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RESEARCH ARTICLE

A Novel Approach to Reduce the Environmental Footprint of Maritime Shipping

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Abstract

Maritime shipping is a strategic sector with a strong international vocation and management. The need to define regulations valid for many different countries without generating disparities of treatment slowed down the formulation of environmental regulations, especially for atmospheric emissions. In particular, regulations pertaining to the reduction of sulphur compounds allowed two distinct approaches: the use of low-sulphur fuels or exhaust gas cleaning systems, the so-called Scrubbers. The actual implementation of these solutions presents specific concerns either related to the toxicity of atmospheric by-products and to the fuel cost or to the generation of polluting washwaters that may need treatment before discharge. In this paper we analyzed the potential environmental benefit deriving from the use of a distillate fuel, not compliant with current IMO Sulphur Regulations, together with a Scrubber. The pilot-scale experimental results indicated that a limited amount of water and/or scrubber volume is needed to reduce sulphur emissions below regulations on maritime shipping, especially with the addition of NaOH reaching a water-saving between 25%-33% compared to the use of pure seawater. Experiments indicated that scrubber washwater PAHs emissions are within the available water quality standards indicated by EU and USA guidelines. A bottom-up analysis on heavy metals concentration shed light on the prominent role of metal-parts corrosion on the washwater emissions. Taking into account for corrosion phenomena, the actual heavy metals concentration in the washwater deriving from scrubbing was normally below the water quality standards.

Keywords Ships environmental footprint · Exhaust gas cleaning system · Washwater emissions · Marine distillate fuels · Marine seawater scrubber · Persistent pollutants

Article Highlights

- A new model to contain emission footprint of maritime shipping is proposed.
- A pilot-scale open-loop scrubber was tested to treat a Diesel engine exhausted gas.
- SO_2 scrubber emissions from MGO fuel were complying with IMO limits.
- 25%-33% of water-savings were achieved by adding NaOH in pure seawater.
- Most of the pollutants in the wash water complied with the Water Quality Standards.
- Heavy metals emissions in wash water were related to corrosion of the set-up alloys

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1 Introduction

Due to the progressive introduction of severe regulations regarding the maximum allowed sulphur content in fuels for on-road vehicles and on the emissions of SO_2 in industrial productions and power plants, the emission of SO_2 in the atmosphere is progressively decreasing since more than 50 years. The maritime sector remained largely unregulated until the International Maritime Organization (IMO) introduced the Revised version of the MARPOL Annex VI guidelines (International Maritime Organization 2008). This was later ratified by many national Governments thus becoming the standard for ship emission worldwide. Until this date, the unbalancing between maritime shipping and land-based activities in terms of sulphur regulation was so large that ships were considered responsible for up to 70% of the SO_2 concentration in the air in some regions in the North and Baltic Sea (Turner et al. 2017) and it was shown that SO_2 emissions from shipping were around three times larger than those derived from road traffic and aviation combined (Eyring et al. 2005).

In order to achieve a reduction of sulphur emissions while preserving the overall economic balances of shipping companies and fuel availability, the MARPOL VI introduced two options to guarantee compliance to their emission targets: 1) to control the sulphur content in the fuel or; 2) to adopt exhaust gas cleaning systems to depurate the gas before they enter the atmosphere. Nowadays, the emission target imposed for all traveling ships is the equivalent emission factor, mg/kWh of sulphur equivalent to that produced by burning a fuel containing 0.5% in weight of sulphur. Besides, the same MARPOL identified some sulphur Emission Control Areas (SECA) within which the equivalent sulphur content is lowered to 0.1% in weight. When International agreements were not signed, some Regional governments impose a similar limit for ships traveling along their territorial waters, as for example in European Union (Derwent et al. 2005).

It is not easy to address properly the advantages and the problems arising from the use of a low Sulphur fuel, especially since the spirit of the original IMO guidelines was meant to provide a shift from heavy fuel oils to distillate fuels, while the market recently responded to the regulatory stimulus by inducing heavy fuel oils at low-sulphur content, whose emissions profile is still under scrutiny (Zetterdahl et al. 2016). For example, many distilled fuels were proved to be responsible for higher emissions of ultrafine particles compared with heavy fuel oils. These particles are considered highly dangerous for exposed people (Wichmann 2007; Schmid et al. 2009; Di Natale and Carotenuto 2015; Oeder et al. 2015; Reis et al. 2018; Liu et al. 2019).

Seawater scrubbers are considered the most efficient and cost-effective gas cleaning systems to remove sulphur compounds from marine diesel exhaust gases. These units used the natural alkalinity of seawater, sometimes improved by the addition of NaOH, to absorb sulphur dioxide from the exhaust gases. This process is used for around one century in coal-fired power plants and its design is well consolidated in the engineering companies. While these units can provide emission of sulphur dioxide well below the target limits, their main drawback is the transfer of other pollutants to the seawater. To this, the IMO introduced guidelines to control the quality of scrubber washwater discharge (International Maritime Organization 2006).

While complying with the reference IMO regulations, several shipping companies performed voluntarily monitoring campaigns which revealed levels of pollutants emission below wastewater regulations for direct discharge in natural waters for similar (FGD scrubbers, municipal waste incinerator, power plants) installations (Hufnagl et al. 2005; Lange and Markus 2015; DNV-GL and Carnival corporation, 2019). Together with the high dilution occurring around the ship's keel (*e.g.* Lange and Markus 2015), these results indicated a low level of water pollution associated with scrubber washwater.

Nevertheless, these evaluations did not attempt to assess the cumulative effect of washwater parameters entering seawater or the potential environmental impact from these emissions. Recently several studies have raised concerns about a negative impact on the marine environment where authors pointed out how these guidelines look inappropriate and claimed for stricter regulations to control, in particular, for the emissions of persistent pollutants as PAH and heavy metals from seawater scrubbers (Turner et al. 2017, 2018; Ytreberg et al. 2019; Dulière et al. 2020). Teuchies et al. (Teuchies et al. 2020) showed that scrubber washwater emissions should be discouraged in areas with high levels of pollutions since the amount of emitted pollutants sum to the already polluted background. This conclusion holds true, however, for all the existing sources of pollutants active in that area.

These publications have led to an extended discussion within the IMOs Sub-Committee on Pollution Prevention & Response (PPR) while some port and regional authorities have banned the use of open-loop scrubbers (International Maritime Organization 2015).

Indeed, PAH and heavy metals derive from the use of carbon-based fuels and are normally emitted in the atmosphere, where they react or disperse, being eventually deposited over the nearby sea or land. When a scrubber is adopted, it is concentrated in a limited amount of water and transferred from the air to the sea. Whether it is better to emit these pollutants in the air or the sea, is a question that requires further investigations.

Independently from the actual fate of emitted pollutants, it is clear that the heavier the fuels the higher the tendency to have PAH and heavy metals in the gas exhausts. Therefore, to reduce ship emissions, lighter fuels should be used. Marine fuels are currently classified according to the ISO 8217:2017 and more recent ISO/PAS 23,263:2019, which indicates two main classes of fuels: marine distillates and marine residual fuels. The first is characterized, among the other properties, by low levels of ashes ($<0.01\%$ in weight) and carbon micro residues ($<0.30\%$ in weight) while the others have different qualities according to the average molecular weight of its constituents (ashes from 0.04% to 0.15% in weight; carbon micro residue from 2.5% to 20% in weight).

Notwithstanding their better properties, not all distillate fuels are able to comply with regulations on sulphur content and the toxicity of the particles they produce in the marine engines appeared even larger than those produced by residual fuels (Wichmann 2007; Schmid et al. 2009; Di Natale and Carotenuto 2015; Oeder et al. 2015; Reis et al. 2018; Liu et al. 2019). In this sense, the use of scrubbers, with their capacity to remove sulphur compounds and partially capture particles (*e.g.* (Lehtoranta et al. 2019; Winnes et al. 2020)) and part of the PAHs (Winnes et al. 2020) shifting them to the washwater and making them harmless from humans and the environment, is a valuable option to reduce the environmental footprint of ships, as suggested in recent studies (Ha et al. 2010; Tang et al. 2014; Di Natale et al. 2015, 2018, 2019a, 2020a, b; Darake et al. 2016; Flagiello et al. 2017, 2018a, b, 2019a, b, 2020a, b, c; Schultes et al. 2018; Iliuta and Iliuta 2019; Iliuta and Larachi 2019; Wang et al. 2019; Kuang et al. 2020; Flagiello 2020).

This paper proposes a possible option to reduce ships' environmental footprint both in terms of air and water impact by using a distillate fuel in combination with a marine scrubber. This kind of fuel can be used easily in most of the existing engines and are largely available on the market. Similarly, the marine scrubber market largely consolidated in the last years, with several suppliers available worldwide.

To this end, this work reported experimental results on a pilot-scale seawater scrubber used to treat a 4-stroke marine diesel engine fueled with a 0.92% sulphur-fuel Marine Gas Oil (MGO). The experiments include both an analysis of gas pollutants removal efficiency and of the concentration of the PAH and the heavy metals in the scrubber washwater. The results are compared with the global and the SECA limits on sulphur emissions imposed by the IMO and with the limits imposed on PAH and heavy metals for land-based installation and with the indication for Natural Waters Quality Standards imposed by several countries.

2 Materials and Methods

2.1 Materials

The use of seawater as scrubbing liquid is related to the natural abundance of dissolved alkaline species in seawater compared to freshwater, which shifts the chemical equilibria towards a greater dissociation of H_2SO_3 (Iliuta and Larachi 2001; Rodríguez-Sevilla et al. 2004; Andreasen and Mayer 2007; Darake et al. 2016; Flagiello et al. 2018a, b, 2019a, b, c), as shown in Eqs. (1)–(6):

$$SO_{2(g)} + H_2O_{(l)} \leftrightarrow H_2SO_{3(aq)} \tag{1}$$

$$H_2SO_{3(aq)} + CO_3^{2-} \leftrightarrow HSO_3^- + HCO_3^- \tag{2}$$

$$HSO_3^- + CO_3^{2-} \leftrightarrow SO_3^{2-} + HCO_3^- \tag{3}$$

$$H_2SO_{3(aq)} + HCO_3^- \leftrightarrow HSO_3^- + H_2CO_{3(aq)} \tag{4}$$

$$HSO_3^- + HSO_3^- \leftrightarrow SO_3^{2-} + H_2CO_{3(aq)} \tag{5}$$

$$H_2CO_{3(aq)} \leftrightarrow CO_{2(g)} + H_2O_{(l)} \tag{6}$$

This larger dissociation of H_2SO_3 occurring under alkaline conditions gives rise to a significant improvement of SO_2 solubility in water: SO_2 dissolves integrally in water as long as there are enough HCO_3^- and CO_3^{2-} ions to complete the reactions (Rodríguez-Sevilla et al. 2004; Andreasen and Mayer 2007; Flagiello et al. 2017, 2018a, 2019b).

In the Mediterranean Sea and in the Oceans, the alkalinity of water is quite high: 2.3–2.4 mmol/L (Lee et al. 2006), allowing an appreciable chemical absorption of sulphur dioxide. On contrary, the Baltic Sea and North Pacific have lower alkalinity. To this hand, a limited amount of NaOH is added to the natural seawater to improve the absorption of sulphur dioxide while containing the risks of precipitation of hydroxides in seawater. The typical reaction mechanism of SO_2 in an aqueous solution containing OH^- ions is shown below:

$$SO_{2(aq)} + OH^- \leftrightarrow HSO_3^- \tag{7}$$

$$HSO_3^- + OH^- \leftrightarrow SO_3^- + H_2O \tag{8}$$

where sulphur dioxide once absorbed from gas-phase in the aqueous-phase ($SO_{2(aq)}$) is hydrolyzed to HSO_3^- and subsequently into SO_3^{2-}.

In this work, the experiments were carried out using the exhaust gas produced by a four-cylinder diesel engine fed with a Marine Gas Oil (MGO) fuel containing 0.92% in weight of sulphur, whose chemical composition is shown in Table 1. The engine oil used at the test bench was a Volvo Penta VDS-3.

The FGD experiments were carried out using a sample of seawater taken from the sea area of Kattegat, located between the Jutlandic peninsula in the west, the Danish Straits islands of Denmark in the south, and the Sweden coasts in the east. This water is indicated as KSW (Kattegat Seawater) in the following and its composition is shown in Tables 2 and 3. The same seawater was eventually doped with 100 mg/L of NaOH until reaching pH = 10.5, to simulate typical water used for scrubbing in the Baltic Sea (Tang et al. 2014; Wang et al. 2019; Kuang et al. 2020). This last water solution is named KSWOH in this paper.

The sodium hydroxide used was purchased from VWR International Chemicals (Sweden) as AR grade (99.99% in weight) to enhance the seawater of Kattegat (see Eqs. (7)–(8)).

Table 1 Chemical composition of the MGO fuel

Name	Methods	Values
Total aromatics	SS 155116	30.2% in volume
Mono-aromatics	SS 155116	21.3% in volume
Di-aromatics	SS 155116	7.76% in volume
Poly aromatics (Tri +)	SS 155116	1.13% in volume
Sulphur (S)	EN ISO 8754	0.92% in weight
Aluminum (Al)	ASTM D 7111	0.35 mg/kg
Barium (Ba)	ASTM D 7111	< 0.1 mg/kg
Calcium (Ca)	ASTM D 7111	< 0.1 mg/kg
Chromium (Cr)	ASTM D 7111	< 0.1 mg/kg
Copper (Cu)	ASTM D 7111	< 0.1 mg/kg
Iron (Fe)	ASTM D 7111	< 0.1 mg/kg
Lead (Pb)	ASTM D 7111	< 0.1 mg/kg
Lithium (Li)	ASTM D 7111	< 0.1 mg/kg
Magnesium (Mg)	ASTM D 7111	< 0.1 mg/kg
Manganese (Mn)	ASTM D 7111	< 0.1 mg/kg
Molybdenum (Mo)	ASTM D 7111	< 0.1 mg/kg
Nickel (Ni)	ASTM D 7111	< 0.1 mg/kg
Potassium (K)	ASTM D 7111	< 0.1 mg/kg
Silicon (Si)	ASTM D 7111	< 0.1 mg/kg
Silver (Ag)	ASTM D 7111	< 0.1 mg/kg
Sodium (Na)	ASTM D 7111	< 0.1 mg/kg
Titanium (Ti)	ASTM D 7111	< 0.1 mg/kg
Vanadium (V)	ASTM D 7111	< 0.1 mg/kg
Zinc (Zn)	ASTM D 7111	< 0.1 mg/kg

2.2 Experimental Set-Up

The experiments were carried out in the Engine lab of the Department of Mechanics and Maritime Sciences, Chalmers University of Technology (Göteborg, Sweden), on a Volvo PENTA four-cylinder 80 kW engine marine diesel engine (D3-110) operated by fixing three different loads at 2000 r/min corresponding to engine loads at 10%, 25% and 50% of the rated maximum load.

The pilot-scale spray tower (i.d.: 400 mm and total length: 500 mm) was made in stainless steel AISI 316L and was positioned horizontally, unlike the common vertical scrubbers. The system was operated at atmospheric pressure. The flowsheet of the experimental plant is shown in Figure 1.

Different engine loads can be tested by varying the engine speed and the hydraulic torque. The load variation influences the fuel consumption, temperature, and composition of the flue-gas generated.

A PLC unit allowed to manage the engine rotation per minute, the hydraulic torque, the cooling water and to measure the temperature and pressure of the engine and the support units. The operating conditions collected during operations were resumed in Table 4.

Table 2 The concentration of ionic species in the Kattegat seawater sample

Heavy metals and ionic composition			Values
Ca	Calcium	mg/L	19.5
Fe	Iron	mg/L	0.0243
K	Potassium	mg/L	< 8
Mg	Magnesium	mg/L	< 2
Na	Sodium	mg/L	13,100
Si	Silicon	mg/L	1.03
Al	Aluminum	μg/L	34.7
Ba	Barium	μg/L	10.2
Cd	Cadmium	μg/L	< 0.05
Co	Cobalt	μg/L	< 0.05
Cr	Chromium	μg/L	0.14
Cu	Copper	μg/L	12.4
Hg	Mercury	μg/L	< 2
Mn	Manganese	μg/L	2.85
Mo	Molybdenum	μg/L	0.245
Ni	Nickel	μg/L	1.38
P	Phosphorus	μg/L	< 40
Pb	Lead	μg/L	< 0.3
Sr	Strontium	μg/L	52.4
Zn	Zinc	μg/L	83.1
NO_3^-	Nitrate	mg/L	1.32
SO_4^{2-}	Sulphate	mg/L	68.9
PO_4^{3-}	Phosphate	mg/L	< 0.04
F^-	Fluoride	mg/L	< 2
Br^-	Bromide	mg/L	< 4
Cl^-	Chloride	mg/L	21,400
NH_4^+	Ammonium	mg/L	< 0.05
HCO_3^-	Bicarbonate	mg/L	219

On the outlet line of the Volvo Penta diesel engine exhausts, a solenoid valve allows to split the gas flow rate into two streams: the first was sent to the engine lab chimney and the second one was sent to the scrubber in order to be treated.

The gas flow rate sent to the scrubber was controlled by using the solenoid valve on the exhaust pipe. The piping connecting the engine to the spray tower was made in Stainless Steel AISI 316L (i.d. 74 mm) and was thermally insulated to reduce the heat losses.

The flue-gas was fed in counter-current flow to the water into the scrubber. The flow rate, temperature, and pressure of the flue-gas after the scrubber were measured by a portable analyzer (Testo 480 Multi-function) equipped with a steel Pitot tube inserted into the outlet scrubber piping.

The liquid flow was fed by a frequency-controlled progressing cavity pump (Getriebebau Nord GmbH & Co.KG, D-22941 model, with a total power of 1.8 kW) and its pressure was controlled by a pressure gauge 0–10 bar (WIKA

Table 3 The concentration of organic compounds in the Kattegat seawater sample

Organics composition (μg/L)	Values
Aliphates > C5-C8	< 10
Aliphates > C8-C10	< 10
Aliphates > C10-C12	< 10
Aliphates > C12-C16	< 10
Aliphates > C5-C16	< 20
Aliphates > C16-C35	< 10
Aromatics > C8-C10	< 0.30
Aromatics > C10-C16	< 0.775
Metylpyrener/metylfluorantener	< 1.0
Methylchrysene/dimethylbenz(a)anthracene	< 1.0
Aromatics C16-C35	< 1.0
Benzene	< 0.20
Toluene	< 0.20
Ethylbenzene	< 0.20
m-p-xylene	< 0.20
o-xylene	< 0.20
Xylenes, sum	< 0.20
Naphthalene	0.038
Acenaphthylene	< 0.010
Acenaphthene	< 0.010
Fluorene	< 0.010
Phenanthrene	0.037
Anthracene	< 0.010
Fluoranthene	< 0.010
Pyrene	< 0.010
Benzo(a)anthracene	< 0.010
Chrysene	< 0.010
Benzo(b)fluoranthene	< 0.010
Benzo(k)fluoranthene	< 0.010
Benzo(a)pyrene	< 0.010
Dibenz(a,h)anthracene	< 0.010
Benzo(g,h,i)perylene	< 0.010
Indeno(1,2,3-cd)pyrene	< 0.010

Instruments, 233.50.63 model). The liquid flow was measured by ROTA Yokogawa liquid rotameter 0–10 L/min before the scrubber. A BETE® spray nozzle (HA 1.50–9020 model, made in stainless steel) was placed at 140 mm of distance from the scrubber inlet. In order to reduce the amount of water dragged by the gas, two honeycomb grid demisters made in stainless steel AISI 316L (i.d.: 400 mm) were put at 140 mm from the scrubber outlet. Six different liquid flow rates (*L*) between 30 and 180 L/h available at 20 °C, were tested. The washwater was stored in a steel tank of about 5 m^3 and then disposed of.

The gas analysis system was a Fuji Electric ZRE type NDIR gas analyzer (SO_2, NO, CO and CO_2) and Ankersmid Sampling (AOX 100 model) NO_x converter. This unit allowed to measure the total NO_x level with Fuji Electric ZRE, while if it was by-passed it only provided the reading of the NO emissions. O_2 was measured using a paramagnetic oxygen sensor (PAROX 1200). Flue-gas sample was previously cleaned from the soot with hot filter (J.U.M. Engineering, heated sample filter 1128 model) and dehumidified with a gas quencher (Ankersmid Sampling gas cooler) at low temperature.

2.3 Experimental Procedure

The pilot scrubber was fed with a flue-gas stream with two different flow rates (*G*): in the first experimental set, it was constant at 70 m^3/h (0.15 m/s), while in the second it was double, 140 m^3/h (0.31 m/s). The characteristics and physical properties of the flue-gas deriving from the Volvo diesel engine were reported in the former Table 4. The input concentrations of the gas pollutants were determined by a gas analyzer, feeding flue-gas into the scrubber without the liquid feed.

The seawater stream (*L*) was sent in counter-current flow with the gas at the different flow rates, from 30 to 180 L/h. The liquid was available at room temperature in June (20 °C), either as pure seawater (Kattegat seawater, KSW) or with additions of 100 mg/L of NaOH (KSWOH).

The scrubber output concentration levels of gas pollutants were monitored and recorded up for about 10 min until reaching stable measurement conditions (*i.e.* steady-state), which corresponded to a deviation of more or less than 5% on the concentration measurement and of about 1 part per million when the concentration values were lower than 20 parts per million. The system behaved stably in all experimental tests, but the data reproducibility is limited by the specific functioning of the engine.

The washwater sample was taken from the bottom of the scrubber and the pH value and temperature were measured soon by a portable pH-meter (pH Tester 30 with accuracy ± 0.1 for pH). For some water samples, the ionic, organic, and heavy metals composition was also analyzed by an accredited chemical analysis laboratory, according to ISO standards.

3 Results and Discussion

3.1 Gas Pollutant Emissions

Figures 2 and 3 show the SO_2 emissions at the scrubber exit as a function of the liquid–gas mass ratio (*L*/*G*) for KSW and KSWOH. The results are referred to two different flue-gas flow rates, equal to 70 and 140 m^3/h and for three different engine loads: 10%, 25%, and 50%. The lines denote the maximum allowed SO_2 emissions in SECAs

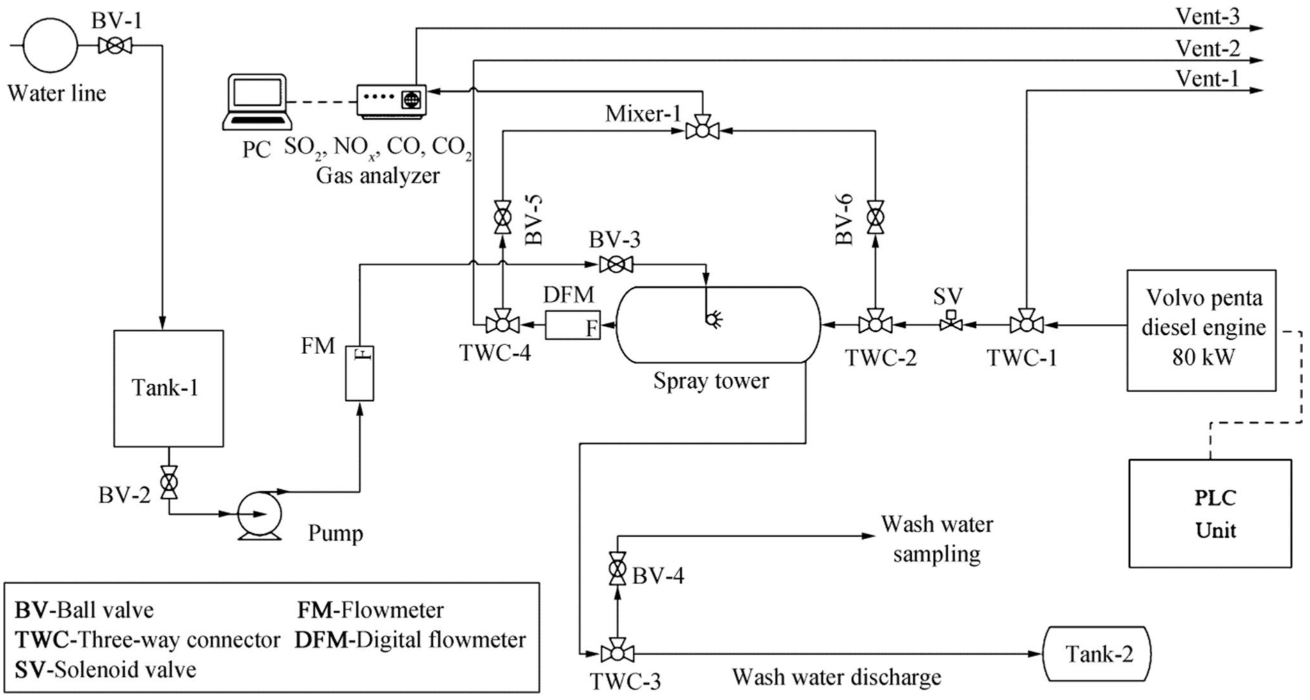


Figure 1 P&ID diagram of the experimental set-up

and open sea (GLOBAL) calculated on the basis of the specific fuel consumptions and the sulphur content of the fuel.

Figures 2 and 3 show how much liquid is required to comply with the global and SECA emission targets for the two-gas flow rate and for the two kinds of seawater. In general, the *L/G* ratio increases with the engine load, due to the higher concentration of SO_2 in the gas stream.

Besides, the experiment showed that, compared with the simple KSW, the KSWOH solution allowed a water-saving of between 7 and 50% to meet the global IMO limit and between 25 and 33% for the SECA limit. It is also worth noticing that the increase of gas flow rate worsened the SO_2 removal. This is probably since most of the scrubbing takes place at the scrubber entrance so that although the gas residence time halved passing from 70 to 140 m^3/h, the overall absorption was scarcely unaltered.

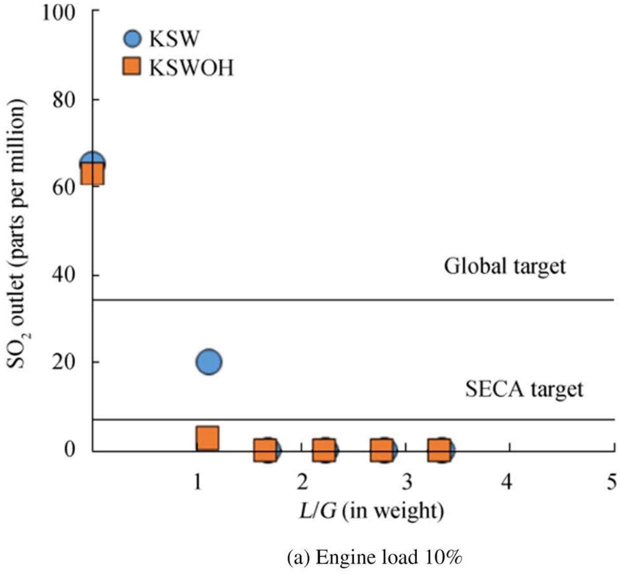
Table 5 shows the inlet/outlet emissions of SO_2 other gas pollutants (NO_x, CO and CO_2) with the gas inlet/outlet temperature as a function of the engine loads and liquid–gas mass ratio (*L/G*) for KSW and KSWOH solutions.

The measured concentrations of NO_x, CO and CO_2 in line with earlier experiments performed with this engine setup (Anderson et al. 2015). As expected, the results showed that seawater scrubbing has negligible effects on the removal of NO_x, CO and CO_2 also when NaOH was added to the liquid. This result mirrored the low solubility of these gases in the seawater acidified by the absorption of SO_2 and why SWS is not commonly used to reduce emissions of these gases. Table 5 also indicated that the gas temperatures decreased due to the contact with the cold scrubbing liquid, fed at 20 °C and that no effect of the limited heat of absorption associated with SO_2 solubilization, which was the only gas pollutant absorbed was to be observed. Despite the inlet temperatures were always higher when the load increased, the outlet temperatures were very similar, with a maximum deviation between 10 and 20 °C when the load is increased at 140 m^3/h.

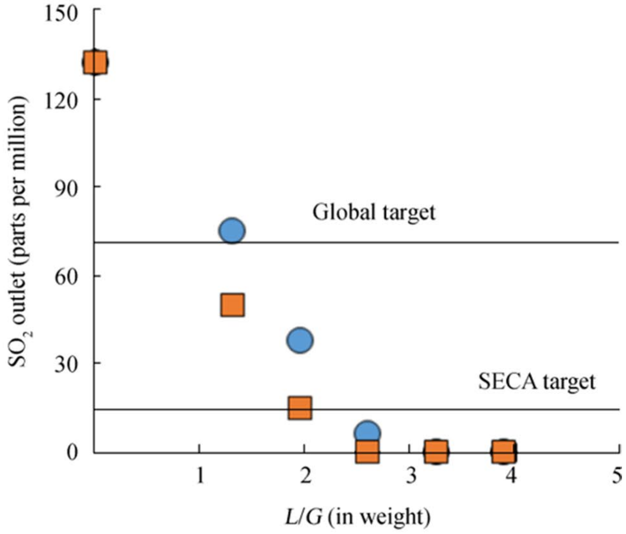
Table 4 Engine data collected for different engine loads (10%, 25%, and 50%)

Engine load (%)	Engine speed (rpm)	Hydraulic. torque (N·m)	Engine power (kW)	Fuel consumption (L/h)	Flue-gas temp (°C)
10	2000	35	8.38	2.7 ± 1	180 ± 6
25	2000	95	19.90	5.5 ± 1	260 ± 5
50	2000	190	39.80	10.1 ± 1	318 ± 2

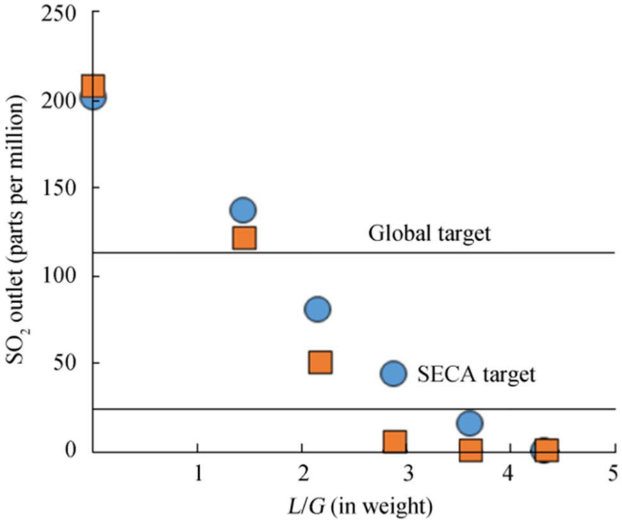
Figure 2 Experimental SO_2 outlet concentrations from FGD pilot ▸ unit with 70 m^3/h of flue-gas stream as a function of the *L*/*G* and parametric with different engine load (10%, 25% and 50%) and different scrubbing solutions at 20 °C (KSW and KSWOH). The horizontal lines indicate the SO_2 corresponding to the GLOBAL and SECA targets. $L/G = 0$ indicate the SO_2 outlet from the scrubber turned off



(a) Engine load 10%



(b) Engine load 25%



(b) Engine load 50%

In a former paper (Anderson et al. 2015) the particle emissions of the same engine unit were analyzed for four different fuels. Independently of fuel, bimodal size distributions by number were shown, with peaks at 10 nm and 45–50 nm for distillates and 10 and 100–110 nm for Heavy Fuel Oil (HFO). The emissions of nanoparticles with a size below 50 nm were the dominating fraction of the total particle number concentration and can be related to both sulfur content and other properties of the fuel.

The experiments showed lower emissions of particles larger than 50 nm and for volatile aerosols for distillate fuels compared with residual fuels. Recently Lethoranta (Lehtoranta et al. 2019) and Winnes and Fridell (Winnes et al. 2020) showed that a conventional scrubber applied on a residual fuel reduces up to 50% of particles mass and may remove from 10 to 80% of particles number, but better reduction of mass emissions (mg/kWh) achieved for distilled fuels (around 50%). The scrubber also removed a portion (35%–60%) of the PAHs normally emitted in the atmosphere (Winnes et al. 2020). The joint action of distilled fuels and scrubber is expected to reduce particle emissions around 75%.

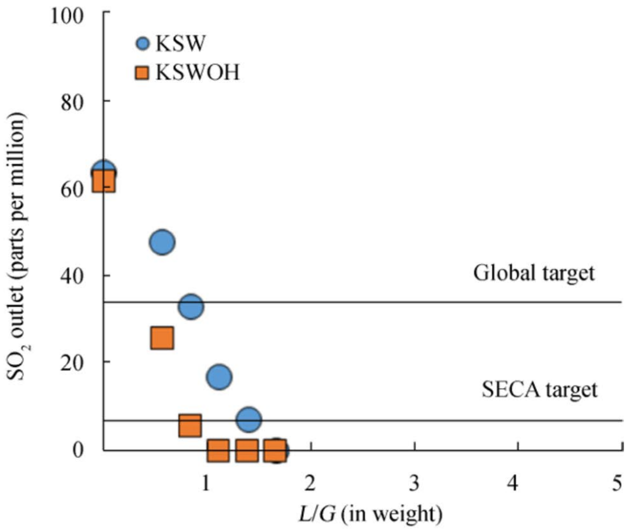
Further reductions of particulate matter can be achieved using electrified scrubbers that were proved to reduce diesel engines particles emissions fueled with distilled and residual fuels by more than 85%–90% in number and mass (Carotenuto et al. 2010; Ha et al. 2010; Di Natale et al. 2015, 2016, 2020a). The same electrification is also able to increase the absorption efficiency of sulphur dioxide (Di Natale et al. 2019a, b, 2020b).

3.2 Washwaters Properties

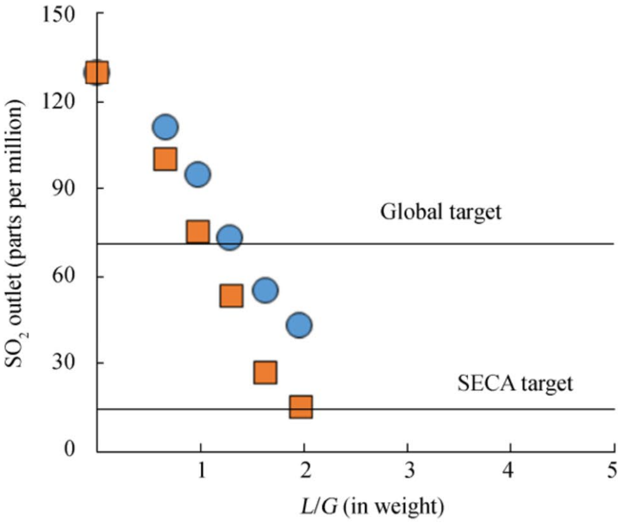
An analysis of the pH and temperatures of the washwater was performed for each FGD test described in the previous section. Although turbidity and total suspended solids (TSS) were not measured, the experimental observations showed a limited increase of turbidity with the presence of fine suspended black particles on the water surface and a smell of sulphur dioxide, which increased as the engine load increased.

Figures 4 and 5 show the pH values of the washwater at the scrubber outlet as a function of the liquid–gas mass ratio for KSW and KSWOH in the different operating conditions, *i.e.* flue-gas flow rates and engine loads.

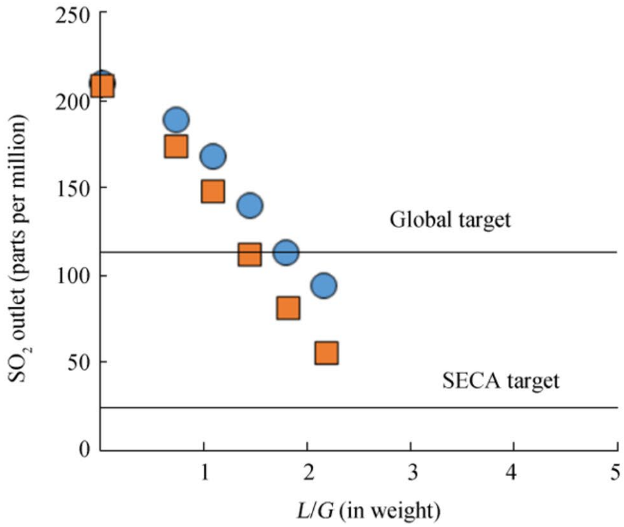
Figure 3 Experimental SO_2 outlet concentrations from FGD pilot ▶ unit with 140 m^3/h of flue-gas stream as a function of the L/G and parametric with different engine load (10%, 25% and 50%) and different scrubbing solutions at 20 °C (KSW and KSWOH). The horizontal lines indicate the SO_2 corresponding to the GLOBAL and SECA targets. $L/G = 0$ indicate the SO_2 outlet from the scrubber turned off



(a) Engine load 10%



(b) Engine load 25%



(c) Engine load 50%

The pH values of the washwater in Figures 4 and 5 were consistent with the SO_2 emission trends. As the engine load increased, the ranges of pH values in the washwaters lowered because more SO_2 was captured. It is worth noting that the seawater samples gave rise to an increase of pH when the complete SO_2 removal was achieved, in particular for all the conditions investigated for a flow rate of 70 m^3/h of flue-gas. Generally, the use of NaOH allowed an increase of pH by at most one pH unit because absorption completed when the water alkalinity and hydroxide content were consumed. The pH values of effluents after the scrubber were in the range 3–5, which is usually considered high enough to guarantee a pH higher than 6.5 at 4 m from the discharge point, as suggested by IMO guidelines 2009, Resolution MEPC 184(59), (Gregory and Confuorto 2012; Endres et al. 2018; IMO (International Maritime Organization) MEPC 74/INF.10, 2019). Generally, the amount of water needed to restore the pH within 4 m is about 1.9 times higher than that used for gas cleaning process (United States Environmental Protection Agency, 2011) and dilution around the keel is fast enough to easily achieve this goal when pH is above 3.5 (*e.g.* Lange and Markus 2015).

Figures 6 and 7 show the temperature of effluents at the scrubber outlet as a function of the liquid–gas mass ratio for KSW and KSWOH in the same different operating conditions reported in Figures 4 and 5.

Figures 6 and 7 showed that the liquid temperature remained almost unvaried with the engine load. This was probably due to the heat losses of the scrubber unit accompanied by the low energy of absorption of SO_2 in water. When the flue-gas flow rate was 140 m^3/h the exit liquid temperature is almost 5 °C higher than in the case of lower gas flow rate.

The temperature of scrubber washwater was generally in the range 30–50 °C.

Effluent discharges with temperatures above 40 °C can cause eutrophication effects, as suggested by IMO guidelines 2009 (Resolution MEPC 184(59)). However, the same mixing with fresh seawater, made to restore the pH (United States Environmental Protection Agency, 2011), is sufficient to cool down the scrubber washwater below critical levels.

3.3 FGD Effect on Heavy Metals and Organics Emissions in Washwaters

To evaluate the effect of the FGD process on heavy metals and organics emissions in the scrubber washwaters, further

Table 5 Experimental results for inlet/outlet of SO_2, NO_x, CO, CO_2 and gas temperature (T_G out) in the all experiments

Scrubbing solution	Engine load	Fuel consumption	G	L/G	SO_2 out	NO_x out	CO out	CO_2 out	T_G out
	(%)	(L/h)	(m^3/h)	(in weight)	(parts per million)			(% in volume)	(°C)
KSW	10	2.7 ± 1	70	0.00	65	176	490	3.80	180
				1.11	20	176	490	3.80	55
				1.67	0	178	488	3.80	40
				2.23	0	175	490	3.81	35
				2.79	0	176	491	3.80	34
				3.35	0	175	492	3.80	30
			140	0.00	64	177	496	3.80	180
				0.56	48	175	494	3.80	95
				0.84	33	173	493	3.81	80
				1.12	17	174	495	3.81	73
				1.40	7	173	493	3.81	62
				1.69	0	175	493	3.80	56
	25	5.5 ± 1	70	0.00	132	352	188	5.90	260
				1.30	75	348	184	5.91	66
				1.94	38	347	185	5.91	51
				2.59	6	346	182	5.90	44
				3.23	0	344	183	5.90	40
				3.88	0	345	183	5.90	35
			140	0.00	130	352	186	5.89	260
				0.65	111	347	188	5.90	95
				0.97	95	347	188	5.91	80
				1.30	73	346	187	5.91	70
				1.63	55	351	184	5.90	60
				1.96	43	347	186	5.90	55
	50	10.1 ± 1	70	0.00	203	686	205	8.30	318
				1.44	137	688	205	8.33	75
				2.15	81	689	204	8.32	63
				2.87	44	690	201	8.30	55
				3.60	15	687	201	8.30	45
				4.31	0	687	201	8.30	40
			140	0.00	208	690	202	8.32	318
				0.72	187	692	201	8.35	98
				1.07	166	694	203	8.36	85
				1.43	138	689	202	8.34	75
				1.80	111	689	202	8.34	67
				2.15	93	689	202	8.34	62

Table 5 (continued)

Scrubbing solution	Engine load (%)	Fuel consumption	G	L/G	SO_2 out	NO_x out	CO out	CO_2 out	T_G out
		(L/h)	(m^3/h)	(in weight)	(parts per million)			(% in volume)	(°C)
KSWOH	10	2.7 ± 1	70	0.00	63	176	486	3.71	180
				1.10	3	176	487	3.80	58
				1.66	0	178	488	3.80	45
				2.21	0	175	488	3.81	37
				2.76	0	176	486	3.80	34
				3.32	0	175	487	3.80	30
			140	0.00	62	175	492	3.74	180
				0.56	26	175	494	3.80	94
				0.84	6	173	493	3.81	82
				1.11	0	174	495	3.81	70
				1.39	0	173	493	3.81	61
				1.66	0	175	493	3.80	56
	25	5.5 ± 1	70	0.00	132	352	188	5.90	260
				1.30	50	348	184	5.91	70
				1.94	15	347	185	5.91	55
				2.59	0	346	182	5.90	45
				3.23	0	344	183	5.90	40
				3.88	0	345	183	5.90	35
			140	0.00	130	352	186	5.89	260
				0.65	100	347	188	5.90	95
				0.97	75	347	188	5.91	80
				1.30	53	346	187	5.91	70
				1.63	27	351	184	5.90	60
				1.95	15	347	186	5.90	55
	50	10.1 ± 1	70	0.00	208	692	204	8.35	318
				1.44	121	690	205	8.33	82
				2.17	50	689	204	8.32	66
				2.90	5	690	201	8.30	58
				3.61	0	690	201	8.30	46
				4.34	0	691	201	8.30	40
			140	0.00	206	695	202	8.37	318
				0.72	172	692	201	8.35	100
				1.08	146	694	203	8.36	92
				1.44	110	689	202	8.34	83
				1.80	80	689	202	8.34	71
				2.17	54	692	202	8.34	66

chemical analyses were performed on three washwater samples collected under the following conditions:

- SAMPLE 1:
  engine load = 10%; $G = 70$ m^3/h; $L = 60$ L/h;
- SAMPLE 2:
  engine load = 25%; $G = 70$ m^3/h; $L = 120$ L/h;
- SAMPLE 3:
  engine load = 50%; $G = 70$ m^3/h; $L = 150$ L/h.

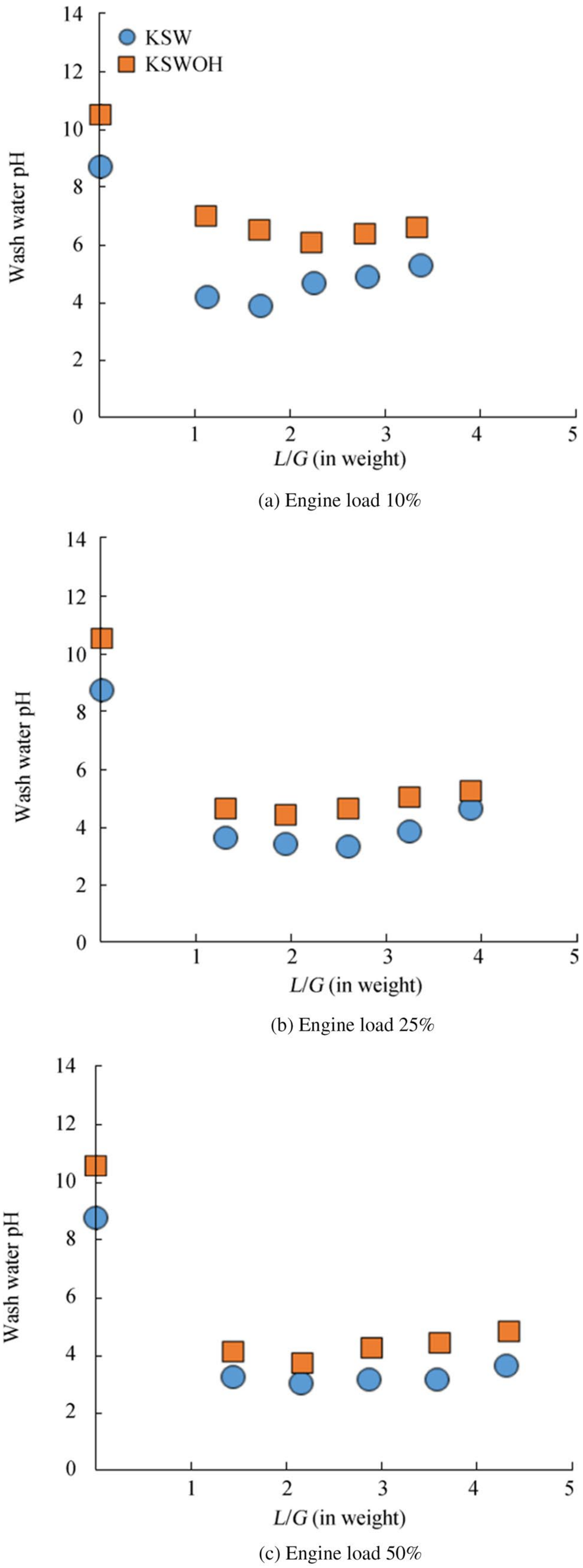
The experimental results are reported in Table 6 for heavy metals content and in Table 7 for organics content.

The concentrations of some metals such as Fe, Al, Co, Cu, Cr, Mn, Mo, Ni, Pb and Zn significantly increased in the washwater. Organics and PAH levels are mostly below the detection limits and only Aliphatics (C10-C12, C12-C16, C5-C16, C16-C35) and Aromatics C8-C10 were detected. Besides, experiments indicated an increase in the metals concentrations by increasing the engine load and liquid flow rate. In particular,

Figure 8 resumes the trends of the washwater concentration of those pollutants that had a most relevant increase, (more than 2 times the value of the parent seawater) as a function of the load engine. The experiments were presented as the ratio between the concentration of pollutant in the washwater sample and that of the parent seawater ($C_{\mathrm{SAMPLE}}/C_{\mathrm{KSW}}$) from Tables 6 and 7.

Figure 8 shows that Zinc, Copper and Aluminum concentration in the washwater increased with the engine load and up to a value between 5 and 10 times that of fresh KSW, while Iron, Cobalt, Manganese, Molybdenum and Lead increased up to 30–100 times. On contrary, a significant

Figure 4 Experimental results of washwater pH value from FGD ▶ pilot unit with 70 m^3/h of flue-gas stream as a function of the *L/G* and parametric with different engine load (10%, 25%, and 50%) and different scrubbing solutions at 20 °C (KSW and KSWOH. *L/G* = 0 indicates the pH value of seawater



(a) Engine load 10%

(b) Engine load 25%

(c) Engine load 50%

increase was observed for chromium which reached a maximum value of almost 4500 times than fresh KSW, while for nickel it reached 650 for the 50% load.

The only two organic species that were higher than KSW were Aliphatics > C16-C35, up to 10 times, and Aromatics > C8-C10, between 3 and 50 times.

Figure 9 compare the discharge concentrations of the heavy metals in the three washwater samples (Tables 6 and 7) with the regulations in Table 8.

- EU-EQS

  Maximum allowed Concentration (MAC) of the Europe Environmental Quality Standards, Directive 2013/39/EC, relating to water quality standards in the European Union (Kjølholt et al. 2012);
- DE-EQS

  Danish Environmental Quality Standards, relating to water quality standards in Denmark (Kjølholt et al. 2012);
- STR-EQS

  Stringent Environmental Quality Standards, relating to more stringent criteria for the inland waters and national territorial waters, established by the Danish Ministry of Environment (Kjølholt et al. 2012);
- EPA-NRWQC

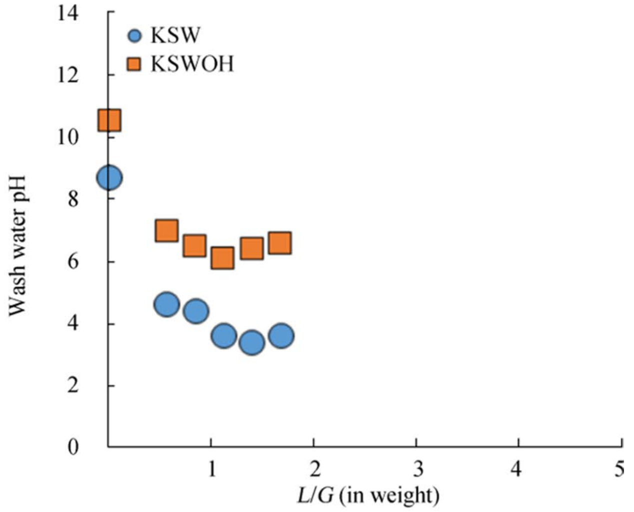
  EPA's National Recommended Water Quality Criteria for saltwater organisms (United States Environmental Protection Agency, 2011);
- IT-DL

  D.Lgs. 3rd April 2006, No. 152 Environmental Regulations (Italian Official Gazette No. 88 of 14th April 2006—suppl. ord. No. 96) (Italian Official Gazette n. 88 del 14 April 2006—suppl. ord. n. 96, 2006a, 2006b);
- GE-DL

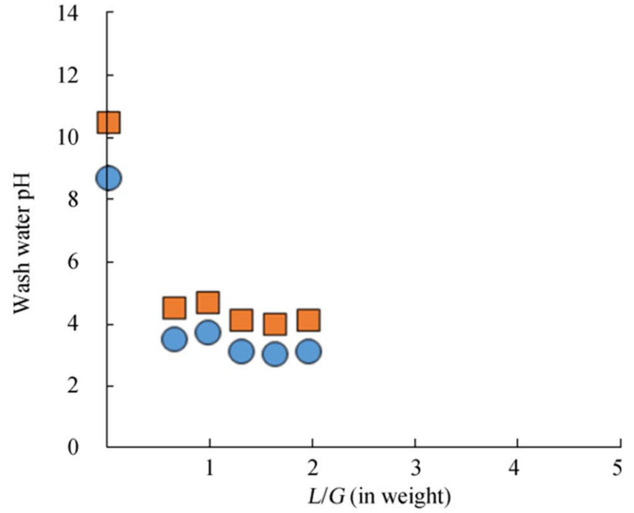
Federal Ministry for the Environment, Nature Conservation and Nuclear Safety, Germany (Promulgation of the New Version of the Ordinance on Requirements for the Discharge of Waste Water into Waters of 17th June 2004) (Federal Ministry for the Environment Nature Conservation and Nuclear Safety Germany 2004).

It is worth remembering that DL and EQS limits are very different. The DLs refers to the concentration of a pollutant at the discharge point, without any dilution, and is defined by the performances of the best available technologies that are commercialized at the time of introduction of regulation. The EQSs refer to the chemical quality of a natural

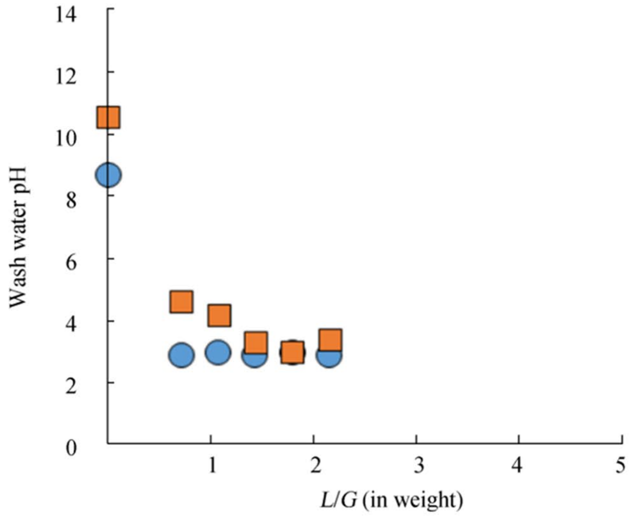
Figure 5 Experimental results of washwater pH value from FGD ▸ pilot unit with 140 m^3/h of flue-gas stream as a function of the L/G and parametric with different engine load (10%, 25%, and 50%) and different scrubbing solutions at 20 °C (KSW and KSWOH. $L/G=0$ indicates the pH value of seawater



(a) Engine load 10%



(b) Engine load 25%



(c) Engine load 50%

water body. Indeed, the actual concentration of a chemical in a water body depends both on the anthropogenic emissions and on the natural background and biological and chemical-physical transformations occurring in the same water body. Besides, this concentration strongly depends on the relevance of turbulence and water currents and their effect on the washwater dilution this is extremely important for sea areas.

Despite this, the EQSs have a repercussion on the discharge limit of nearby sources of wastewater emissions: when EQS is exceeded or is close to limit in a certain area, local authorities are entitled to introduce further reduction to the discharge limit of the emission sources affecting the quality of that area. Therefore, while scrubber washwater composition must be compared with the DL limits, their comparison with the EQS and the knowledge of washwater flow rate may be an index of how much the scrubber can contribute to the pollution of a certain sea area.

Figure 9 showed that most of the heavy metals, *e.g.* Cr, Cu, Ni, Pb and Zn, have quite high concentrations, and failed to comply with the EQS and NRWQC Regulations for water quality standards. Most organics and PAHs (from Table 7) are below the detection limit of the analytic instrument, only Benzene, Naphthalene and Phenanthrene in the first sample (SAMPLE 1) were detected. Their concentration is below the UE-EQS and EPA-NRWQC targets.

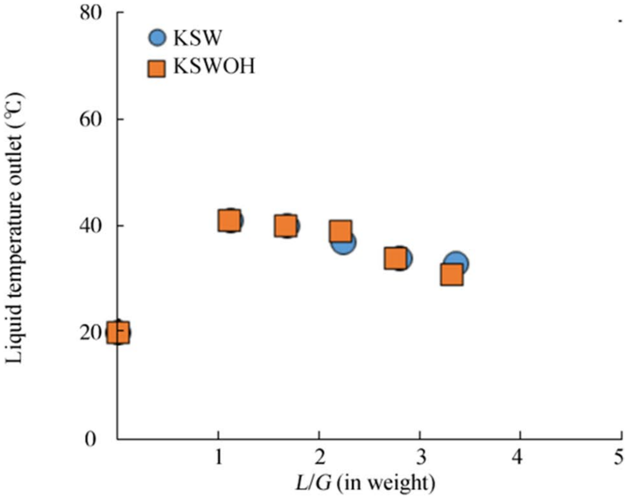
The comparison of metals concentration with the IT-DL and GE-DL Regulations, which refer directly to the discharge of washwater from industrial activities or scrubbers, showed that the limits are almost all verified: only Fe and Cr exceed the limits by almost 30%.

Starting from the analysis of fuel samples and their consumption during tests and assuming that all the metals in the fuel are transferred to the water, it is possible to calculate the fraction of heavy metals in the fuel that is transferred to the scrubber washwater as:

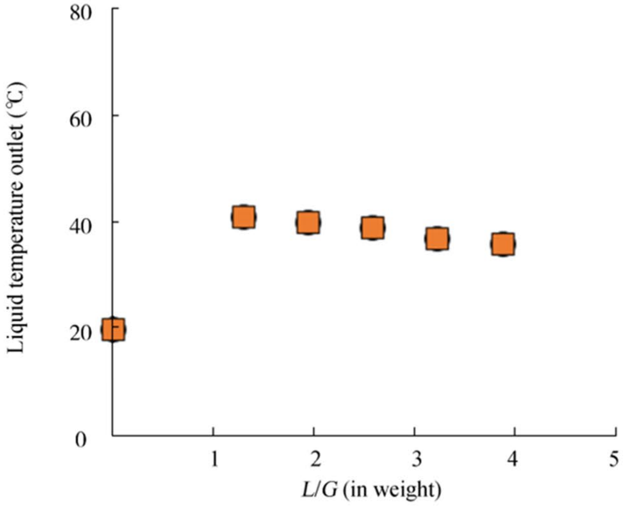
$$f = \frac{C}{\frac{\mathrm{FC}\cdot\rho_f\cdot C_M}{L}\cdot\frac{G}{G_{\mathrm{eng}}}} \tag{9}$$

where C is the difference between the concentration of a given heavy metal in the washwater (C_{SAMPLE}) and the baseline concentration of the same heavy metals in the raw Kattegat seawater (C_{KSW}). The denominator of Eq. (9) indicated the maximum concentration in the washwater deriving from the fuel: C_M (mg/kg) indicates the mass

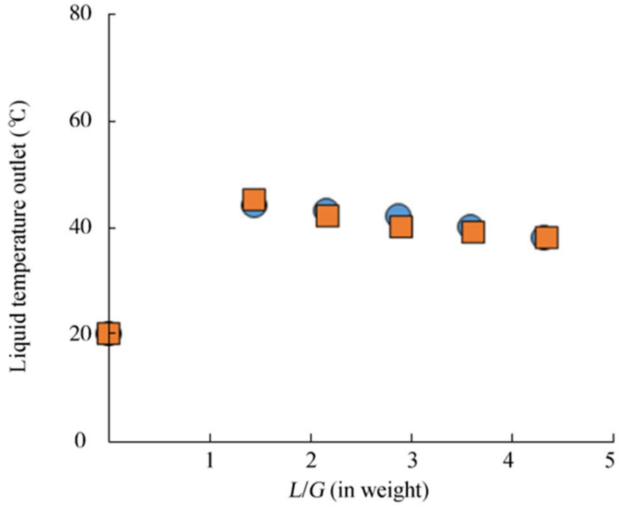
Figure 6 Experimental results of washwater temperatures from FGD pilot unit with 70 m^3/h of flue-gas stream as a function of the L/G and parametric with different engine load (10%, 25% and 50%) and different scrubbing solutions at 20 °C (KSW and KSWOH). $L/G = 0$ indicate the inlet temperature of seawater



(a) Engine load 10%



(b) Engine load 25%



(c) Engine load 50%

concentration of metals in the fuel, FC (L/h) is fuel consumption for each engine load (see Table 4), $\rho_F = 0.84$ kg/L is the MGO fuel density, L (L/h) is the seawater flow rate fed to the scrubber, G (m^3/h) is the flue-gas flow rate fed to the scrubber, G_{eng} (m^3/h) is the total exhaust gas flow rate produced by the engine (estimated as 144 Nm^3/h, on the bases of the engine speed and size). The effect of lubricating oil combustion in the exhaust gases is negligible for this kind of engine. The fractions f for different metals are reported in Table 9.

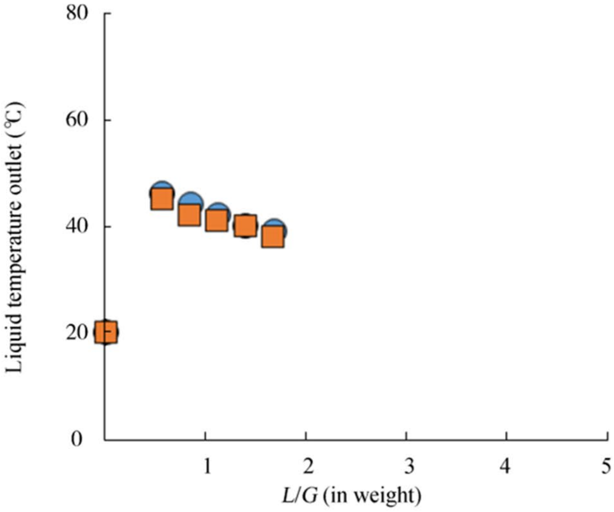
Table 9 demonstrates that, awkwardly, almost all the metals in the scrubber washwater do not derive from the fuel (corresponding to a ratio $f > 1$). As suggested by former works (Hufnagl et al. 2005), the authors envisage that the origin of these metals (Fe, Al, Cr, Cu, Mn, Co, Ni, Pb, Zn) can be related to the corrosion of scrubber and pipeline metals. This result makes the choice of the right material of material for FGD systems very important in order to keep emissions of these metals low. Manufacturers usually adopt nickel-based alloys, titanium, or non-metallic materials such as epoxy and composites to prevent or minimize corrosion.

4 Conclusions

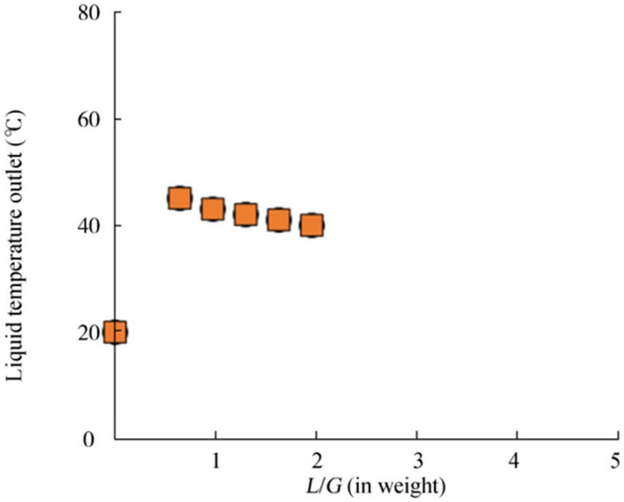
This work analyzes the potential reduction of the environmental footprint of ships achievable by the use of an MGO fuel in combination with a scrubber. The tests were carried out in a pilot spray FGD column used to clean the gases deriving from a marine Diesel engine (Volvo Penta 80 kW) operated at different loads with a 0.92% in weight of sulphur in the MGO. The tested scrubbing liquid was a sample Kattegat seawater, used either as is or doped with NaOH.

The rationale for this solution is in its capacity to simultaneously assure a strong reduction of both gas and water emissions. The better quality of the fuel allows reducing the overall emissions of PAHs and heavy metals, while the scrubber reduces sulphur emissions, keeping the concentration of these persistent pollutants well below current washwater limitations, with a limited impact over the environmental quality standard for seawater. Among the metal contaminants, only Fe and Cr exceed the allowed limits by about 30%. It should be noted that for the examined

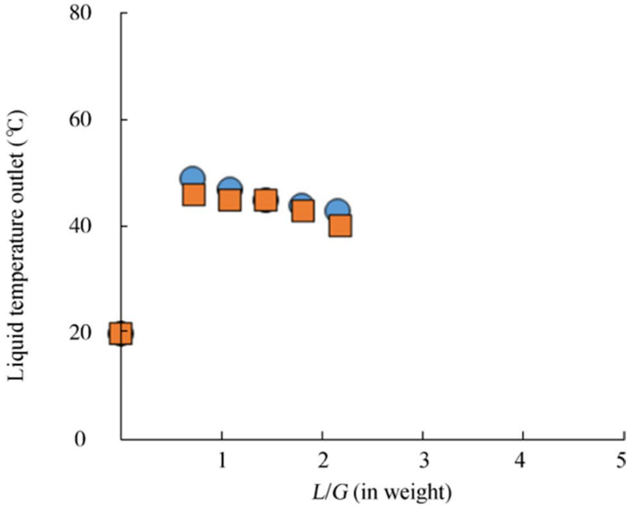
Figure 7 Experimental results of washwater temperatures from FGD ▶ pilot unit with 140 m^3/h of flue-gas stream as a function of the L/G and parametric with different engine load (10%, 25% and 50%) and different scrubbing solutions at 20 °C (KSW and KSWOH). $L/G = 0$ indicate the inlet temperature of seawater



(a) Engine load 10%



(b) Engine load 25%



(c) Engine load 50%

samples the seawater fed flow rate does not offer a significant driving effect on the dilution of the volatile organic and polycyclic aromatic contaminants which are often not detectable with analysis instruments, only Benzene, Naphthalene and Phenanthrene in the first sample were detected but compliant with water quality standards.

As the long-lasting experience of marine scrubbing clearly demonstrated, sulphur emissions control is not a problem, and the pilot-scale scrubber was able to easily cut the SO_2 emissions below the SECA and GLOBAL targets. The addition of 100 mg/L of NaOH in seawater determines a further and significant increase in desulphurization efficiencies, reaching the targets required in maritime transport with a water-saving up to 33% compared to the use of pure seawater.

Unfortunately, this process had scarce effects on other gas pollutants (NO_x, CO and CO_2) because their scarce solubility in water. The experiments also showed that PAHs emissions are within the available water quality standards indicated by the EU and the USA and that corrosion of metallic surfaces of the scrubber and the discharge pipelines is a major source of heavy metals in the scrubber washwater, overwhelming the actual contribution deriving from the transfer of fuel-derived metals to the scrubber effluents. Among the metal contaminants with the highest impact due to corrosion were Iron, Chromium, Nickel and Zinc. Such corrosion problems are probably a relevant contribution to scrubber washwater quality also for Intermediate Fuel Oil (IFO) fueled ships and should be considered also for conventional cooling systems onboard ships, which are commonly used to dilute scrubber effluents before discharge as secondary metals source.

It is worth noticing that a shift to distillate fuels was probably the original intention of the MARPOL VI regulation, but the cost and availability of distillates posed a limit in its use favoring the adoption of desulphurized residual fuels. However, these last kind of fuels do not reduce the actual emissions of other components as ashes or aromatic compounds, limiting the actual environmental benefit of fuel shift.

Indeed, while distillates are the preferred choice for this solution, a benefit can also come from the use of lighter residual marine fuels as RMA10 or RMB30, for which a massive reduction of ashes and carbon micro-residue can be achieved with respect to conventional RMG380/RMK380 fuels.

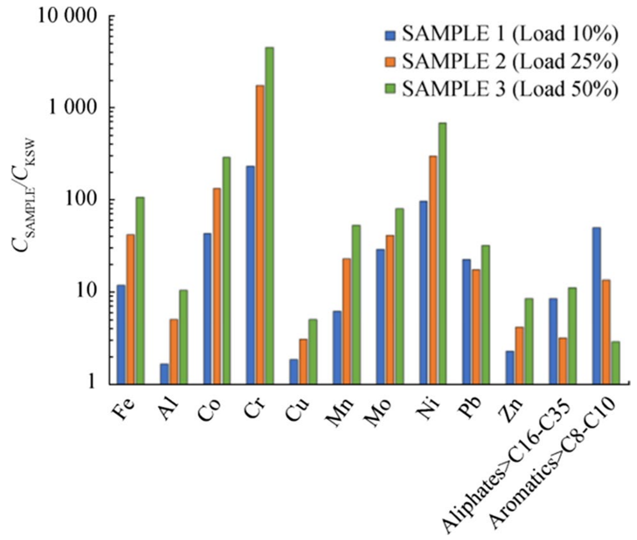


Figure 8 Comparison between the concentrations of the heavy metals and organic species that varied at least two times compared with the background values measured in Kattegat seawater in the SAMPLES 1, 2 and 3

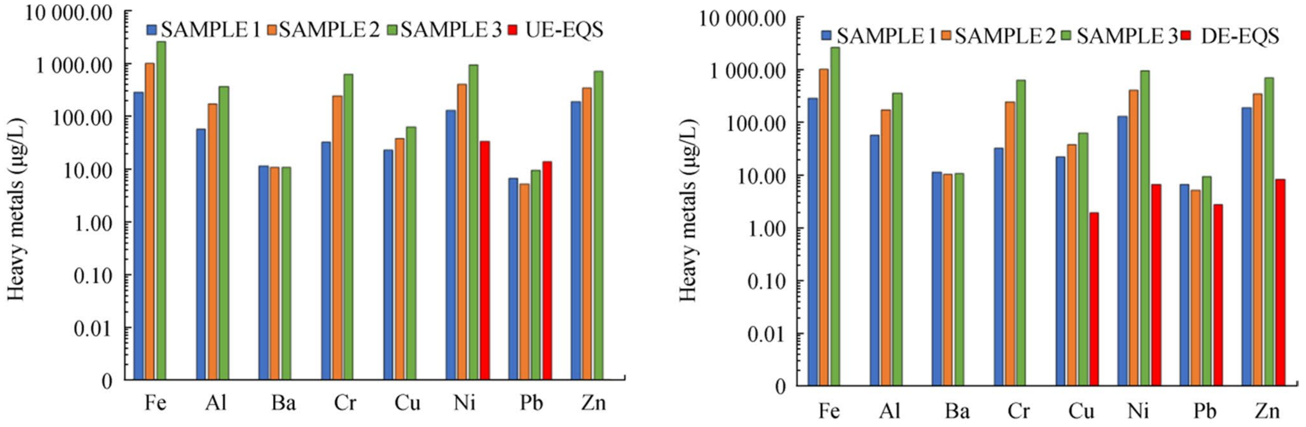
While the cost of the combined use of lighter fuels and scrubber after-treatment has to be carefully considered and is surely well above those currently adopted to comply with the sulphur limits requirements, it is worth noticing that the proposed solution is able to provide a superior reduction of both the atmospheric and the water emission of ships. Besides, it is worth noticing that both the technologies of

Table 6 Heavy metals concentration values in the KSW and for the three washwater samples

Heavy metals		KSW INLET	SAMPLE 1	SAMPLE 2	SAMPLE 3
Ca	mg/L	19.5	21.15	20.30	20.58
Fe	mg/L	0.0243	0.29	1.02	2.59
K	mg/L	<8	8.40	8.40	9.29
Mg	mg/L	<2	2.17	3.24	6.35
Na	mg/L	13,100	13,102	13,122	13,181
Si	mg/L	1.03	1.09	1.06	1.07
Al	μg/L	34.7	57.1	173.70	363.70
Ba	μg/L	10.2	11.4	10.68	10.70
Cd	μg/L	<0.05	<0.05	<0.05	<0.05
Co	μg/L	<0.05	2.16	6.65	14.45
Cr	μg/L	0.14	32.54	243.14	630.14
Cu	μg/L	12.4	22.8	38.30	62.80
Hg	ng/L	<2	<2	<2	<2
Mn	μg/L	2.85	17.6	64.85	150.85
Mo	μg/L	0.245	7.12	10.095	19.64
Ni	μg/L	1.38	132.38	409.38	947.38
Pb	μg/L	<0.3	6.77	5.25	9.47
Sr	μg/L	52.4	55.75	64.5	73.30
Zn	μg/L	83.1	190.10	347.10	707.10

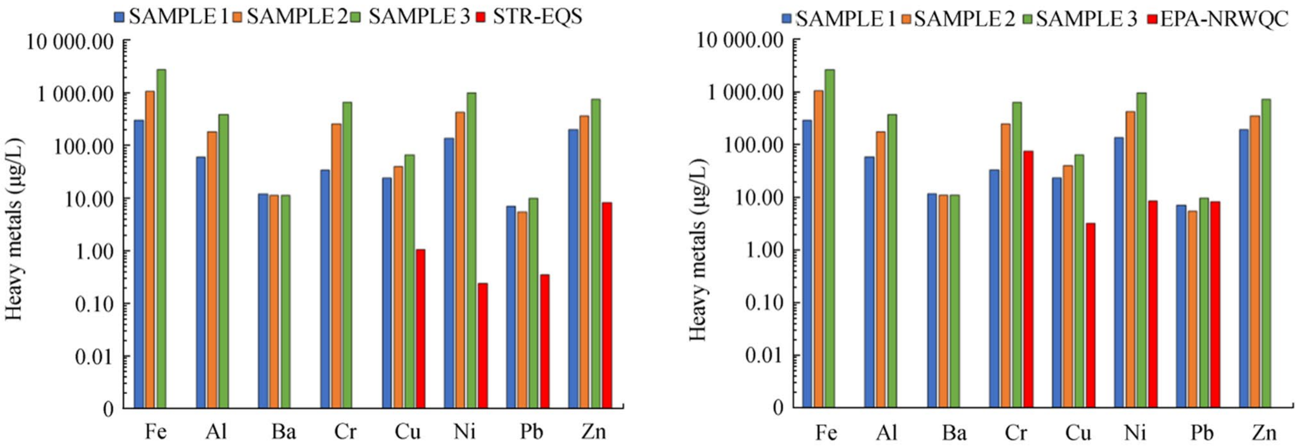
Table 7 Organics concentration values in the KSW and for the three washwater samples

Organics composition (μg/L)	KSW INLET	SAMPLE 1	SAMPLE 2	SAMPLE 3
Aliphatics > C5-C8	10	<10	<10	<10
Aliphatics > C8-C10	10	<10	<10	<10
Aliphatics > C10-C12	10	32	23	25
Aliphatics > C12-C16	10	36	21	26
Aliphatics > C5-C16	20	68	44	51
Aliphatics > C16-C35	10	75	125	102
Aromatics > C8-C10	0.30	14.5	1.64	<0.57
Aromatics > C10-C16	<0.775	<1.49	<1.49	<1.49
Metylpyrene/ metylfluorantene	<1.0	<1.0	<1.0	<1.0
Methylchrysene/ dimethylbenz(a) anthracene	<1.0	<1.0	<1.0	<1.0
Aromatics C16-C35	<1.0	<1.0	<1.0	<1.0
Benzene	<0.20	0.23	<0.20	<0.20
Toluene	<0.20	<0.20	<0.20	<0.20
Ethylbenzene	<0.20	<0.20	<0.20	<0.20
m-p-xylene	<0.20	<0.20	<0.20	<0.20
o-xylene	<0.20	<0.20	<0.20	<0.20
Xylenes, sum	<0.20	<0.20	<0.20	<0.20
Naphthalene	0.038	0.217	<0.048	<0.048
Acenaphthylene	<0.010	<0.048	<0.048	<0.048
Acenaphthene	<0.010	<0.048	<0.048	<0.048
Fluorene	<0.010	<0.048	<0.048	<0.048
Phenanthrene	0.037	0.135	<0.048	<0.048
Anthracene	<0.010	<0.048	<0.048	<0.048
Fluoranthene	<0.010	<0.048	<0.048	<0.048
Pyrene	<0.010	<0.048	<0.048	<0.048
Benzo(a)anthracene	<0.010	<0.048	<0.048	<0.048
Chrysene	<0.010	<0.048	<0.048	<0.048
Benzo(b)fluoranthene	<0.010	<0.048	<0.048	<0.048
Benzo(k)fluoranthene	<0.010	<0.048	<0.048	<0.048
Benzo(a)pyrene	<0.010	<0.048	<0.048	<0.048
Dibenz(a,h)anthracene	<0.010	<0.048	<0.048	<0.048
Benzo(g,h,i)perylene	<0.010	<0.048	<0.048	<0.048
Indeno(1,2,3-cd) pyrene	<0.010	<0.048	<0.048	<0.048
PAH, sum 16	0.075	0.355	<0.38	<0.38
PAH, sum carcinogens	<0.035	<0.17	<0.17	<0.17
PAH, sum others	0.075	0.355	<0.22	<0.22
PAH, sum L	0.038	0.218	<0.072	<0.072
PAH, sum M	0.037	0.135	<0.12	<0.12
PAH, sum H	<0.04	<0.19	<0.19	<0.19



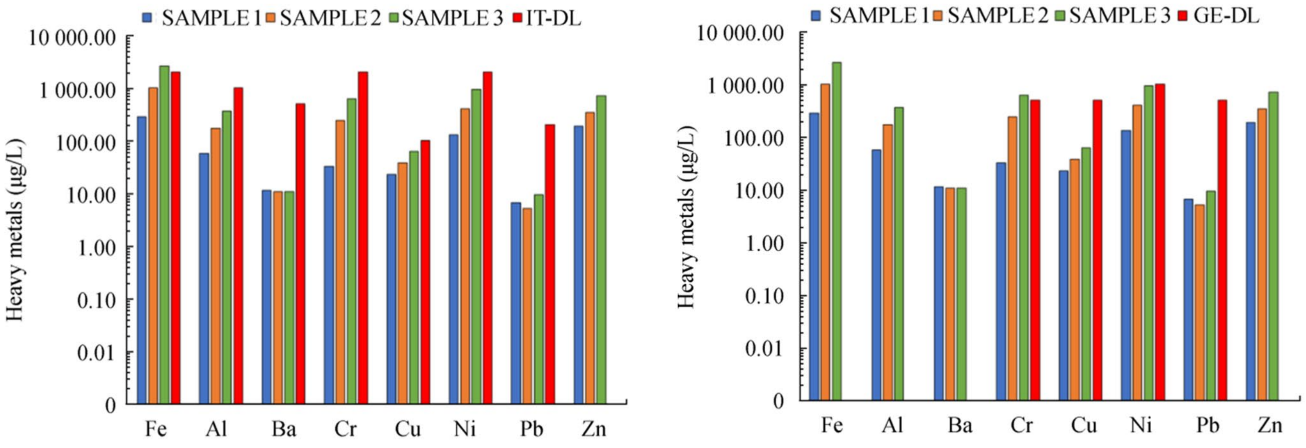
(a) EU-EQS

(b) DE-EQS



(c) STR-EQS

(d) EPA-NRWQC



(e) IT-DL

(f) GE-DL

Figure 9 Comparison between the concentrations of the heavy metals in the three washwater samples with the available regulations

Table 8 Discharge limits in the washwater of heavy metals, organics and PAHs according to some of the available EU and USA regulations and guidelines

			EU-EQS	DE-EQS	STR-EQS	EPA-NRWQC	IT-DL	GE-DL
Heavy metals	Lead	µg/L	14	2.8	0.34	8.1	200	500
	Mercury	µg/L	0.07	0.07	0.05	N/A	5	50
	Nickel	µg/L	34	6.8	0.23	8.2	2000	1000
	Copper	µg/L	N/A	2	1	3.1	100	500
	Vanadium	µg/L	N/A	57.8	4.1	N/A	N/A	N/A
	Zinc	µg/L	N/A	8.4	7.8	N/A	N/A	N/A
	Arsenic	µg/L	N/A	1.1	0.11	36	N/A	N/A
	Chromium	µg/L	N/A	N/A	N/A	74	2000	500
	Selenium	µg/L	N/A	N/A	N/A	71	N/A	N/A
	Cadmium	µg/L	0.45	1.5	0.2	N/A	20	100
	Iron	µg/L	N/A	N/A	N/A	N/A	2000	N/A
	Alluminium	µg/L	N/A	N/A	N/A	N/A	1000	N/A
	Barium	µg/L	N/A	N/A	N/A	N/A	500	N/A
Organics and PAHs	Benz[*a*]anthracene	ng/L	N/A	N/A	N/A	18	N/A	N/A
	Benzo[*a*]pyrene	ng/L	27	N/A	N/A	18	N/A	N/A
	Benzo[*b/k*]fluoranthene	ng/L	0.17	N/A	N/A	18	N/A	N/A
	Chrysene	ng/L	N/A	N/A	N/A	18	N/A	N/A
	Dibenz[*a,h*]anthracene	ng/L	N/A	N/A	N/A	18	N/A	N/A
	Fluorene	mg/L	N/A	N/A	N/A	5.3	N/A	N/A
	Indeno[1,2,3-*cd*]pyrene	ng/L	N/A	N/A	N/A	18	N/A	N/A
	Phenanthrene	µg/L	N/A	N/A	N/A	N/A	N/A	N/A
	Pyrene	mg/L	N/A	N/A	N/A	4	N/A	N/A
	Benzene	µg/L	50	N/A	N/A	N/A	N/A	N/A
	Naphthalene	µg/L	130	N/A	N/A	N/A	N/A	N/A
	Anthracene	µg/L	0.1	N/A	N/A	N/A	N/A	N/A
	Fluoranthene	µg/L	0.12	N/A	N/A	N/A	N/A	N/A
	Benzo(*g,h,i*)perylene	ng/L	8.2	N/A	N/A	N/A	N/A	N/A

engine tuning and modifications required for fuel switching from residual to distillate fuels and for scrubber installation and management are now mature and their implementation in a combined solution is not expected to pose unexpected problems or complexities.

In light of these considerations, the Authors believe that the proposed solution of a combined use of lighter fuels and scrubber after-treatment earns a chance to be considered as a valid option for reducing the environmental footprint of new and existing ships.

Table 9 Ratio between net metal addition found in washwater samples (total concentration in scrubber washwater minus the background value deriving from raw KSW) and maximum possible metal content deriving from the fuel (*f*)

Heavy metals		SAMPLE 1	SAMPLE 2	SAMPLE 3
Fe	Iron	237	1026	2003
Si	Silicon	53	31	31
Al	Aluminum	6	41	73
Ba	Barium	1	0.5	0.4
Cr	Chromium	29	250	492
Cu	Copper	9	27	39
Mo	Molybdenum	6	10	15
Ni	Nickel	117	420	739
Pb	Lead	6	5	7
Zn	Zinc	95	272	487

Abbreviations ASTM: American Society for Testing and Materials; DE-EQS: Danish Environmental Quality Standards; EPA: Environmental Protection Agency; EPA-NRWQ: EPA's National Recommended Water Quality Criteria for saltwater organisms; EU-EQS: Europe Environmental Quality Standards; FGD: Flue-Gas Desulphurization; GE-DL: German D.Lgs on discharge of waste water into waters; HFO: Heavy Fuel Oil; IFO: Intermediate Fuel Oil; IMO: International Maritime Organization; ISO: Organization for Standardization; IT-DL: Italian D.Lgs on Environmental Regulations; KSW: Kattegat seawater; KSWOH: Kattegat seawater with NaOH addition; MAC: Maximum allowed concentration; MEPC: Marine Environment Protection Committee; MGO: Marine Gas Oil; PAH: Polycyclic Aromatic Hydrocarbon; PPR: Pollution Prevention & Response Sub-Committee; SECA: Sulphur Emission Control Area; STR-EQS: Stringent Environmental Quality Standards; TSS: Total suspended solids

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