



How do different marine engine fuels and wet scrubbing affect gaseous air pollutants and ozone formation potential from ship emissions?

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ABSTRACT

Sulphur Emission Control Areas (SECAs), mandated by the International Maritime Organization (IMO), regulate fuel sulphur content (FSC) to mitigate the environmental and health impact of shipping emissions in coastal areas. Currently, FSC is limited to 0.1% (w/w) within and 0.5% (w/w) outside SECAs, with exceptions for ships employing wet sulphur scrubbers. These scrubbers enable vessels using non-compliant fuels such as high-sulphur heavy fuel oils (HFOs) to enter SECAs. However, while sulphur reduction via scrubbers is effective, their efficiency in capturing other potentially harmful gases remains uncertain. Moreover, emerging compliant fuels like highly aromatic fuels or low-sulphur blends lack characterisation and may pose risks.

Over three years, we assessed emissions from an experimental marine engine at 25% and 75% load, representative of manoeuvring and cruising, respectively. First, characterizing emissions from five different compliant and non-compliant fuels (marine gas oil MGO, hydro-treated vegetable oil HVO, high-, low- and ultra-low sulphur HFOs), we calculated emission factors (EF). Then, the wet scrubber gas-phase capture efficiency was measured using compliant and non-compliant HFOs.

NO_x EF varied among fuels (5200–19700 mg/kWh), with limited scrubber reduction. CO (EF 750–13700 mg/kWh) and hydrocarbons (HC; EF 122–1851 mg/kWh) showed also insufficient abatement. Carcinogenic benzene was notably higher at 25% load and about an order of magnitude higher with HFOs compared to MGO and HVO, with no observed scrubber reduction. In contrast, carbonyls such as carcinogenic formaldehyde and acetaldehyde, acting as ozone precursors, were effectively scrubbed due to their polarity and water solubility. The ozone formation potential (OFP) of all fuels was examined.

Significant EF differences between fuels and engine loads were observed, with the wet scrubber providing limited or no reduction of gaseous emissions. We suggest enhanced regulations and emission abatements in the marine sector to mitigate gaseous pollutants harmful to human health and the environment.

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1. Introduction

and, for road traffic, regulated in the framework of the HC sum value [Russel, 2013]. Nevertheless, benzene is known to be a human carcin-

Abbreviations

CCAI	Calculated Carbon Aromaticity Index	IMO	International Maritime Organization
DMA	Distillate Marine Fuel (category according to ISO 8217)	LS-HFO	Low Sulphur HFO
ECA	Emission-Controlled Area	MC	Measurement Campaign
EF	Emission Factor	MGO	Marine Gas Oil
FAME	Fatty Acid Methyl Ester	MIR	Maximum Incremental Reactivity
FID	Flame Ionization Detector	NECA	Nitrogen ECA
FTIR	Fourier Transform Infrared Spectroscopy	OFP	Ozone Formation Potential
FSC	Fuel Sulphur Content	RME	Rapeseed Oil Methyl Ester
HFO	Heavy Fuel Oil	RMG	Residual Marine Gasoil
HVO	Hydrotreated Vegetable Oil	SECA	Sulphur ECA
		ULS-HFO _{ar}	Ultra-Low Sulphur Aromatic HFO
		VOC	Volatile Organic Compounds

About 90% of global trade goods is transported by ships [Federal Government of Germany, 2017]. As a consequence, international maritime transport significantly contributes to pollutants related to global warming, water quality, and air pollution [e.g. Eyring et al., 2010, European Parliament, 2015, Toscano and Murena, 2019]. The latter is well known to cause serious adverse human health effects, such as lung cancer, chronic obstructive pulmonary disease (COPD), lower respiratory infections, cardiovascular disease, and diabetes [e.g. Health Effects Institute, 2019]. Ship engines are a significant source of anthropogenic combustion emissions, such as nitrogen oxides (NO_x), sulphur oxides (SO_x), particulate matter (PM), carbon monoxide (CO), and volatile organic compounds (VOCs). This is a major concern especially for coastal communities [e.g. Aakko-Saksa et al., 2023, Corbett 2007, Chu-Van et al., 2018]. Besides these primary pollutants, the emissions are important sources for secondary aerosol formation and also contribute to increased ground level ozone (O₃) concentrations, another important secondary air pollutant especially at local and regional scales [Perez et al., 2016, Tang et al., 2020].

Regarding the health effects, NO_x causes inflammation of the lungs, with the primary site of toxicity being the lower respiratory tract. Populations that may be particularly sensitive to NO_x include asthmatics and those with COPD and heart disease [CDC 2014]. Furthermore, NO_x contributes to particle and ozone formation and also potentially causes acidification and eutrophication upon deposition on land, lakes, and seas. It can be transported in the atmosphere over long distances [Karl et al., 2019]. A review of model studies on ship emissions showed that NO_x emissions from international shipping on European seas could be equal to land-based emission sources in Europe (EU-27) from 2020 onwards [EEA 2013].

CO in combustion emissions has its origin in incomplete combustion of hydrocarbons from the fuel in particular through lack of oxygen. The adverse health effects are due to the binding with haemoglobin to form carboxyhaemoglobin, which affects gas exchange and cellular respiration. Inhaling excessive concentrations of CO can lead to hypoxic injury, nervous system damage, and death [Wilbur et al., 2012].

Hydrocarbon (HC) emissions is a collective term for VOC substances comprising hundreds of different compounds, some of them being toxic or even carcinogenic. In addition, many HC compounds act as ozone precursors. HC combustion emissions have their origin in the incomplete combustion of the fuels. Thereby, HC constituents from the fuels can either combust incompletely or pass unburned through the combustion process [Russel, 2013].

Benzene is a natural constituent of fossil fuels and originates in combustion emissions from incomplete combustion of organic substances as well as its non-decomposition during the combustion process. It is one of the numerous unregulated HC constituents being measured

and, for road traffic, regulated in the framework of the HC sum value [Russel, 2013]. Nevertheless, benzene is known to be a human carcin-

ogen due to sufficient evidence that it causes leukemia i.e. it is classified by the International Agency for Research on Cancer (IARC) as a class 1 carcinogen [IARC 2006]. Due to this extraordinary hazard to human health, special attention is drawn to this compound in this study.

Carbonyl compounds can be present in combustion emissions due to incomplete combustion and partially due to oxidation of HC. These oxygenated HC are a group of intermediates formed during lower-temperature reactions during the combustion process. This group of species predominantly consists of formaldehyde and acetaldehyde [e.g. Lemel et al., 2005]. Carbonyls are well known to play an important role in atmospheric chemistry [e.g. Sawant et al., 2007] and also act as ozone precursors [Bhattacharya and Tulsawani, 2008, IARC 2006, European Commission 2002, Karavalakis et al., 2011]. In addition, some attract attention due to their adverse health effects and thus have been identified as hazardous air pollutants for humans [Weng et al., 2010]. In this regard, acetaldehyde is classified by IARC as a class 2B carcinogen i.e. possibly carcinogenic to humans, and formaldehyde even as a class 1 carcinogen i.e. carcinogenic to humans.

Over the last two decades, there have been strong efforts to reduce the environmental impact of maritime transport. The International Maritime Organization (IMO) adopted strict regulations under Annex VI of the International Convention for the Prevention of Marine Pollution from Ships (MARPOL) by implementing so-called Emission Control Areas (ECAs). These ECAs include e.g. Baltic Sea, North Sea, English Channel, North America, and U.S. Caribbean Sea for all vessels over 300 gross tons. Within these designated ECAs, SO_x emissions are indirectly controlled by regulating the marine fuel sulphur content (FSC). Since 2015 there is a maximum value of 0.1% (w/w). On January 1, 2020 outside ECAs (also called SECAs as sulphur ECAs) the max. FSC was reduced from 3.5% to 0.5% [IMO, 2008a]. Global NO_x ship emissions are regulated under the IMO treaty [IMO, 2008b] in three progressively more stringent tiers. Tier 1 (since 2000) and Tier 2 (since 2011) limits are valid worldwide and apply to all new marine diesel engines. Tier 3 only affects vessels sailing inside designated Nitrogen ECAs (NECAs) and came into force in the North American and the U.S. Caribbean ECAs on January 1, 2016 and in the Baltic Sea, North Sea, and British Channel ECAs on January 1, 2021.

Common marine low-speed engines have been designed to burn heavy fuel oil (HFO) or marine gas oil (MGO). HFO is produced from residuals of the crude oil refining process and, therefore, contains higher values of inorganic components, such as sulphur, ash, and metals as well as organic compounds such as polycyclic aromatic hydrocarbons (PAHs) and asphaltenes in comparison to MGO [Streibel et al., 2017].

MGO is a middle distillate fuel, which usually consists of a blend of various distillates. It is similar to diesel fuel but has a higher density and is typically compliant to the open sea as well as within an ECA due to low

sulphur contents [Jeong et al., 2023]. Therefore, conventional low-grade HFOs have been replaced by distillate fuels or low-sulphur HFOs (LS-HFO). However, alternative shipping fuels are increasingly entering the market such as e.g. liquefied natural gas (LNG) and hydrotreated vegetable oils (HVO). Hydrotreatment of vegetable oils is an alternative process to esterification to form paraffinic hydrocarbons similar to those found in petroleum-based diesel. It is an option to produce renewable diesel fuels since HVO is made from the same biomass as fatty acid methyl ester (FAME), but it may also be produced from residual crops and industrial waste like wood spills [Szeto and Leung, 2022]. Apart from this other (modern) fuel types may enter the market depending on availability, political situation, and price.

Another option to comply with IMO regulations is the usage of emission abatement systems to reduce pollutants. In this regard, a legal and effective approach to reduce SO_x emissions is the usage of a scrubber. This alternative allows vessels to run on high sulphur and potentially less expensive HFOs instead of higher quality fuels. For the maritime sector, wet scrubbers are usually applied to remove SO_x emissions, whereby the exhaust is directed through a liquid media i.e. sprays of seawater or chemically treated fresh water [Oikawa et al., 2003, Andreasen and Mayer, 2007]. Wet scrubbers can be operated in open-loop and closed-loop modes, whereby hybrid systems are also common [Zetterdahl et al., 2016]. In open-loop systems, seawater is used to wash out SO_x from the exhaust. The contaminated wash water is then discharged to the sea with minimal or no treatment [Teuchies et al., 2020]. Pollutants thus enter the aquatic ecosystem and become a potential source of marine pollution. [Oikawa et al., 2003, Ushakov et al., 2020, Endres et al., 2018]. In the closed-loop mode, fresh or sea water together with some added sodium hydroxide is used to take up SO_x from the exhaust. The washing water is continuously circulating and cleaned in the system and finally discharged and purified on-land in a treatment plant to remove the polluted residue sludge [Zetterdahl et al., 2016, Lehtoranta et al., 2019].

Fuel type as well as engine load have been shown to significantly influence chemical and physical properties of exhaust gas components. It is known that, besides SO_2 , high FSC in HFO can also cause elevated PM emissions [Winnes and Fridell, 2009, Cordtz 2013]. Therefore, in most studies, the focus has been on the physicochemical properties of particles in relation to various FSCs [e.g. Lehtoranta et al., 2019, Winnes and Fridell, 2009]. Some papers have also reported significant emission reductions from NO_x and CO by the use of low sulphur HFO [e.g. Zetterdahl et al., 2016, Yusuf et al., 2012, McCaffery 2021]. Furthermore, several studies have dealt with the investigation of marine engine exhaust after passing through scrubber systems. Several studies report the reduction of SO_x and a few other main gaseous components, such as NO_x as well as PM [Lack et al., 2009, Petzold et al., 2010, Petzold et al., 2011]. However, while SO_x removal efficiency is undisputed, studies investigating other, less targeted gaseous pollutants are rare.

Therefore, in this study, we investigated how different marine fuels (i) as well as wet scrubbing (ii) can affect gaseous air pollutants in exhaust emissions of a marine test-bed engine operated at different engine loads. The focus is on a comprehensive overview of gaseous (trace) compounds relevant to the environment and human health. A comparable study of this depth could not be found in the literature.

- (i) Five different fuels were applied, namely two HFOs with various FSC (2.2% and 0.5% w/w), conventional MGO, HVO, and a test fuel not available on the free market yet (ULS-HFO_{ar}).
- (ii) The influence of wet scrubbing on the exhaust was examined by comparing the gaseous emission before and after having passed a scrubber system. This investigation has been carried out on the same two HFO fuels (2.2% and 0.5%).

In all test series, a comprehensive chemical analysis of the exhaust was carried out by investigating more than 40 individual gaseous constituents, several of them being climate-damaging, toxic, or even

cancerogenic. 26 of them belong to the list of 30 main ozone precursors in ambient air according to the European directive 2002/3/EC [European Commission 2002]. Subsequently, the corresponding ozone formation potentials (OFP) of all settings and fuels were determined and compared. Particle emissions are not the subject of this paper but have been thoroughly discussed by the authors in another publication [Jeong et al., 2023].

2. Materials & methods

All marine engine emission measurements were conducted during three different campaigns, each lasting several weeks between June 2020 and April 2022 at the Chair of Piston Machines and Internal Combustion Engines (Lehrstuhl für Kolbenmaschinen und Verbrennungsmotoren, LKV), Faculty of Mechanical Engineering and Marine Technology at the University of Rostock, Germany.

2.1. Marine engine & test series

A single-cylinder four-stroke research engine was used (1 VDS 18/15 CR, Elbwerk, Roßlau). The layout of the engine represents a typical modern medium-speed marine diesel engine with a displacement of 3.18 L and a rated power of 80 kW at 1500 rpm. It can be operated with various fuels from distillates and paraffinic fuels to high-sulphur and high-viscosity marine fuels. Though the engine has a maximum output of 80 kW, its combustion processes are comparable to those of full-size engines. It features common-rail injection and adjustable external charge air compression as well as adjustable exhaust gas back pressure. The engine was operated at constant speed but with varying loads of the maximum continuous rate (MCR) in accordance with the E2 test cycle for heavy-duty, constant speed marine propulsion engines based on ISO 8178-4. For the comparison of the five different fuels, the engine was operated during measurement campaign 1 (MC1) at 25% (20 kW), 50% (40 kW), 75% (60 kW), and 100% (80 kW) load. In contrast, for the investigation of the effects of wet scrubbing, it was run during two further test series i.e. measurement campaign 2 (MC2) and measurement campaign 3 (MC3) at 25% (20 kW) and 75% (60 kW) engine loads. For all tests and fuel types three replicates during three different days have been performed. This was followed by a change of the lubricating oil for the next test cycle when a new fuel type was introduced. The exchange of the lubrication oil took one day and consisted of full draining of the used oil over night, four flushing cycles, exchange of oil filters, and a running-in program on different engine loads with MGO for 2 h. The order of fuel tests was from light to heavy.

Thereby, the 75% engine load stands for the typical optimum fuel oil consumption point. This engine load was considered to be representative of cruising speeds at open sea as well as for stationary power generation operation [Klein Woud and Stapersma, 2002]. In contrast, the engine load of 25% represents typical manoeuvring operation at ports and harbours. Engine type and related combustion emissions have been described in former studies [Sippula et al., 2014; Streibel et al., 2017], however, engine parameters had to be modified for this study and differ from previous works, with the exception of the particle phase characterization paper [Jeong et al., 2023] and other recent studies [Anders et al., 2023, Schneider 2023].

2.2. Fuels

For MC1 the engine was fed with the following five fuels: high sulphur heavy fuel oil with 2.2% S (HFO 2.2), low sulphur heavy fuel oil with 0.5% S (HFO 0.5), marine gas oil (MGO), hydrotreated vegetable oil (HVO), and ultra-low sulphur aromatic heavy fuel oil (ULS-HFO_{ar}). Latter fuel was a test fuel provided by a ship engine manufacturer, which is not commercially available yet. The four other fuels were provided by a marine fuel supplier (not named due to non-disclosure agreement). The physicochemical characterization of the fuels was conducted

according to ISO 8217 and is presented in Table 1.

MGO is considered one of the highest quality marine fuels due to its naturally low sulphur content. The distillate fuel had concentrations of metals commonly found in HFO fuels, such as V, Ni, and Fe, below the limit of detection.

HVO is a synthetic premium fuel, obtained by hydrogenation and cracking of vegetable oils. It can be regarded as a second-generation biofuel and diesel substitute with good ignition properties. Its density is significantly lower than MGO, however, in almost all other specified parameters it is comparable to traditional diesel. In principle, HVO can be used in a diesel engine neat or blended with other fuels. Currently, it is rarely used in practice due to its higher price. In this study, HVO represents the extreme case for a high paraffinic fuel.

HFO fuels typically have a much higher density and viscosity and contain residues from refinery processes [Fritt-Rasmussen et al., 2018]. Therefore, HFOs can contain significant amounts of metals (mainly V, Ni, Fe), sulphur, and nitrogen. By definition, HFO has a density at 15 °C greater than 0.9 g/cm³ or a kinematic viscosity exceeding 180 mm²/s¹ at 50 °C. Therefore, a wide range of marine fuels can be produced by blending different product streams from crude oil refining.

HFO 0.5 is an example of a commercial low sulphur fuel oil, which is not allowed inside ECA zones but is compliant for open-sea operation. It should be noted that in-house analyses showed a sulphur content of actually 0.51%. However, this issue of marginal violations near the 0.5% sulphur cap was reported to happen in the IMO 2020 transition phase quite regularly. Therefore, in the framework of this study, this HFO 0.5 fuel is considered as compliant outside an ECA. Compared to HVO and MGO, the much higher density, viscosity, and content of metals refers to the presence of residue fractions.

HFO 2.2 is a commercial non-compliant high sulphur fuel (2.2% S) and was included to account for open-sea operation before January 1, 2020. Nowadays, this fuel must be used in combination with a scrubber. Density and viscosity are similar to HFO 0.5, however, the flashpoint is lower.

ULS-HFO_{ar} is very similar to high-quality distillate fuels such as MGO, although it is classified as HFO. However, ULS-HFO_{ar} may exhibit low ignition quality (low cetane number), resulting in poor combustion at low loads, potentially leading to increased emissions of organic compounds and operational challenges. It refers to a clarified cycle oil, that was produced by fluid catalytic cracking, and contains mainly alkylated 2- to 4-ring aromatics (ar) [Käfer et al., 2019]. Its density of 0.975 exceeds ISO 8217 specification significantly and its high carbon-to-hydrogen ratio, as well as high content of aromatics (illustrated as a Calculated Carbon Aromaticity Index CCAI, where lower values indicate better ignition quality), resulted in a rather poor ignition behaviour in comparison to the other investigated fuels [Latarche

Table 1
Physicochemical properties of the applied fuels.

	Method	MGO	HVO	ULS-HFO _{ar}	HFO 0.5	HFO 2.2
Classification	ISO 8217	DMA	DMA	RME 180	RMG 380	RMG 380
Density@15 °C [g/cm ³]	ISO 12185	0.835	0.78	0.975	0.96	0.990
Viscosity@50 °C [mm ² /s]	ASTM D7042	2	2.47	6	340	350
Sulphur [% w/w]		0.001	<LOD	0.048	0.51	2.16
Water [mg/kg]		23	20	214	423	586
Flash point [°C]		72	80	75	156	135
Ash [% w/w]	ISO 6245	0.001	0.001	<0.001	0.019	0.051
Heating value [MJ/kg]		42.7	43.8	40.3	41.1	40.1
C [%]	DIN 51732	87.4	86.4	88.5	86.8	85.6
CCAI	ISO 8217	796	739	907.4	822	852

2021]. However, shipowners could decide on this fuel in the future depending on price and availability, since there is no obligation to follow ISO 8217. Consequently, it would be a compliant marine fuel in an ECA.

For MC2 and MC3, the two commercial heavy fuel oils HFO 0.5 and HFO 2.2 were applied.

2.3. Wet scrubber

A downscaled research open-loop wet sulphur scrubber (EGCS40HB, SAACKE, Germany, schematic in SI) was used, operated with Baltic Sea water with a salinity of 10.5 ± 3.6 in practical salinity unit (PSU) and a pH of about 8. The components of the scrubber consisted of a quench with three sprays, a wash tower with a total volume of 0.9 m³ including the spray, a randomly structured filling body and a demister structure. During operation, the SO₂/CO₂ ratio was maintained at a maximum of 4.3 SO₂ (ppm)/CO₂ (% v/v), corresponding to the emission of fuel oil with 0.1% w/w of sulphur content [IMO, 2015]. Prior to introducing the exhaust gas into the wash tower, the exhaust gas temperature was reduced by adjusting the sprays inside the quench to optimize the solubility of SO_x in the wash water [Bandyopadhyaya and Biswasa, 2006]. The cooled exhaust gas was then introduced into the wash tower, which was equipped with a filling body package of metal saddle rings to improve the mass transfer of SO_x from the gas to the liquid phase and to remove particles in the exhaust gas.

2.4. Experimental set-up

Measurements were conducted during three measurements campaigns (MC). For MC2/MC3 (with vs. without scrubber; Fig. 1), two sampling points in the stack were used for comparison between the scrubber upstream (before scrubber; A_u in Fig. 1) and downstream (after scrubber; A_d) consisting of two identical multi-hole perforated sampling probes and heated transfer lines. A heat-resistant ball valve and insulated Y-connector were used to switch between up- and downstream. The temperature of the transfer lines and the valve was always set at 200 °C. In the case of MC1 (fuel comparison, no scrubber), only one sampling point was used (A_u) with the same temperature setting. In all campaigns, the exhaust gas was sampled undiluted for the investigation of the main gas phase compounds and VOCs.

In addition, sampling of the DNPH cartridges for the investigation of carbonyls was performed after a primary dilution step of the raw emissions (Fig. 1, probes B_u and B_d). The temperature of the transfer line

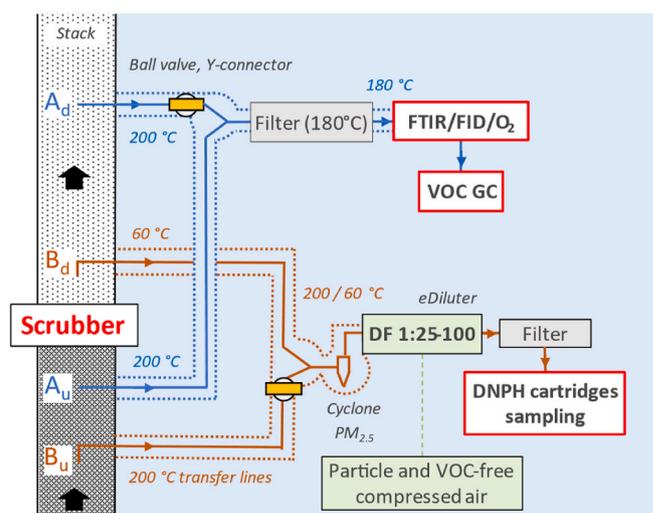


Fig. 1. Illustration of the exhaust sampling setup for MC1: five fuels, no scrubber, sampling probes A_u and B_u only; and MC2/MC3: two fuels, with scrubber (sampling probes A_d and B_d) vs. without scrubber (A_u and B_u).

and ball valve was set to 200 °C for upstream (B_1) and 60 °C for downstream (B_4) measurements due to cooled emissions after the scrubber.

The primary dilution factor (DF) of the exhaust sample from the engine stack was adjusted according to the fuel types using a two-stage ejector diluter system (eDiluter Pro, Dekati Ltd., Finland). A dilution ratio of 1:25 was set for MGO, HVO, and ULS-HFO_{ar} and between 1:50 and 1:100 for the two HFOs. VOC- and particle-free air (737-15, Aadco Instruments Inc., USA) preheated to transfer line temperature was used for dilution. After the primary dilution step, the exhaust flow was split into different sampling lines with individual dilution ratios for online analysers and offline sampling, respectively. Fig. 1 illustrates the experimental setup for this study, while other measurements and analyses are shown in previous papers [Anders et al., 2023, Jeong et al., 2023, Schneider 2023]. The instrumentation is described in the following sections.

It should be noted that the emission factors for identical fuels and conditions could have slightly varied between MC1 (no scrubber installed) and MC2/MC3 (scrubber installed) because the exhaust back-pressure in the experimental setup might have been influenced, which could also have affected the emission pattern.

2.5. Analytical techniques

2.5.1. Main exhaust components

The main exhaust gas components CO₂, CO, CH₄, NO, NO₂, N₂O, and SO₂ were analysed by Fourier transform infrared spectroscopy (FTIR; model: DX4000; Gaset Technologies, Finland) with the results reported on a wet basis as this is the more realistic way of expressing the data according to the instrument manufacturer. The system also included an O₂-analyser (PMA 10, M&C TechGroup, Ratingen, Germany) and a flame ionization detector (FID; Thermo-FID EN 15267, SK-Elektronik, Leverkusen, Germany) for total hydrocarbon (THC) content, measured as an equivalent of C₃ (propane). Sampling was carried out undiluted with sampling rates of 3 L/min by a 5-m heated transfer line (Winkler GmbH, Heidelberg, Germany) at 180 °C. A Portable Gas Sample Probe (PSP4000-H, M&C, Germany) containing the filter heated to 180 °C was installed upstream of the heated transfer line. The FTIR measurements were checked at least once a week using standard gas mixtures containing the main exhaust gas compounds and cross-checked with another FTIR system on site.

2.5.2. Carbonyls

In total, nine carbonyls were investigated in this work, see SI. For sampling the diluted exhaust was directed through 2,4-dinitrophenyl hydrazine (DNPH) cartridges (Supelco, Orbo 555 at MC1 and Waters, Sep-Pak DNPH-Silica Short Cartridge, 350 mg of Sorbent, 55–105 µm at MC2 and MC3) to rapidly produce the carbonyls' stable hydrazone derivatives. Sampling rates were 500 mL/min for a total sampling time of 20 min using a two-channel sampling pump (BIVOC2V2, Umweltanalytik Holbach GmbH, Germany). The cartridges were collected immediately after the test and frozen (−20 °C) until further treatment in the lab. There, hydrazones have been eluted with 5 mL of acetonitrile (Roth, Rotisolv HPLC gradient). These extracts have been concentrated to a final volume of 0.5 mL using a nitrogen solvent evaporation system (Biotage, TurboVap). Extracts have been re-diluted with acetonitrile to a final volume of 1 mL and filtered through a 0.2 µm syringe filter (VWR, 0.2 PTFE).

Analysis was done by high-performance liquid chromatography with diode array detection (HPLC-DAD; Agilent 1260 Infinity II). Separation has been performed using an Eclipse plus C18 column (4.6 × 150 mm, 1.8 µm) coupled with an Eclipse plus C18 pre-column (4.6 × 5 mm, 1.8 µm) column working under gradient conditions. Calibration standard lines of 5, 10, 50, 100, 200, 500, 1000 ng/mL and 7.85, 15.7, 157, 785, 1570, 3140 ng/mL respectively have been used for the quantification. The calibration standard lines have been prepared from the single initial

calibration verification standard (Sigma-Aldrich, DNPH-standard).

2.5.3. VOC

Regarding VOCs, the focus was on the C₂ - C₉ hydrocarbons being listed as ozone precursors for ambient air in the EU directive 2002/3/EC [European Commission 2002]. Sampling and chemical analysis were performed immediately afterwards on-site by using a sample enrichment and thermal desorption (TD) module (KORI-Xr water condenser and Unity-Xr thermal desorber, Markes International Ltd, Bridgend, United Kingdom), followed by a 2D gas chromatograph (GC, 8890, Agilent Inc., USA) consisting of two analytical columns (DB-1 50 m × 320 µm × 1.2 µm and HP-AL/KCL, 50 m × 320 µm × 8 µm and Al₂O₃/KCl, both from Agilent Inc., USA), each connected to an FID. The sampling volume was set to 50 N mL for all experiments. The thermal desorption gas chromatography system (TD-VOC-GC) was directly connected to the output of the absorption cell of the FTIR beside the FID and O₂ sensor. The functional principle of the TD-VOC-GC and other applications e.g. measurements of ozone precursor levels in ambient air and in motor vehicle combustion have been described in detail in Latella et al. [Latella et al., 2005]. Identification and quantitative measurement of the C₂ - C₉ hydrocarbons were achieved by using a certified standard mixture containing the ozone precursors (approximately 200 ppbV each, National Physical Laboratory, Teddington, United Kingdom). In so doing, 22 VOCs could be addressed, see Table S1 in the Supplementary Material.

2.5.4. Calculations

Emission factors were calculated as mass pollutant per engine energy in mg/kWh and are illustrated in excerpts in Table 2, Fig. 2a–g as well as the entire data set in Table S1 in the Supplementary Material. Emission factors expressed in mass pollutant per exhaust volume as well as mass pollutant per mass fuel can be also found in the Supplementary Material.

In addition, the ship emission factors were compared to two different road-traffic emission standards for heavy-duty (HD) engines in Europe, EURO III (EU Directive 98/69/EC) and EURO VI (EU Directive 715/2007). Although this approach seems bold, it enables us to better classify the ship emission factors since exhaust gases from road traffic have been regulated and stepwise reduced by technical measures for decades. HD engines had to comply with EURO III emission standards from the year 2000–2005. It therefore represents outdated but still frequently encountered engine technology on European roads. In contrast, EURO VI emission standards, established in 2013, are the current standards and remain compliant with legislation. The introduction of EURO VII is not expected before 2025. Therefore, EURO VI emission standards represent modern engine technology. Legislative HD emission factors can slightly differ depending on the applied homologation procedure. In this study, exhaust limits of ramped steady-state test cycles were chosen (ESC for EURO III and WHSC for EURO VI) because these cycles are more similar to the applied E2 test cycle for ship engines than transient HD test cycles. However, emission factors of road traffic and ship emissions are not one-to-one comparable but should be considered as an approach to classify the results.

The concept of maximum incremental reactivity (MIR) of ozone formation was applied to evaluate the ozone formation potential (OFP) of the emissions. In general, the MIR method is based on a scenario in which optimum conditions of precursor/NO_x ratios yield maximum ozone formation. For all sorts of ozone precursors, MIR factors have been derived, whose product with the compound's emission factor results in the potential amount of ozone formed [Carter, 1994]. The OFP of a mixture is determined by adding up the individual contributions of all emission constituents. By following this procedure OFP of VOC, carbonyls, and CO were calculated.

3. Results

The following sections present the experimental results of the

Table 2

Emission factors and OFP of gaseous air pollutants for the engine loads 20 kW (25%) and 60 kW (75%) operated with the ship fuels MGO, HVO, ULS-HFO_{ar}, HFO 0.5, and HFO 2.2 from MC1. For HFO 0.5 and HFO 2.2 comparative tests with and without wet scrubbing have been carried out at MC2 and MC3. Emission factors are illustrated in pollutant mass per generated energy [mg/kWh].

20 kW	MGO	HVO	ULS-HFO _{ar}	HFO 0.5 Scr	HFO 2.2 Scr	HFO 0.5	HFO 2.2
NO _x	9462 ± 298	5207 ± 103	19728 ± 932	9736 ± 218	10361 ± 345	8983 ± 467	9307 ± 605
CO	2461 ± 98	1919 ± 580	12508 ± 624	6169 ± 1014	8132 ± 279	7973 ± 414	9954 ± 214
HC	512 ± 37	408 ± 8	1160 ± 120	965 ± 25	1411 ± 246	1468 ± 84	1851 ± 102
Acetylene	18.0 ± 0.3	1.6 ± 0.8	87.2 ± 10.4	61.3 ± 3.2	84.4 ± 6.2	175.2 ± 5.5	146.4 ± 7.7
Ethylene	40.4 ± 0.4	22.2 ± 1.6	63.2 ± 11.3	144.5 ± 19.0	221 ± 0.5	219.7 ± 3.8	246.9 ± 15.0
Benzene	4.0 ± 0.03	2.0 ± 0.3	13.3 ± 4.9	33.4 ± 2.2	47.7 ± 4.8	36.9 ± 1.8	34.9 ± 4.0
Formaldehyde	39.3 ± 3.8	31.8 ± 1.8	83.4 ± 5.7	3.7 ± 1.7	6.6 ± 5.3	141.5 ± 13.1	150.3 ± 52.4
Acetaldehyde	14.9 ± 1.5	13.2 ± 1.1	40.7 ± 2.2	6.6 ± 2.1	8.7 ± 3.5	54.7 ± 7.8	74.7 ± 18.4
OFP	1376 ± 107	1061 ± 119	2586 ± 125	2003 ± 190	2827 ± 59	5048 ± 154	5787 ± 560
60 kW	MGO	HVO	ULS-HFO _{ar}	HFO 0.5 Scr	HFO 2.2 Scr	HFO 0.5	HFO 2.2
NO _x	7857 ± 117	6915 ± 104	13668 ± 428	8376 ± 181	7793 ± 237	7488 ± 264	8330 ± 392
CO	1556 ± 279	1570 ± 230	750 ± 81	1183 ± 24	1138 ± 124	1706 ± 167	1367 ± 114
HC	182 ± 33	186 ± 17	122 ± 2	138 ± 18	156 ± 37	218 ± 29	147 ± 12
Acetylene	6.4 ± 0.8	1.0 ± 0.4	3.4 ± 0.4	1.9 ± 0.1	1.4 ± 0.2	8.6 ± 1.6	5.7 ± 0.5
Ethylene	31.4 ± 5.6	27.6 ± 4.66	7.9 ± 0.8	11.6 ± 0.8	9.7 ± 1.2	34.7 ± 5.2	16.8 ± 2.5
Benzene	2.5 ± 0.3	2.1 ± 0.1	1.4 ± 0.1	2.6 ± 0.2	2.2 ± 0.2	5.1 ± 0.4	2.8 ± 0.4
Formaldehyde	32.7 ± 5.8	37.2 ± 3.6	15.8 ± 2.4	2.8 ± 0.5	1.7 ± 1.9	34.7 ± 16	17.9 ± 4.2
Acetaldehyde	9.9 ± 2.2	11.8 ± 1.2	11.4 ± 3.5	<LOQ	1.9 ± 0.7	15.6 ± 2.9	18.8 ± 4.9
OFP	837 ± 90	891 ± 80	406 ± 35	249 ± 25	278 ± 99	923 ± 153	925 ± 163

gaseous emissions for the comparison of the five investigated ship fuels MGO, HVO, ULS-HFO_{ar}, HFO 0.5, and HFO 2.2 as well as the pre- and post-scrubber analyses for HFO 0.5 and HFO 2.2. In marine engine technology, scrubbers are implemented to remove SO₂ from the emission. Results in this study confirm the high effectivity of this application (see Table S1 in Supplementary Material), however, this is not the subject of the presented paper and will not be discussed further. The results of all test series and investigated compounds can be found in excerpts in Table 2 and the entire data set in Table S1 in the Supplementary Material. Fig. 2a–f illustrate the emission factors of the air pollutants NO_x, CO, HC, benzene, formaldehyde, and acetaldehyde operated under 20 kW (25% engine load) and 60 kW (75% engine load) for the five different fuels. Results for MGO, HVO, ULS-HFO_{ar}, HFO 0.5, and HFO 2.2, the latter two without wet scrubbing, originate from MC1. Results for HFO 0.5 and HFO 2.2 with wet scrubbing (Scr) originate from MC2 and MC3, respectively.

3.1. NO_x

Emission factors of NO_x (Fig. 2a) were in the same range for all fuels and engine loads except HVO and ULS-HFO_{ar}. Operation with the latter fuel resulted in extraordinarily high NO_x values between 13668 ± 428 mg/kWh (60 kW) and 19728 ± 932 mg/kWh (20 kW) whereas HVO at 20 kW featured the lowest NO_x emission factors with 5207 ± 103 mg/kWh. All other fuels and engine loads ranged from 7488 ± 264 mg/kWh (HFO 0.5, 60 kW) to 10361 ± 345 mg/kWh (HFO 2.2 Scr, 20 kW). For all fuels except HVO, NO_x emission factors were slightly lower at 60 kW in comparison to 20 kW ranging from a 25% reduction for HFO 2.2 Scr to 10% for HFO 2.2.

NO_x in ship emission is dependent on the combustion parameters and temperatures inside the engine, which leads to the generation of thermal NO_x by the Zeldovich mechanism [Heywood, 2018]. Harsh conditions result in higher degradation rates of excess atmospheric oxygen and nitrogen during the compression ignition process, which in turn, recombines to NO, which is partially further oxidized to NO₂ [Heywood, 2018]. Differing NO_x values from the same engine but operated with different fuels, as observed in this study, originate from different engine settings. The injection timing for ULS-HFO_{ar} had to be advanced to compensate for its low estimated cetane number (ECN), resulting in relatively poor ignition qualities, especially at the lowest load.

According to the NO_x limits in MARPOL Annex VI, the NO_x emission factor for this engine should be below 8180 mg/kWh (Tier 2 and n = 1500 rpm), which was not completely fulfilled. For comparison Tier 1

would be 10420 mg/kWh and Tier 3 2080 mg/kWh. This means that for this engine a shift from Tier 2 to Tier 3 entails a NO_x reduction by the factor of 4. Tier 1 to 3 are also illustrated in Fig. 2a.

NO_x emission limits for road-based HD engines are 5000 mg/kWh for EURO III and 400 mg/kWh for EURO VI. Therefore, it can be seen that all ship emission factors exceeded EURO III limits – between 4% for HVO at 20 kW and almost 400% for ULS-HFO_{ar} at 20 kW – and were far beyond EURO VI limits. It can also be noted that wet scrubbing does not seem to have any effect on NO_x emission.

In conclusion, when compared to road-traffic HD engines, ship emissions resulted in significantly elevated NO_x levels regardless of which ship fuel is used. The compliance with stepwise stricter NO_x limits in road traffic was technically achieved by the implementation of primary and secondary exhaust after-treatment devices like exhaust gas circulation and selective catalytic reduction, which is not yet state-of-the-art in ship engine technology.

3.2. CO

Emission factors of CO are illustrated in Fig. 2b. For this compound significant differences between fuel type and engine load could be determined. All fuels showed higher CO values for 20 kW in comparison to 60 kW with the only exception of HVO where no influence of the engine load could be observed. While the differences for MGO were smaller (20 kW: 2461 ± 98 mg/kWh, 60 kW: 1556 ± 279 mg/kWh → −36%) the HFO fuels showed tremendous absolute values and differences with ULS-HFO_{ar} the highest ranging from 12508 ± 624 mg/kWh (20 kW) to 750 ± 81 mg/kWh (60 kW), which is equivalent to a reduction of 95%. Emission factors and reduction rates for the commercial HFO-fuels were with scrubber −84% (HFO 0.5 Scr: 6169 ± 1013 mg/kWh to 1183 ± 24 mg/kWh) and −86% (HFO 2.2 Scr: 8132 ± 279 mg/kWh to 1138 ± 124 mg/kWh) as well as −79% (HFO 0.5: 7973 ± 414 mg/kWh to 1706 ± 167 mg/kWh) and −86% (HFO 2.2: 9954 ± 214 mg/kWh to 1367 ± 114 mg/kWh) without scrubber. In general, the HFO fuels generated about 2.5 (MGO to HFO 0.5 Scr) to 5.5 (HVO to ULS-HFO_{ar}) times higher CO emission factors for the 20 kW engine load. For the engine load of 60 kW, the CO emissions were much more balanced and reached values between 1183 ± 124 mg/kWh (HFO 0.5 Scr) and 1706 ± 167 mg/kWh (HFO 2.2 Scr) except ULS-HFO_{ar}.

The CO emission limits for HD engines in Europe are 2100 mg/kWh for EURO III and 1500 mg/kWh for EURO VI. All 60 kW test series in this study as well as HVO 20 kW fell below this road-traffic threshold. MGO 20 kW exceeded the EURO III threshold by +17% (2461 ± 98 mg/kWh),

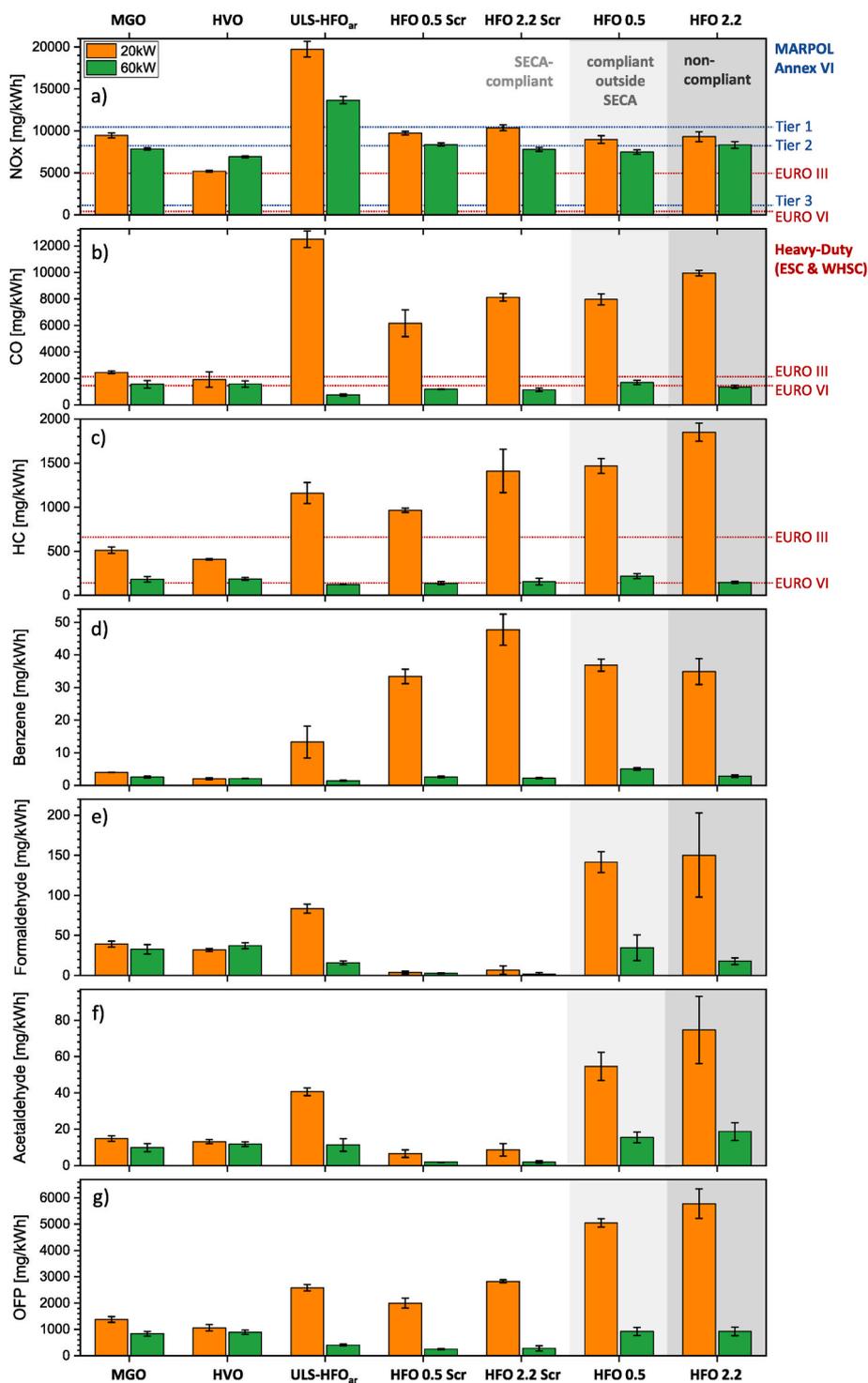


Fig. 2. a-g (in color): Emission factors of the air pollutants NO_x (Fig. 2a), CO (Fig. 2b), HC (Fig. 2c), Benzene (Fig. 2d), Formaldehyde (Fig. 2e), Acetaldehyde (Fig. 2f) as well as OFP (Fig. 2g) for 20 kW (25% engine load) and 60 kW (75% engine load) for the ship fuels MGO, HVO, ULS-HFO_{ar}, HFO 0.5, and HFO 2.2. Latter two fuels with (Scr) and without wet scrubbing. EURO III and EURO VI emission limits of heavy-duty engines (ESC and WHSC test cycles) are added for NO_x, CO, and HC for comparison. MARPOL Annex VI NO_x limits for Tier 1, 2, and 3 are added for this engine (rpm 1500).

whereby the HFO fuels with and without wet scrubbing resulted in much higher emission factors ranging from 6169 ± 1014 mg/kWh for HFO 0.5 Scr to 12508 ± 624 mg/kWh for ULS-HFO_{ar}. All 60 kW CO emission factors were below or in the range of the EURO VI road traffic limit. This proves that optimized combustion conditions can significantly lower the CO emissions of ship engines.

Wet scrubbing had no or insignificant effects on CO emissions, which becomes even clearer when the post-scrubbing emissions (Fig. 2b and

Table 2) are directly compared with the corresponding pre-scrubbing values of the same test series, which is illustrated in Table S1 in the Supplementary Material. Neither for HFO 0.5 (pre-scrubber at MC3: 5468 ± 90 mg/kWh, post-scrubber at MC3: 6169 ± 1014 mg/kWh) nor for HFO 2.2 (pre-scrubber at MC3: 8263 ± 398 mg/kWh, post-scrubber at MC3: 8132 ± 279 mg/kWh) significant effects of wet-scrubbing could be determined.

3.3. Hydrocarbons

Emission factors of HC are shown in Fig. 2c. When operating the engine at 60 kW, HC emissions were comparable throughout all fuels and resulted in values between 122 ± 2 mg/kWh (ULS-HFO_{ar}) and 218 ± 29 mg/kWh (HFO 0.5). However, at lower engine loads (20 kW) HC emissions increased significantly between factors of 2.2 (HVO) to 12.6 (HFO 2.2) and ranging from 408 ± 8 mg/kWh (HVO) to 1851 ± 102 mg/kWh (HFO 2.2). For this engine load, MGO and HVO featured similar HC emissions, whereas fuels containing HFO had significantly higher yields.

The HC limits for HD engines in Europe are 660 mg/kWh for EURO III and 130 mg/kWh for EURO VI. The EURO III threshold was met for all fuels at 60 kW engine load ranging from 122 ± 3 mg/kWh for ULS-HFO_{ar} to 218 ± 29 mg/kWh for HFO 0.5 and exceeded significantly for all HFO-fuels at 20 kW with emission factors from 965 ± 25 mg/kWh for HFO 0.5 Scr up to 1851 ± 102 mg/kWh for HFO 2.2. In contrast, MGO and HVO complied with the EURO III emission limits. The EURO VI HC emission limit was only met by ULS-HFO_{ar} at 60 kW, however, the exceedances of the other fuels were relatively low ranging from 138 ± 18 mg/kWh for HFO 0.5 Scr to 218 ± 29 mg/kWh for HFO 0.5.

In contrast to NO_x and CO, some reductions of HC emissions could be observed at 20 kW engine load when a wet scrubber was applied (see Table 2). For HFO 2.2 a reduction rate of 30% (2015 ± 265 mg/kWh to 1411 ± 246 mg/kWh) and for HFO 0.5 of 36% (1498 ± 142 mg/kWh to 965 ± 25 mg/kWh) was determined. However, engine loads of 60 kW did not feature significantly lowered HC emission factors.

3.4. Benzene

The emission factors of benzene are illustrated in Fig. 2d. Similar to the HC sum values all fuels featured relatively low numbers for the engine load of 60 kW with emission factors from 2.2 ± 0.16 mg/kWh (HFO 2.2 Scr) to 5.07 ± 0.42 mg/kWh (HFO 0.5). When running at 20 kW engine load, benzene emission increased significantly, particularly, for the commercial HFO fuels. In doing so, the benzene yields ranged from 33.4 ± 2.2 mg/kWh (HFO 0.5 Scr) to 47.7 ± 4.8 mg/kWh (HFO 2.2 Scr), which corresponds to increase rates of more than 20 for HFO 2.2 Scr. MGO (3.96 ± 0.03 mg/kWh) and HVO (2.02 ± 0.3 mg/kWh) resulted in about one order of magnitude lower values whereby for them, no significant differences between the engine loads could be determined. The same trend has been observed for HC. Wet scrubbing showed no influence on the benzene emissions.

3.5. Carbonyls

The carbonylic compounds formaldehyde and acetaldehyde featured a unique behaviour in comparison to the previously presented emission constituents. The commercial HFO fuels had the highest emission factors when operated without a scrubber at 20 kW engine load. For formaldehyde (Fig. 2e), values reached 141.5 ± 13.1 mg/kWh (HFO 0.5) and 150.3 ± 52.4 mg/kWh (HFO 2.2), for acetaldehyde (Fig. 2f) 54.7 ± 7.8 mg/kWh (HFO 0.5) and 74.7 ± 18.4 mg/kWh (HFO 2.2). At 60 kW engine load without scrubber emission factors for both HFO fuels were reduced significantly to 34.7 ± 16 mg/kWh (HFO 0.5; 72% reduction) and 17.9 ± 4.2 mg/kWh (HFO 2.2; 88% reduction) for formaldehyde as well as 15.6 ± 2.9 mg/kWh (HFO 0.5; 71% reduction) and 18.8 ± 4.9 mg/kWh (HFO 2.2; 75% reduction) for acetaldehyde. These values were in the same range as for the non-HFO-fuels MGO (formaldehyde 20 kW: 39.3 ± 3.8 mg/kWh and 60 kW: 32.7 ± 5.8 mg/kWh; acetaldehyde 20 kW: 14.9 ± 1.5 mg/kWh and 60 kW: 9.9 ± 2.2 mg/kWh) and HVO (formaldehyde 20 kW: 31.8 ± 1.8 mg/kWh and 60 kW: 37.2 ± 3.6 mg/kWh; acetaldehyde 20 kW: 13.2 ± 1.1 mg/kWh and 60 kW: 11.8 ± 1.2 mg/kWh). However, for MGO and HVO no significant differences between high and low engine loads could be determined. Interestingly, when wet scrubbing was applied, the emissions of both carbonyl

compounds were significantly reduced resulting in reduction rates between 97% for formaldehyde with HFO 0.5 to 88% for acetaldehyde with HFO 2.2. Obviously, these polar organic compounds were washed out almost completely from the exhaust by wet scrubbing. The same reduction effect was observed for the engine load of 60 kW. The fuel ULS-HFO_{ar} featured the same trend as the commercial HFOs but with lower emission factors.

3.6. OPF

Values of OPF are illustrated in Fig. 2g. For the 20 kW engine load, three main groups can be observed. HVO showed the lowest OPF with 1061 ± 119 mg/kWh closely followed by MGO with 1376 ± 107 mg/kWh. The commercial HFO fuels with operating scrubber as well as ULS-HFO_{ar} featured OPF varying between 2003 ± 190 mg/kWh (HFO 0.5 Scr) and 2827 ± 59 mg/kWh (HFO 2.2 Scr). As a third group, both commercial HFOs without wet scrubbing could be identified as having the highest OPF with 5048 ± 154 mg/kWh (HFO 0.5) and 5787 ± 560 mg/kWh (HFO 2.2). Subsequently, from the fuel with the lowest OPF to the fuel with the highest OPF, a ratio of more than 1:5 was determined. For higher engine loads e.g. 60 kW a somewhat different picture emerges. In this case, the fuels MGO, HVO as well as HFO 0.5 and HFO 2.2, both without scrubbing, lead to similar OPF ranging from 837 ± 90 mg/kWh (MGO) to 925 ± 163 mg/kWh (HFO 2.2). In contrast, after scrubbing HFO 0.5 (249 ± 25 mg/kWh) and HFO 2.2 (278 ± 99 mg/kWh) had the lowest OPF. In conclusion, the pattern of OPF for all experiments (Fig. 2g) resembled the pattern of HC (Fig. 2c) with the exception that OPF yields with scrubber operation (HFO 0.5 Scr and HFO 2.2 Scr) were lowered due to the almost absent OPF contributions by carbonylic compounds.

In general, OPF is strongly influenced by CO and certain hydrocarbons. Although CO has a relatively weak ozone formation potential with a MIR factor of 0.057, the high CO emissions still result in a notable fraction. Hydrocarbons contributing the most to OPF have (alternating) C–C double bonds or C–O double bonds. This leads to MIR-factors from 0.31 for ethane to e.g. 13.47 for benzene, 7.877 for formaldehyde, and 6.829 for acetaldehyde (see Table 2). The percentage contribution of CO as well as hydrocarbons separated in carbonyl compounds and VOC (without carbonyls) to the OPF of the different fuels is illustrated in Fig. 3.

Remarkable is the modified pattern for both test series with/without scrubber where the percentage contribution without scrubber changed from 8 to 10% from CO, 55% from VOC, and 35–37% from carbonyls to 13–23% from CO, 66–83% from VOC and only 4–10% from carbonyls

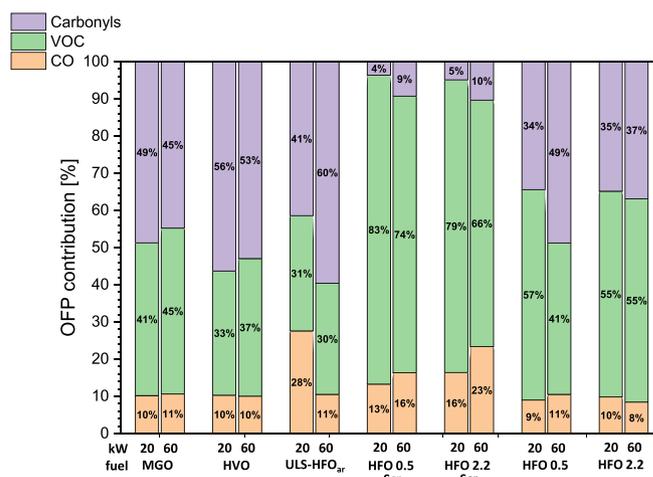


Fig. 3. (in color): Percentage contribution of CO, VOC (without carbonyls) and carbonyls to the OPF for the ship fuels MGO, HVO, ULS-HFO_{ar}, HFO 0.5 and HFO 2.2. Latter two fuels with (Scr) and without wet scrubbing.

with scrubber. Subsequently, the above-mentioned removal of carbonyl compounds by wet scrubbing modifies the overall matrix of chemical constituents in the gaseous emission and significantly influences the secondary formation of ozone. In contrast, the emission patterns of MGO, HVO and commercial HFO without scrubbing were similar besides the different absolute values.

4. Discussion

Regarding the presence of gaseous air pollutants in marine exhaust, a clear relation to the engine operation was observed. At the lowest engine load of 20 kW, the commercial HFO fuels (without scrubbing) as well as the ULS-HFO_{ar} featured significantly higher emissions for most studied pollutants than MGO and HVO. Emissions of the latter two fuels were mostly in the same range with sometimes slightly lower values for HVO e.g. for HC. With higher engine loads the differences in emissions between all fuels were converging (see Fig. 2 and Table 2).

4.1. Environmental benefits from sulphur cap outside a SECA

On January 1, 2020 the upper limit for FSC was reduced from 3.5% (w/w) to 0.5% [IMO, 2008a]. In our study, the effects of this regulation tightening should be noticed when comparing any emission factors of HFO 0.5 with HFO 2.2 (both without scrubber). However, for the investigated gaseous air pollutants, with the exception of SO₂, only little to no significant effects could be determined by this act. Although at 20 kW engine load CO and HC emission factors of HFO 0.5 were lower than that of HFO 2.2 (CO: 20%; HC: 21%), this positive effect was not seen at 60 kW, which should be the far more important engine load at open sea. However, the benefits of this regulation tightening on SO₂ emission and other directly related effects like aerosol formation from SO_x, which are not subject in this paper, are out of the question.

4.2. Environmental benefits from sulphur cap inside a SECA

Since January 1, 2015 the upper limit for FSC in a SECA has been reduced from 1.0% (w/w) to 0.1% [IMO, 2008a]. Compliance with this regulation can be achieved by either (i) operating on (modern) fuels with reduced FSC or (ii) by implementing a proven effective exhaust after-treatment technology for SO₂. In this study i) is addressed by running test series on the fuels MGO, HVO, and ULS-HFO_{ar} in comparison to HFO 0.5, whereas ii) is investigated by running test series on commercial HFO fuels (here HFO 0.5 and HFO 2.2) with and without wet scrubbing.

- i) The transformation from HFO 0.5 to the commercial cleaner fuels MGO and HVO showed positive effects for almost all pollutants (except NO_x) when operating the engine at low speeds. Reduction rates in the range of one order of magnitude were feasible e.g. 1:18 (HVO) and 1:9 (MGO) for benzene, 1:3 (MGO) and 1:4 (HVO) for CO, 1:4 (MGO) and 1:4 (HVO) for formaldehyde or 1:4 (MGO) and 1:5 (HVO) for OFP. The benefits of ULS-HFO_{ar} are less pronounced, for some compounds like NO_x and CO even negative. At higher engine loads little (e.g. benzene) to no significant effects could be observed. Taking into account that ships often undergo manoeuvring operations at ports and close to coastal areas, which brings the focus to lower engine loads, residents should have profited from the switch to better fuel qualities like MGO and HVO in terms of air quality.
- ii) Many air pollutants were not significantly affected by the wet scrubbing process i.e. their emission factors with or without scrubbing were about the same. However, this was not the case for carbonylic compounds, first and foremost formaldehyde and acetaldehyde as the two dominating representatives. These compounds were significantly reduced, sometimes even almost entirely removed by wet scrubbing, most likely due to the molecules' polarity, which makes them very water-soluble. Reduction rates of up to 97% could

be determined. Although higher engine loads resulted also here in lower emissions wet scrubbing further reduced these values. This behaviour is also reflected in OFP, where values for scrubbed HFO fuels were in between unscrubbed HFO fuels and the cleaner fuels MGO and HVO.

Consequently, a clear positive effect on air quality by these technical measures can be derived for these specific pollutants.

4.3. Environmental benefits of different fuels inside a SECA

For this evaluation, the five fuels/conditions MGO, HVO, ULS-HFO_{ar}, HFO 0.5 Scr, and HFO 2.2 Scr were compared. In general, it can be said that emission factors of different fuels partially differed significantly at low engine loads but converged at higher rates. This brings the situation in harbours, estuaries etc. more into focus where ship engines might run more often on low speeds/loads. The test fuel ULS-HFO_{ar} did not entail substantial improvements. Some emission factors were lower than those of scrubbed HFO fuels (e.g. benzene), some even higher (e.g. NO_x, CO), or in the same range as commercial scrubbed HFO fuels (e.g. HC). The fuels MGO and HVO generated the lowest air pollutant yields and featured, in general, a similar behaviour for most compounds with HVO being the even cleaner fuel (e.g. NO_x). However, differences between MGO and HVO were marginal. Commercial HFO fuels (with scrubber) featured the highest emission factors for most of the investigated air pollutants. Increase rates of one order of magnitude were common in comparison to MGO/HVO (e.g. CO, benzene) except for carbonylic compounds. Representatives of this compound class (formaldehyde, acetaldehyde) were very effectively removed by wet scrubbing.

4.4. Environmental benefits from a NECA

Since January 1, 2016 in the U.S. and since January 1, 2021 in Europe NECA's were established where new ships must comply with Tier 3. This law tightening entails great environmental benefits as the permitted NO_x emissions have been reduced significantly. These NO_x emission standards are only to be fulfilled by the implementation of NO_x emission abatement systems, which have been state-of-the-art in road traffic for a long time.

These and other well-established technical measures to reduce air pollutants should finally also find entry into the marine engine sector. From this implementation of modern emission abatement systems (e.g. oxidation catalyst, selective catalytic reduction catalyst, diesel particle filter, wet scrubber) in combination with high-quality fuels, accompanied with (stricter) emission standards, coastal residents and the marine ecosystem would profit likewise. Based on our results we emphasize that the wet sulphur scrubber alone cannot sufficiently reduce NO_x, so an additional abatement system would be required.

5. Conclusion

Significant differences in gaseous emission factors between different fuels and engine operation were revealed, with the wet scrubber providing limited or no reduction of gaseous emissions, especially for water-insoluble gases. We suggest enhanced regulations and emission abatements in the marine sector to mitigate gaseous pollutants harmful to human health and the environment.

In future research, it will be important to explore the interaction between gas phase plume chemistry and particulate emissions, especially in context of secondary PM formation.

CRediT authorship contribution statement

Jan Bendl: Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Conceptualization. **Mohammad Reza Saraji-Bozorgzad:** Writing – review & editing, Writing –

original draft, Visualization, Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Uwe Käfer**: Writing – review & editing, Validation, Methodology, Investigation, Formal analysis, Data curation. **Sara Padoan**: Writing – review & editing, Writing – original draft, Investigation, Data curation, Conceptualization. **Ajit Mudan**: Investigation, Data curation. **Uwe Etzien**: Writing – review & editing, Methodology, Investigation, Conceptualization. **Barbara Giocastro**: Writing – review & editing, Investigation. **Julian Schade**: Writing – review & editing, Investigation. **Seongho Jeong**: Writing – review & editing, Investigation. **Evelyn Kuhn**: Investigation. **Martin Sklorz**: Supervision, Methodology, Conceptualization. **Christoph Grimmer**: Investigation. **Thorsten Streibel**: Writing – review & editing, Supervision, Resources, Project administration, Conceptualization. **Bert Buchholz**: Resources, Project administration. **Ralf Zimmermann**: Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition. **Thomas Adam**: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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