust gas temperatures. However, they are large in size and electrical risks are considerable in installations. Furthermore, storage and disposal of removed PM is needed and energy consumption increases. Material limitations may lead to the need for flue gas cooling [45], [110].

9. Methane and some gaseous emissions

9.1 General

Many less common emission species than already discussed are present in the exhaust gas from marine engines. Studies on individual gaseous emissions from marine engines are rare, and thus the results here originate only from a few studies reported by Aakko-Saksa et al., Timonen et al., Teinilä et al. and Lehtoranta et al. [25][27][28][59]. In these studies, FTIR instruments (Gasmeter) were used for measurements having mostly the following detection limits (DL):

- Methane DL 2 ppm, 1 mg/m³, 0.026 g/kg fuel
- Formaldehyde DL 5 ppm, 7 mg/m³, 0.184 g/kg fuel
- Nitrogen dioxide DL 2 ppm, 4 mg/m³, 0.105 g/kg fuel
- Ammonia DL 2 ppm, 2 mg/m³, 0.053 g/kg fuel
- Nitrous oxide DL 4 ppm, 8 mg/m³, 0.210 g/kg fuel

When using FTIR instrument for measuring gaseous emissions in the presence of high SO₂ concentrations, measurement artefacts may be induced. However, this aspect is not discussed in this report.

9.2 Methane, THC, CO and formaldehyde emissions

Hydrocarbon and carbon monoxide emissions are the products of incomplete combustion of fuel. Typically, these emissions are low for diesel engines. When utilizing natural gas as a fuel, one could expect to have some methane emissions, if small quantities of fuel escapes the combustion process, since natural gas is mainly composed of methane.

Methane emission is important to consider since methane is a strong greenhouse gas. Global warming potential (GWP) of methane is 28 times higher than that of CO₂ over a 100-year perspective [1]. Methane emissions could be reduced e.g. by better fuel mixing conditions, by combustion chamber design and by reducing crevices. One option could also be the use of oxidation catalysts, but further research is needed to solve the long-term performance of the methane catalysts.

Measurements on marine engines using natural gas are sparse, and even fewer studies include measurements of methane emissions. So far, methane emissions measured from LNG ships have been high when compared to extremely low methane emissions from marine diesel engines (Fig. 14)¹². Anderson et al. [54] reported of results obtained onboard a LNG ship (DF engine). Methane emissions were on average 7 g/kg fuel (appr. 1.4 g/kWh) at high engine loads, but higher at low engine loads (appr. 20-28 g/kg fuel). Higher methane emissions were reported by Lehtoranta et al. [59] for an natural gas fuelled engine in testbed, however, this may be related to the specific engine measured.

Stenersen and Thonstad [114] reported general methane emission factor of 31 g/kg fuel for LNG ships, which is high methane emission factor reflecting different gas engine technologies available for using LNG as a fuel, and higher methane emissions at lower engine loads. On the other hand, Stenersen and Thonstad [114] also claimed that a high-pressure DF engine technology for LNG use does not emit methane, which is promising when considering possibilities to reduce methane emission from LNG fuelled ships.

¹² Agrawal et al. [39] found close to ambient levels of methane concentrations (1.3-2.2 ppmv) from marine diesel engine of tanker. Concentrations of non-methane organic compounds were also below 4.2 ppmv.

As mentioned in Chapter 3, with certain assumptions, methane emissions of approximately 29 g/kg fuel (5.8 g/kWh) are estimated to compensate GHG mitigation potential of LNG. Substantially lower methane emission (7 g/kg fuel, 1.4 g/kWh) from a LNG DF engine was measured at high engine loads [54], however, higher methane emissions were reported at lower engine loads. Methane emission from LNG fuelled ships vary, for example depending on engine technology and engine load. It seems that, also the modern dual fuel engines might need improvements to reach the methane limit values planned in China (1-2 g/kWh). Generally, effective methane control measures for LNG use are still needed.

No data on methane emissions is available for marine engines using methanol as a fuel. However, an alcohol engine (Scania EEV Ethanol DC9 270 hp) using additised methanol showed methane emission below detection limit [60].

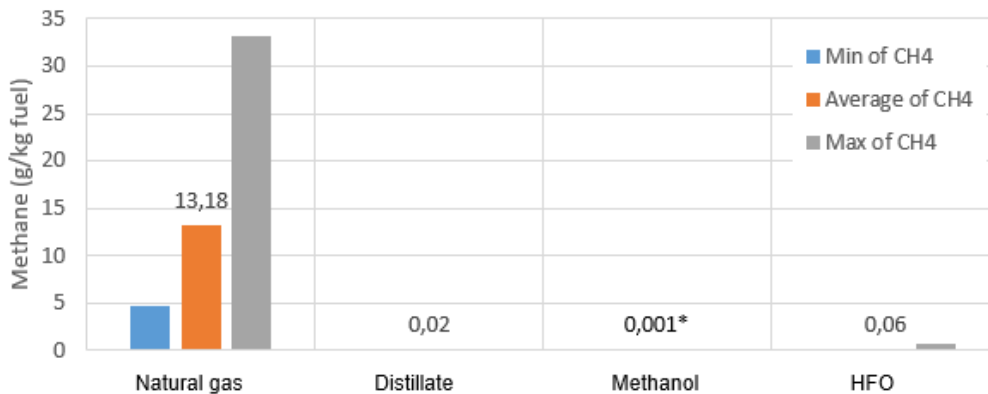


Figure 14. Methane emissions from marine engines using different fuels (with and without exhaust gas treatment technologies). MSD and SSD engines at engine loads above 50% MCR. Four studies referred for marine diesel engines ([25][27][28] [35]), two studies for natural gas [54][59] and one for methanol (* high-speed engine [60]).

Transport sector is a source of ambient concentrations of formaldehyde through incomplete combustion of fuel and through photochemical activity, although formaldehyde is present predominantly indoors. Formaldehyde is an irritant to the eyes, skin, and respiratory tract in humans possibly inducing asthma [80]. IARC has defined formaldehyde as carcinogenic to humans, Group 1 [82]. Formaldehyde is one of the reactive volatile organic compounds contributing to the formation of tropospheric ozone [115]. Formaldehyde emissions from mobile sources have been limited for decades in the US, e.g. to 4 mg/mi in California for LEV III cars (2015-2025, FTP-75 test) [2]. This is equivalent to formaldehyde emissions of approximately 0.042 g/kg fuel.

Formaldehyde emissions measured from marine engines using residual or distillate fuels were below detection level or very low for all marine engines measured (Fig. 15). Higher formaldehyde emission than the detection limit was observed for NG fueled engine on testbed [59], however, this engine showed generally higher emissions than commercial LNG DF engine in the onboard measurements [54].

For methanol DF engines, formaldehyde results are not available. For smaller alcohol diesel engine using methanol (additised with ignition improver), formaldehyde emission was 0.02-0.07 g/kg fuel, which is approximately at the same level as formaldehyde emissions observed for marine diesel engines using residual fuels [60].

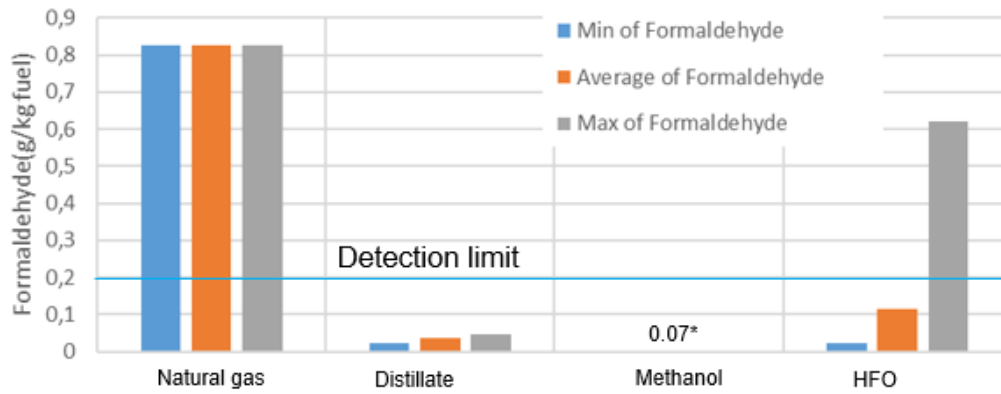


Figure 15. Formaldehyde emissions from marine engines using different fuels (with and without exhaust gas treatment technologies). MSD and SSD engines, engine loads above 50% MCR. [59] [25][27][28][39] *high-speed diesel engine [60].

9.3 Nitrogen dioxide (NO₂) and nitrous oxide (N₂O) and ammonia (NH₃) emissions

Engine-out NO_x emission consists mainly of NO emission, and typically only a small portion of NO₂ emission is present. Since early 1990s, the ratio of NO₂ to NO_x in atmosphere in urban areas has increased despite of decreasing NO_x emissions from vehicles. This is related to the increased market penetration of diesel cars as NO₂ is generated by purpose for the regeneration of some diesel particulate filters to enhance combustion of the soot at lower temperatures¹³, however, this may lead to NO₂ slip at low soot concentration in the exhaust gas. For road transport sector, the US EPA limits NO₂ emission from diesel retrofit technologies: NO₂ should be lower than 20% of baseline engine levels. [116]. In the studies evaluated here for marine engines, NO₂ share of NO_x was low, for example below 1% or 2% for modern medium-speed engines.

Nitrous oxide (N₂O) emissions are not related to combustion of fuels, while they are induced by catalyst chemistry, particularly by three-way catalysts of the spark-ignited cars [117]. Global warming potential (GWP) of N₂O is 298 times higher than that for CO₂ over a 100-year perspective [1]. In the studies evaluated, N₂O emissions from marine engines were below detection limit (0.2 g/kg fuel) [25][27][28][54][35].

Ammonia (NH₃) is also not a product of combustion of fuels, while it may be formed in exhaust treatment technologies [117]. Ammonia is associated with harmful effects on health and vegetation, and can form ammonium aerosols that affect climate and visibility. Ammonia is corrosive and can cause permanent injuries (eyes, alkali burns etc.). Exposure to a high concentration of ammonia gas may be fatal within minutes. [118].

Concern of traffic sources of ammonia increased with the use of urea-based SCR systems for NO_x control for diesel engines. In road transport sector, ammonia limit is 10 ppm for Euro VI heavy-duty diesel and gas engines. Ammonia emissions are not limited for cars, although high ammonia concentrations are commonly formed in three-way catalyst of spark-ignition cars, e.g. peak concentrations in the range of 300–500 ppm have been observed for model [119]. Ammonia emission from marine engines is not limited. However, the IMO 2017 has

¹³ The continuously regenerated trap (CRT) operates in the temperature window of 200–450 °C (200 °C for CO and HC oxidation; NO₂ is not favoured above 450 °C). Presence of water is beneficial for the NO₂-soot reaction. Addition of Rh, Pd or V in Pt reduces SO₂ oxidation when compared with 100% Pt. [121]

guidelines¹⁴ for measures to minimize reductant slip: “When SCR uses urea solution, ammonia solution or ammonia gas as reductant, measures to prevent reductant slip should be provided to avoid the supply of an excessive amount of reductant in the system. The reductant injection system should be designed to prevent emissions of any harmful substance from the system.”

In the studies evaluated, ammonia emissions from marine engines exceeded the detection limit only for SCR equipped marine engines without scrubber (Fig. 14). Even in this case, ammonia emission was only slightly above the detection limit. However, very few results are available and ammonia emissions may depend on the SCR system and operational conditions. Ammonia is water-soluble, and thus it may be dissolved in scrubber water to some extent.

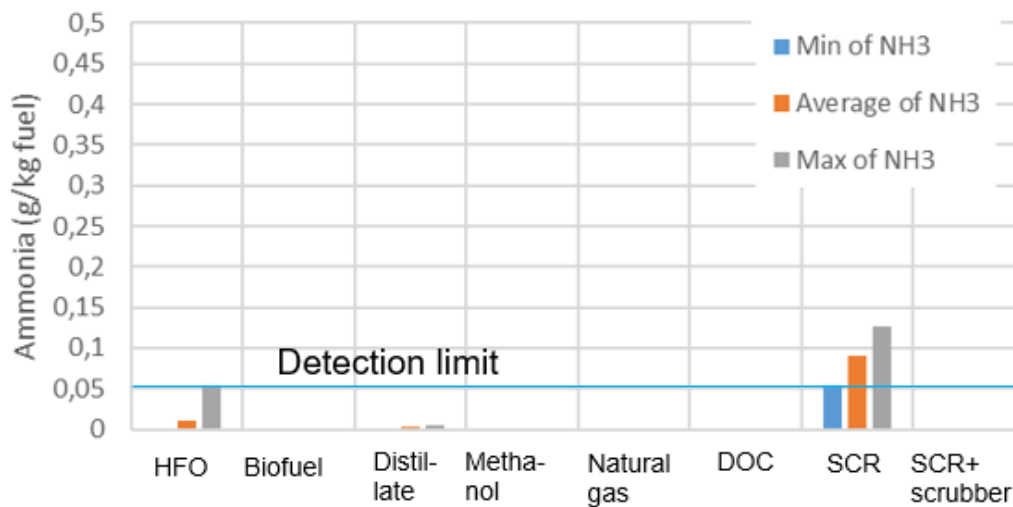


Figure 16. Ammonia emissions from marine engines using different fuels and exhaust gas treatment technologies. MSD and SSD engines at engine loads above 50% MCR. [25][27][28][54][35].

¹⁴ 2017 Guidelines addressing additional aspects of the NO_x Technical Code.

10. Summary

The IMO regulates NO_x and SO_x, emissions globally, and emission regulations are set also e.g. by EU, USA and China. This review considers the ship exhaust emissions already regulated, and the emissions anticipated to be regulated in the near future, namely particulate matter, particle number and black carbon emissions. Other emission components, such as methane emission, are presented shortly. Furthermore, technologies to reduce these emissions are discussed.

Emission measurements from a LNG powered ship have shown reduction of SO_x and PM emissions of almost 100% and NO_x emissions about 90% compared to marine fuel oils. This indicates that LNG is a possible way to handle the regulation of NO_x emissions from ship operation in NECA's. However, CO and HC emissions were found to be higher for LNG than for marine fuel oils. Methanol as marine fuel has slightly lower emission reduction potential (99% for SO_x, 60% for NO_x and 95% for PM) than LNG.

Exhaust treatment with SO_x scrubber removes SO_x emissions almost completely. SCR is efficient for reduction of NO_x. SO_x scrubber, SCR and DOC may also remove PM to some extent and possibly some other emission species. Combination of e.g. distillate fuel, SCR and particulate filter reduces almost 100% of SO_x and PM emissions, and more than 90% of NO_x emissions. However, particulate filters are not yet in commercial use for marine diesel engines using marine fuels, or proven for long-term durability.

When approaching climate-neutral shipping, renewable fuels (methane, methanol, distillate-type fuels, hydrogen), and renewable electricity (batteries) are potential options. From fossil fuels, LNG shows lower CO₂ emissions than marine fuel oils, and thus also GHG mitigation potential, however, compensated to some extent by methane emissions from LNG use.

Summary of the evaluation of the exhaust emissions using different marine fuels and exhaust treatment technologies compared with residual fuel use in marine diesel engine without exhaust treatment is presented in Table 11. There are several technologies capable to meet the present and future emission regulations for ships, although some of these technologies are still developing, and some have other limitations (e.g. regarding retrofits). However, low-emission performance of ships could be achieved by different choices depending on edge-conditions for specific ships (regions, routes etc.).

Table 11. Evaluation of impacts of different technologies on exhaust gas from marine engines compared with residual fuel use in marine diesel engine without exhaust treatment (base). Green = better than residual fuel, Grey = close to residual fuel, ? = missing data.*

	SO _x	NO _x	PM	PN _{solid}	BC	Score
Fuel						
Distillate fuel	+		+			2
Biodiesel	+		+		+	3
LNG *	+	+	+	+	+	5
Methanol *	+	+	+	?	+	4
Exhaust treatment						
SCR		+		?		1
SO _x scrubber	+		+	?		2
Dist+SCR+DPF	+	+	+	+	+	5
Other						
Hydrogen/FC or batteries	+	+	+	+	+	5
<i>Note: Substantial GHG benefits require renewable fuels</i>						

* Other emission species of concern are e.g. PAH, metals, methane, formaldehyde and ammonia.

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