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Comparing emissions of polyaromatic hydrocarbons and metals from marine fuels and scrubbers

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ABSTRACT

In January 2020, new global regulations were implemented to limit the maximum sulphur content in marine fuels. As an alternative to switch to compliant fuels, the regulations allow for installations of exhaust gas cleaning systems, e.g. scrubbers, that enables a continued use of less expensive heavy fuel oils (HFOs). Characterization of scrubber discharge water shows that the acidified water also becomes enriched with contaminants, and large quantities of metals and polyaromatic hydrocarbons (PAHs) are thus being discharged directly to the marine environment. When emissions of contaminants to the atmosphere and the marine environment are evaluated simultaneously, the results show that HFO, with scrubbers installed, generates higher emission factors of both metals and PAHs compared to MGO. This highlights the importance of including both the marine and the atmospheric perspective when comparing environmental loads and impact of contaminants from shipping.

1. Introduction

Shipping is a major emission source of carbon dioxide (CO_2), sulphur oxides (SO_X), nitrogen oxides (NO_X) and particulate matter (PM) to the atmosphere (Eyring et al., 2010; Ausmeel et al., 2020). These emissions deteriorate air quality, impact global climate and have adverse effects on ecosystems and human health (Corbett and Winebrake, 2008; Hassellöv et al., 2013; Corbin et al., 2018; Zhao et al., 2019). As of January 2020, stricter global regulations apply with the main target to reduce the negative impacts of ship-derived SO_X and PM on air quality and the International Maritime Organization (IMO) has now reduced the global maximum sulphur (S) content in marine fuels from 3.5% to 0.5% m/m S (IMO Annex VI of MARPOL 73/78, Regulations for the Prevention of Air Pollution from Ships Reg. 14). In sulphur emission control areas (SECAs), a maximum of 0.1% m/m S in marine fuels has been the limit since 2015 (IMO, 2020). To comply with the new regulations, shipowners are required to switch to compliant fuels, of lower sulphur content, or to install an exhaust gas cleaning system (EGCS), commonly known as a scrubber, that will allow for continued use of cheaper high sulphur heavy fuel oils (HFOs). Scrubbers are developed to reduce SO_X emissions; the exhausts are led through a fine spray of water where SO_X readily dissolve and as a result, the water then becomes acidified (Karle and Turner, 2007). Other contaminants (e.g. polyaromatic hydrocarbons (PAHs) and metals) are also washed out during the scrubbing process, turning the scrubber discharge water into a toxic cocktail (Tao et al., 2013; Turner et al., 2017).

Based on forecasts made by the International Energy Agency (IEA, 2019), there will be a shift in the market following the new

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regulations and by 2024, which is the final year of the IEA forecast, three marine bunker products are predicted to dominate: HFO with the use of a scrubber (22%), marine gas oil (MGO) (40%) and very low sulphur fuel oils (VLSFOs) (37%), also called hybrid fuels, which is an emerging type of fuel blends primarily consisting of residual oil. Since data describing hybrid fuels, such as VLSFO and ultra-low sulphur fuel oils (ULSFO), is scarce, this study will be limited to the comparison of HFO combustion with two other compliance alternatives: MGO-use (including marine diesel oil, MDO) and HFO-use with scrubber installations.

Emissions and impact from scrubbers are and have been debated within the scientific and the decision-making communities, yet, this is the first study that simultaneously addresses emissions to the atmosphere and the marine environment, adding an important perspective to the ongoing discussion. The research presented has resulted in a database of emission factors (EFs) of metals and PAHs from conventional combustion, using HFO or MGO, and from HFO combustion when scrubbers are used. The characterization of the scrubber discharge water and the calculated EFs are based on all data available to the research team as of December 2020 and can be used and extended in future studies on the environmental impact from scrubbers. As the atmospheric and marine environmental compartments are interconnected, taking a holistic approach is paramount when determining how a switch from HFO to low sulphur fuels or an installation of scrubbers, with continuous use of HFO, will affect the environmental load derived from shipping operations. The aim of this study is to compare the previously dominating combustion of HFO, with two available alternative strategies to meet the new global sulphur cap. EFs of metals and PAHs from the combustion of different marine fuels are compared to the EFs derived from the use of open and closed loop scrubbers. Based on the produced EFs, contaminant-specific loads to the marine environment and to the atmosphere are estimated and compared with respect to different fuel-use and exhaust gas cleaning scenarios.

2. Emissions from marine bunker fuels and scrubbers

Since the mid-1900s, residual fuels, i.e. HFO, has dominated the marine fuel market (Corbett and Fischbeck, 1997) and during the last ten years the global bunker fuel demand has increased by approximately 2.5% annually (IEA, 2019). HFOs are high viscosity rest products from the refinery process, during which metals, ash and sulphur are enriched (Jang and Choi, 2016; Uhler et al., 2016). When using HFO, a large part of the emitted SO_2 is converted to sulphate through atmospheric oxidation, contributing to the PM which is the main pollutant causing adverse health effects. SO_2 conversion to sulphate is also causing acidification of marine and land ecosystems (Hassellöv et al., 2013; Turner et al., 2017). In addition, particles consisting mainly of soot, ash, organic carbon and metals are also emitted directly from the ship stacks (Agrawal et al., 2008a; Moldanová et al., 2009). The new regulations, limiting the sulphur content in the fuel and thus limiting the use of HFO, have created a momentum where new techniques (e.g. scrubbers) and compliant fuels are being developed. The different types of compliant fuels all have a sulphur content of $\leq 0.5\%$ m/m S, in accordance to the new global regulations but there are other major differences in the fuels' chemical composition, e.g. due to how they are produced. Marine distillates belong to the middle-class distillate fraction (Czech et al., 2017) and can be used exclusively (named MGO) or blended with traces of residual oils (named MDO) (Lehtoranta et al., 2019).

Due to the difference in fuel characteristics, the use of HFO and MGO will result in different EFs of sulphur as well as contaminants such as PAHs and heavy metals. While exhaust from shipping are traditionally analysed with respect to CO_2, CO, SO_X, NO_X and PM (e.g. Corbett and Fischbeck, 1997; Jalkanen et al., 2014; Claremar et al., 2017), scrubber discharge water has rather been assessed with emphasis on contaminants such as heavy metals and PAHs (e.g. CESA, 2018; Teuchies et al., 2020; Schmolke et al., 2020). Despite the apparent focus of other pollutants, HFO and MGO combustion, when a scrubber is not in operation, result in emission of metals and PAHs to the air.

The PAHs emitted to the atmosphere are transported within the marine boundary layer (MBL) while undergoing transformation processes that changes the properties prior to their dry and wet deposition (Eyring et al., 2010) (Fig. 1). The atmospheric processes are partly determined by the phase distribution, where low molecular weight (LMW) PAHs are found in gas phase, while high molecular weight (HMW) PAHs are sorbed to particles such as soot (adsorbed) and organic matter (absorbed) (Arey and Atkinson, 2003; Keyte et al., 2013; Ke et al., 2017). A major atmospheric sink is photochemical degradation, primarily initiated by hydroxyl radical (·OH)

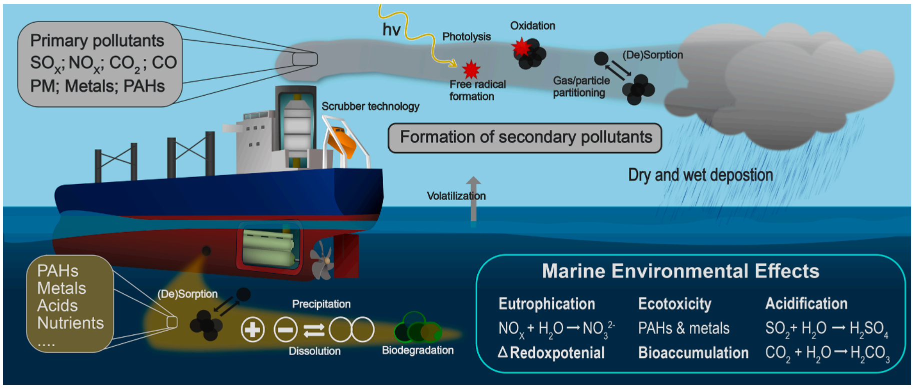

Fig. 1. An overview of pollutants found in exhaust and scrubber discharge water and some potential reaction pathways, transportation and effects on the marine environment.

reactions but it can also be initiated by other oxidants such as NO_3 and O_3 (Atkinson and Arey, 1994; Atkinson and Arey, 2007; Keyte et al., 2013). Atmospheric reactions of PAHs often result in more polar derivatives (Atkinson and Arey, 1994; Arey and Atkinson, 2003), affecting the environmental fate of the parent PAH and its congeners as well as the toxicity (Arey and Atkinson, 2003). The scrubbers potentially introduce a new mode-of-entry for HFO combustion products, where the atmospheric processes are bypassed, and the contaminants are being discharged directly to the water column (Fig. 1). Once in the marine environment, LMW PAHs can be degraded by microorganisms while HMW PAHs are removed through sedimentation, the concentrations of PAHs in the water column are therefore generally low (Burgess et al., 2003). As PAHs and their derivatives are toxic to marine organisms, some being mutagenic and carcinogenic (Achten and Andersson, 2015; Zhao et al., 2019; Honda and Suzuki, 2020) and metals can cause adverse effects (Morales et al., 2016), changing the primary recipient of pollutants, from air to water, will also alter the environmental impact.

A scrubber can be operated in two different modes: open and closed loop mode respectively. The most common system, with an estimated 80% of the scrubber market (DNV-GL, 2021), offers only open loop operation, where large volumes of seawater are continuously pumped in, used as wash water and then discharged, without any additional cleaning step. A medium sized (12 MW) vessel is typically running 13 000 m^3 seawater per day through the scrubber system (Ytreberg et al., 2019). The scrubber wash water is often directly discharged to the sea resulting in a transfer of atmospheric pollutants to the marine environment. The seawater generally has a high buffer capacity, i.e. alkalinity, which is needed to neutralize the acidic discharge, but little is known regarding other implications when bypassing the atmospheric pathway. In a closed loop system, installed by less than 2% of the scrubber fleet (DNV-GL, 2021), internal process water is circulated and reused under the addition of base, usually sodium hydroxide (NaOH). The closed loop system includes cleaning steps where contaminants are collected as sludge that is later disposed in port reception facilities. The discharge water volumes from the closed loop system, also called bleed-off, are smaller, in the range of 100 m^3 wash water per day on a similar medium sized vessel mentioned previously. Approximately 17% of the scrubber fleet have been equipped with hybrid scrubbers that can shift between operation in either open or closed loop mode (DNV-GL, 2021).

PAHs and heavy metals are examples of contaminants found in the scrubber discharge water as they, to some degree, are being scavenged by the scrubber spray (Turner et al., 2017). The emissions of some contaminants, such as SO_X and the transition metals vanadium (V) and nickel (Ni), are related to the parent fuel content while others, such as NO_X, are primarily formed during the combustion process (Moldanová et al., 2011). Emissions of PAHs can be attributed to both the fuel content and the combustion processes (Su et al., 2019; Zhao et al., 2020). Many of the contaminants are not captured entirely by the scrubber but are still emitted in the smokestack. There is no consensus regarding the efficiency of scrubbers in collecting contaminants, other than SO_X. Most researchers agree that PM mass is reduced significantly over the scrubber (Fridell and Salo, 2016; Winnes et al., 2020) but new results indicate that the particle number concentration is unaffected (Lehtoranta et al., 2019), suggesting that the submicron particles are not collected by the scrubber and are emitted with the exhaust (Zhou et al., 2017). The exact chemical composition of these particles is often not known but previous studies show that PM originating from HFO have higher toxicity potential, e.g. oxidative stress, compared to PM from distillate fuels (Streibel et al., 2017; Wu et al., 2018). In case of a ship equipped with a scrubber, it can be challenging to determine where in the scrubber process the enrichment of contaminations occur. This is especially true for metals as there are several potential sources within the ship domain. Anti-fouling paint used in the sea chest or the use of sacrificial anodes can result in elevated levels of zinc (Zn) and copper (Cu) in the water that feeds the scrubber (Kjølholt et al., 2012; Koski et al., 2017). When the ship operates in open loop mode, the volume of water transported from the sea chest and through the piping system of the ship will increase substantially, potentially resulting in increased leakage of metals. More importantly, enrichment of metals in the scrubber discharge water can be attributed to the construction of the engine and/or operation of the scrubber, where leakage of metals occur from piping, wearing of the engine and excess corrosion and abrasion due to the acidic and reactive nature of the scrubber water (Aragon et al., 2009; Kim and Jeong, 2019). Fuel additives, claiming to reduce fuel consumption and emissions and to supress soot formation, can contain both metals and organic compounds that could partly explain some of the discrepancies and variations (Jang and Choi, 2016; Ntziachristos et al., 2016). Lubrication oil has also been identified as a source of both metals and organic compounds emitted during combustion (Eichler et al., 2017; Winnes et al., 2020). To summarize, although the relative importance of the specific sources is not fully understood, the use of scrubbers may imply new sources of metals, resulting in an increased load of metals to the environment.

Several PAHs (e.g. benzo[*a*]pyrene (BaP), benzo[*ghi*]perylene (BghiP)) and metals (e.g. nickel (Ni), lead (Pb)) found in scrubber discharge water are listed as priority substances under the European Union Water Framework Directive (WFD) (Directive 2000/60/EC) and under regional conventions such as the Helsinki convention (HELCOM) and the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR). There are several countries and ports (e.g. in Germany and Belgium) that have already introduced restrictions regarding the use of scrubbers, banning discharge of scrubber water in certain areas (Nepia, 2021), and the International Council for the Exploration of the Sea (ICES) has also highlighted the risk for the marine environment following wide-scale discharge of scrubber water (Hassellöv et al., 2020; ICES, 2020). Previous ecotoxicological studies on marine organisms show that exposure to scrubber discharge water result in adverse effects, and that the mixture itself is more toxic than what could be predicted evaluating the toxicity of each individual compound (Koski et al., 2017; Magnusson et al., 2018). Despite the rapid increase of scrubber installations, when shipowners of more than 4500 vessels today have opted on installing scrubbers (DNV-GL, 2021), there is a lack of studies where emissions to the marine environment and atmosphere are studied and evaluated simultaneously.

3. Material and methods

An extensive literature study was conducted (all references listed in Table A.1-A.2 of Appendix A) to collect and compile EFs of the 16 US EPA priority PAHs (described in Keith, 2015), metals and other elements from ships running on either HFO (>0.5% m/m S), with and without scrubbers, or MGO/MDO (≤0.5% m/m S) (Fig. 2). The EFs to the air and to the sea were subsequently used to compare the loads of contaminants to the environment depending on fuel type and mode of operation of the scrubber. Data of the chemical characterization of scrubber discharge water, the characterization of fuels and the EFs to the atmosphere and marine environment were collected from peer-reviewed literature and reports published between 2004 and 2020 (in Table A.1-A.2 of Appendix A).

3.1. Scrubber discharge water characterisation

The dataset (Appendix B) includes measurements of scrubber inlet water and discharge water from a total of 41 vessels equipped with scrubbers, operated in closed or open loop mode on the main and/or auxiliary engine. Every sample in the dataset corresponds to a measuring point, implying that one vessel can sometimes be represented more than one time but that the sampling occurred at different occasions. For every measuring point, discharge water concentrations of 10 metals and 16 PAHs (Table 2) were extracted from the literature source together with the pH of the same water and the sulphur content of the fuel.

The average concentrations of the contaminants (Table 2) were calculated from all available measuring points. Values below limit of detection (LOD) were included as ½ LOD, and the variation was expressed with the 95% confidence interval (CI). A weighted approach was used to calculate the average sulphur content of the fuel, where a default fuel consumption of 180 kg/MWh (Section 3.2) and the ship-specific engine load were taken into account. First, the fraction (%) of sulphur in the fuel was expressed as kg S/kg fuel and the hourly consumption (kg S/h) could be estimated by multiplying with the default fuel consumption (kg/MWh) and the ship-specific engine load (MW) before summarising for all vessels. Similarly, the hourly fuel consumption for all vessels were calculated by multiplying the ship-specific engine load with the default fuel consumption before summarising. Finally, the weighted average was calculated by dividing the summarised hourly consumption of sulphur with the summarised hourly consumption of fuel. The difference between inlet and outlet water, for specific ships running in open loop mode, were calculated for the pH and the metal and PAH concentrations (Table A.3 of Appendix A) using a two-tailed *t*-test assuming unequal variances. The significance in all statistical test was defined by the $p < 0.05$ level and the analyses were carried out using Microsoft Excel. The inlet water corresponds to water that was sampled from the scrubber system, prior to the scrubbing process i.e. before the water reached the exhaust from the combustion engine.

3.2. Determination of EFs

The EFs measured and calculated for low engine loads (<30% of the maximum continuous rate (MCR)) were excluded as previous studies have shown a higher variation in atmospheric emissions at low engine loads as compared to higher loads ≥ 50% (Jalkanen et al., 2012; Teinilä et al., 2018; Zhao et al., 2020). To limit the variability, the EFs at engine loads in cruising mode, i.e. above 50% of MCR, were chosen for further analysis.

The EFs to the marine environment (mg/MWh) were calculated for those vessels where the discharge water flow (m^3/MWh), or enough information so that the discharge water flow could be calculated, was provided.

$$EF_{Water}\left(\frac{mg}{MWh}\right) = c\left(\frac{mg}{m^3}\right) \times Q\left(\frac{m^3}{MWh}\right) \tag{1}$$

The calculated EFs are based on the ships' unique discharge flow rates (Q), at the time of sampling, and the contaminant concentration (c) in that specific discharge water. This reduced the number of samples but increased the accuracy for each vessel and allowed for a better comparison with the atmospheric EFs.

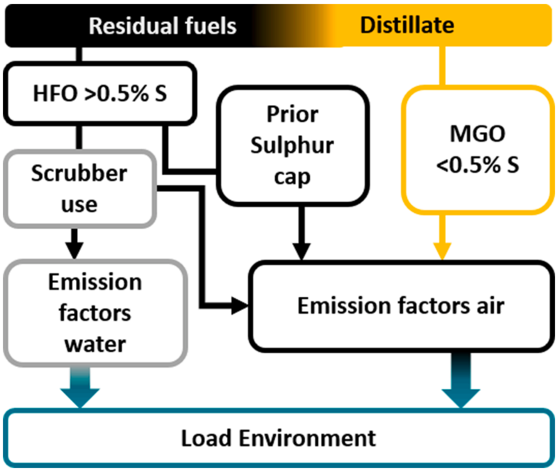

Fig. 2. Flow scheme of the setup of the study with the comparison of heavy fuel oil (HFO) with/without scrubber, where both open and closed loop operation modes will be investigated, and marine gas/diesel oil (MGO/MDO).

For the atmospheric emissions, most studies present EFs as fuel/mass-based (g/kg burned fuel). To be comparable with the EFs calculated from scrubber discharge water, the mass-based EFs was converted into power-based EFs (mg/MWh) (Eq. (2)).

$$EF_{Air,Power}\left(\frac{mg}{MWh}\right) = EF_{Mass}\left(\frac{mg}{kgfuel}\right) \times SFOC\left(\frac{kgfuel}{MWh}\right) \tag{2}$$

where $EF_{Air,Power}$ is the power-based EF, EF_{Mass} is the mass-based EF and SFOC is the specific fuel oil consumption of the ship. When SFOC was not given, a default fuel consumption of 180 kg/MWh was assumed, based on previous studies (Moldanová et al., 2009; Zetterdahl et al., 2016; Teinilä et al., 2018; Winnes et al., 2018). The compound specific EFs were compared for ships operating at the same engine load conditions (Figs. 4–7). When PAHs had only been sampled and measured as part of the particulate fraction, the 8 lighter PAHs (LMW PAHs in Table 2) were not included when calculating the EFs as these compounds are primarily found in gas phase (Moldanová et al., 2011; Fridell and Salo, 2016). The remaining 8 PAHs (HMW PAHs in Table 2) were considered to be primarily associated to particles. The median of the EFs for metals and PAHs (Table A.4) were further used when calculating the relative load to the environment (Figs. 8–9). All calculations and construction of the box and whisker plots for illustration were conducted using MATLAB (MATLAB R2020a, Mathworks Inc.)

3.3. *Comparison of environmental load based on scenarios*

Since there is a lack of measurements of metals and PAHs in the exhaust downstream the scrubber process, the total emission factors of these species for ships using HFO and scrubber (exhaust plus effluent) cannot be properly calculated. As the EFs resulting from scrubbers (Figs. 4–7) are only based on direct discharges to the sea, they are most likely underestimated. To account for this when assessing the total load of contaminants from open and closed loop scrubbers in the different scenarios, it was assumed that the power-based EFs for the combustion of HFO (originating from in-stack measurements on HFO-burning ships without or upstream the scrubber) remained constant, but that the receiving environment changed from atmosphere to sea. The estimated atmospheric EFs downstream a scrubber was calculated by subtracting the median EFs for open loop discharge water from the median EFs for the same compounds from HFO combustion without a scrubber. For closed loop scrubbers, being equipped with a sludge collector, the contaminants that were not accounted for in exhaust or discharge water were assumed to be collected in the sludge with no impact on the environmental load. When estimating the atmospheric emissions in conjunction with open loop scrubber-use (Table A.5 of Appendix A), if the EFs for HFO combustion were larger than the EFs for the discharges to the sea, the difference was assumed to be emitted to the atmosphere. If the opposite was true, it was assumed that the scrubber scavenged the compound completely, i.e. no emission of that compound to the atmosphere, and no additional emission was included in the calculations of the relative load (Table A.5 of Appendix A). For the scenarios, based on the calculations of atmospheric emissions downstream a scrubber, it was assumed that the scrubber scavenged almost all metal compounds (except Ni Table A.5 of Appendix A). This is also supported by Celo et al. (2015), showing that most elements in exhaust PM have a solubility of > 85%. In contrast, some studies show that metals are associated to soot particles (Moldanová et al., 2009; Moldanová et al., 2013; Corbin et al., 2018) that are not scavenged by the scrubber, which suggests that some metals might still be released to the atmosphere (Lack and Corbett, 2012; Lieke et al., 2013).

Statistics and forecasts from the Oil report (IEA, 2019), regarding marine bunker fuel demand (million barrels per day (mb/d)), were used to design the different fuel consumption scenarios (Table 1).

The 1st scenario (Pre-2020 scenario) corresponds to the market prior to the 2020 sulphur cap where ships were primarily using HFO or MGO without any abatement measures. In this scenario, HFO represents 80% of the bunker fuel demand and MGO covers the remaining 20%. The Open- and Closed loop scenarios reflect the post-2020 sulphur cap situation with the introduction of scrubbers, where a large fraction of HFO-users changes to MGO and where some of the HFO users will install scrubbers. In this scenario, MGO corresponds to 77% of the total bunker fuel demand while continued HFO-use with scrubbers correspond to 22% of the total fuel demand. The remaining 1% is assumed to be non-compliant, i.e. continue to use HFO without any abatement methods.

The mode of operation of the scrubber will affect the environmental load and for the Open loop scenario it is assumed that all vessels equipped with a hybrid scrubber will operate in open loop mode. In the Closed loop scenario, open loop scrubbers are removed from the market and all scrubbers are thus operating in closed loop mode.

Finally, in the MGO/MDO scenario (MGO scenario from here on), all the scrubber-users switch to compliant fuels leaving MGO/MDO to dominate the total marine bunker fuel demand. In this scenario, it is still assumed that 1% of the fuel demand will be covered by non-compliant HFO use. For comparison, the Pre-2020 scenario was used as baseline and all scenarios were normalised with respect to the baseline and presented as relative load to the environment (Figs. 8–9). All calculations and construction of the bar charts for illustration were conducted using MATLAB (MATLAB R2020a, Mathworks Inc.)

4. Results and discussion

The average fuel content of inorganic elements was higher in HFO as compared to MGO (Fig. 3). For HFO, V is the most abundant metal, followed by phosphorous (P), Ni, sodium (Na) and iron (Fe) (Fig. 3), which is in line with other studies, (e.g. Moldanová et al., 2013; Celo et al., 2015; Streibel et al., 2017; Corbin et al., 2018)). Ni and V concentrations of the fuel increase with increasing sulphur content (Moldanová et al., 2011; Moldanová et al., 2012; Celo et al., 2015; Streibel et al., 2017) and is significantly higher in HFO compared to MGO/MDO (Moldanová et al., 2011; Moldanová et al., 2012; Streibel et al., 2017). Since V and Ni are rarely present in distillate fuels (Corbin et al., 2018), these metals can be used as tracers of HFO combustion (Tao et al., 2013; Streibel et al., 2017).

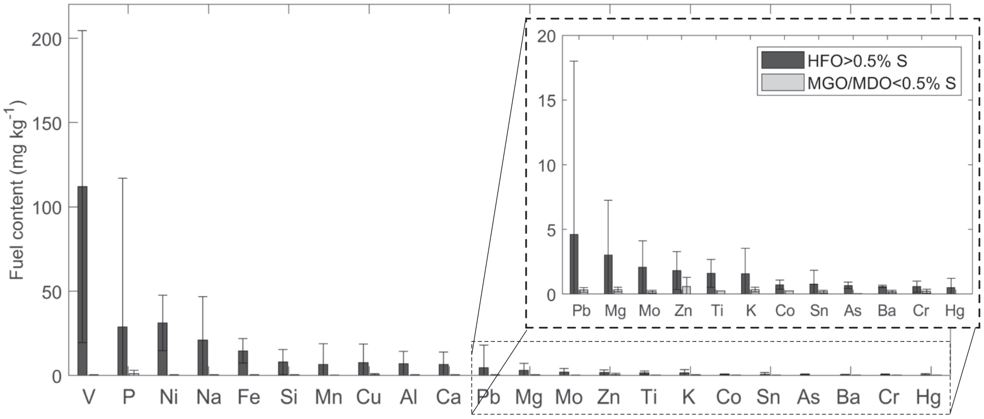

Fig. 3. Comparison of average metal and element content between HFO (>0.5% m/m S) and MGO/MDO (<0.5% m/m S) with error bars showing the standard deviation. References are listed in Table A.2 and raw data in Appendix B.

4.1. *Characterization of scrubber discharge water*

A total of 92 samples were available in the open loop water discharge dataset, out of which 53 included discharge flow rates at an average of 91 ± 13 m^3/MWh (Appendix B). 31 of these were operating at engine loads ≥ 50% of MCR and was further used for the EF calculations, the average discharge flow rate of this selection was 68 ± 9 m^3/MWh. For closed loop mode, 9 out of a total of 25 samples reported discharge flow rates with an average of 0.42 ± 0.2 m^3/MWh. Only 6 operated at engine loads ≥ 50% of MCR with an average discharge flow rate of 0.35 ± 0.3 m^3/MWh and were further used for the EF calculations. All discharge flow rate averages, irrespective of the engine load range, are higher than those that have previously been provided by the IMO and that are used as the default discharge flow rates (45 m^3/MWh for open loop operations and 0.25 m^3/MWh for closed loop operations (IMO, 2008)). It is paramount to use accurate discharge rates when predicting the environmental load associated to scrubber use and, as shown here, assuming discharge rates according to the IMO standard will underestimate the EFs.

The sulphur content of the HFOs used during open loop scrubber operations ranged between 0.7 and 3.2% m/m S with a weighted average of 2.2% m/m S (n = 46). The weighted average sulphur content was slightly lower for closed loop vessels at 1.8% m/m S (n = 13) but with an equal range (0.7–3.2% m/m S). The average pH of the open loop scrubber discharge water was 3.9 ± 0.2 (n = 36). This can be compared to the average pH of the inlet water of 7.7 ± 0.2 (n = 29) and closed loop discharge water that had an average pH of 4.5 ± 0.5 (n = 11) despite the addition of base (Appendix B). There was a significant difference ($p < .001$) between inlet water pH and the outlet water pH of the same ship (Table A.3 of Appendix A). The average difference between inlet and outlet water pH was 2.05, meaning that on average, the outlet water was $10^{2.05}$ (=110) times more acidic than the inlet water (Table A.3 of Appendix A).

Listed in Table 2 are the average concentrations, with 95% CI, of 10 metals and 16 PAHs found in open and closed loop scrubber discharge water. In addition, Table 2 includes the average concentrations of the inlet water of the open loop system and of pristine seawater for comparison. Pristine seawater is here referred to as typical open ocean surface water concentrations, expected to be found in unpolluted areas (Law et al., 1997; Bruland and Lohan, 2003). The PAHs listed in Table 2 are ordered based on their molecular weight, with the LMW PAHs at the beginning and HMW PAHs further down in the table. The LMW PAHs are found in highest concentrations with naphthalene (Nap) and phenanthrene (Phe) as the dominating species in both open and closed loop discharge water. Most of the PAH measurements conducted on inlet water were below LOD (within brackets Table 2) and the PAH concentrations of the inlet water presented in Table 2 is rather a representation of the average of the ½ LODs for these measurements.

There was a significant difference between inlet and outlet water concentrations of V, Ni ($p < .001$) and all but four of the 16 PAHs (Table A.3 of Appendix A). Ni and V are known indicators of HFO combustion and are clearly accumulated in the scrubber discharge water. None of the other metals showed a significant difference between open loop inlet and outlet water, this can partly be attributed to the large variability in the dataset and also highlight the difficulties when tracing the contaminants of scrubber discharge water. There are several potential sources (e.g. marine growth protection systems and corrosion in the pipes and engine) related to shipping that could explain the elevated levels of metals in the inlet water (see Introduction). Despite the large variability, most compounds are enriched in the scrubber discharge water from both open and closed loop operations and the contaminants can thus be associated to the scrubber process and system. As the closed loop system does not have an intake of seawater, the accumulated contaminants found in the bleed-off water (Table 2) are strictly related to the combustion and scrubber system. The extension of piping systems, the addition of the scrubber itself and the increased flow of hot and acidic water through the system all contribute to the elevated levels of contaminants in the scrubber discharge water. As this study focus on the total environmental load derived from the use of scrubbers, inlet concentrations are not subtracted from the open loop discharge concentrations before the EFs are calculated. The concentrations found in pristine seawater (Table 2) are at least one order of magnitude lower hence the seawater used in the scrubber is not making any significant contributions to the calculated loads.

4.2. Emission factors

The power-based EFs (mg/MWh) (Figs. 4–7) can be used to compare the environmental loads originating from the same ship, using different types of fuel or abatement methods. In general, the EFs show that a ship running on HFO will emit more contaminants per power output than vessels running on MGO. This is best illustrated for V, Ni and Fe (Fig. 4), that are common constituents of HFO, where the EFs of V and Ni are on average 175 and 150 times higher and the EF of Fe are almost 20 times higher when using HFO as compared to MGO/MDO.

The EFs for V and Ni from HFO combustion (as exhaust and as scrubber discharge water) overlaps, suggesting that these emissions to a large degree are transferred from the exhaust to the water (Fig. 4). For V and Ni, it is thus not likely that other onboard sources (e.g. anti-fouling and sacrificial anodes) are contributing to the EFs which can be seen e.g. for Cu and Zn, where the EFs calculated from the open loop scrubber discharge water are 4 (Zn) to 30 (Cu) times higher than the EFs for HFO combustion (Fig. 4). The results support that V and Ni can act as tracers of HFO combustion in water, with the use of a scrubber, as well as in air, during non-compliance.

The trend of higher concentrations of metals in HFOs (Fig. 3) propagates to the specific EFs, confirming that combustion of HFO will

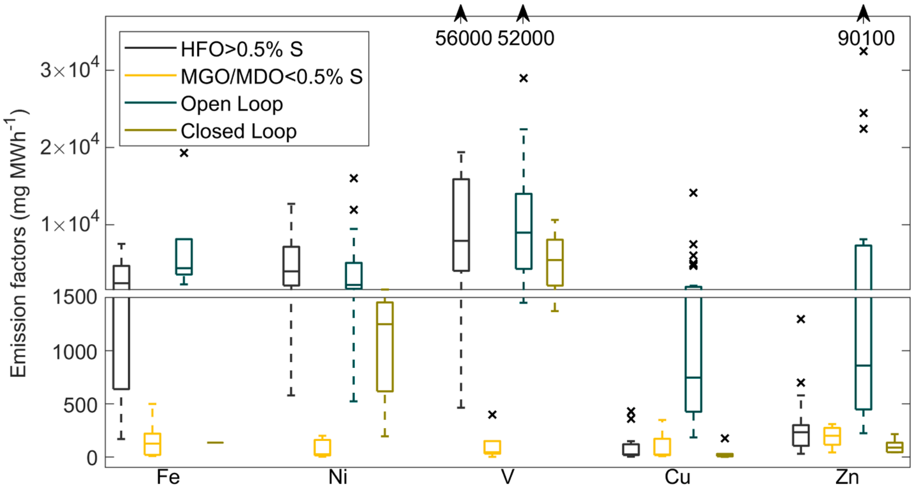

Fig. 4. Emission factors (EFs) of a selection of metals where HFO and MGO/MDO represent EFs to the atmosphere while open and closed loop represent EFs to water. Fe, Ni and V represent typical metals associated with HFO combustion while Cu and Zn are associated with other sources connected to shipping such as anti-fouling. The box represents the 25th (bottom) and 75th (top) percentile with the mid-line being the median. The whiskers show the range of min and max values and the outliers are marked as crosses (if not visible within the range of the plot they are marked with an arrow and the corresponding value of the outlier). The scale of the Y-axis is altered with lower range: −100–1500 mg/MWh and upper range: 1500–37000 mg/MWh.

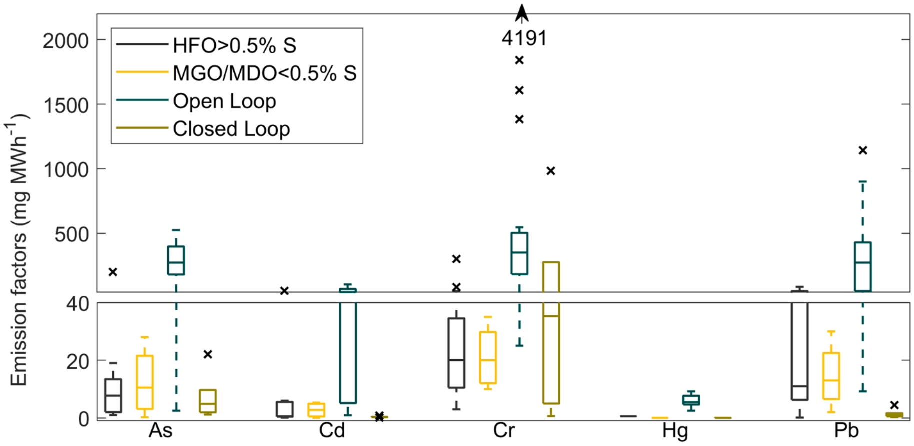

Fig. 5. Emission factors (EFs) of a selection of metals where HFO and MGO/MDO represent EFs to the atmosphere while open and closed loop represent EFs to water. The box represents the 25th (bottom) and 75th (top) percentile with the mid-line being the median. The whiskers show the range of min and max values and the outliers are marked as crosses (if not visible within the range of the plot they are marked with an arrow and the corresponding value of the outlier). The scale of the Y-axis is altered with lower range: 0–50 mg/MWh and upper range: 55–2200 mg/MWh.

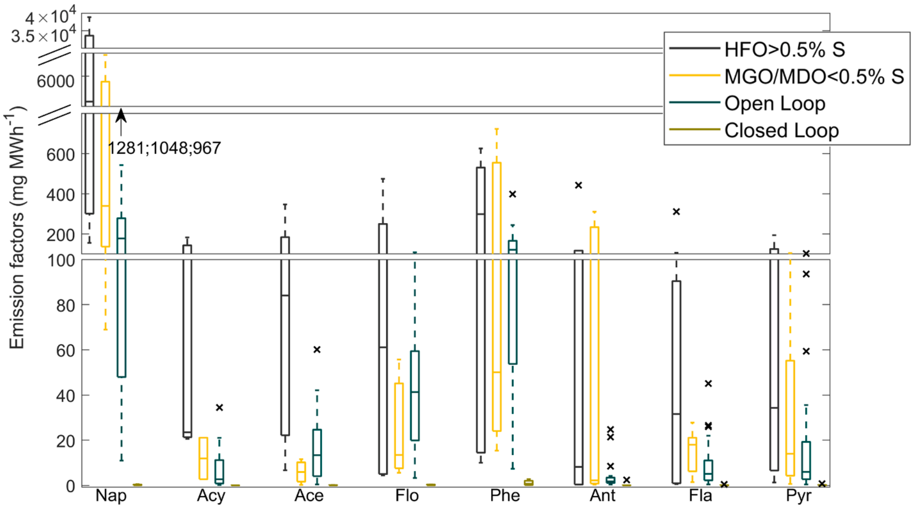

Fig. 6. Emission factors (EFs) of LMW PAHs where HFO and MGO/MDO represent EFs to the atmosphere while open and closed loop represent EFs to the water. The PAHs are listed in the order of molecular mass with the lowest molecular weight to the left. The box represents the 25th (bottom) and 75th (top) percentile with the mid-line being the median. The whiskers show the range of min and max values and the outliers are marked as crosses (if not visible within the range of the plot they are marked with an arrow and the corresponding value of the outlier). The scale of the Y-axis have been altered where the lower panel ranges from 0 to 100 mg/MWh, the second panel from 100 to 800 mg/MWh, the third panel from 400 to 7400 mg/MWh and the top panel 30000–40000 mg/MWh.

generate a larger metal load to the environment compared to MGO combustion. Like Zn and Cu, the EFs for As, Cd, Cr, Fe, and Pb are higher in the open loop scrubber discharge compared to EFs for the same compounds from HFO combustion (Fig. 5). The elevated EFs for Fe, being twice as high in open loop discharge water, and Cr, being almost 20 times higher in the scrubber discharge water, could be an indication of increased corrosion. This is also supported by previous studies (Aragon et al., 2009; Kim and Jeong, 2019) showing that seawater and sulphuric acid mixtures creates corrosive conditions and that piping of the scrubber system are especially prone to damage by corrosion. Since Cr is used in stainless-steel constructions (Aragon et al., 2009), often part of the scrubber system, the use of scrubbers would thus introduce a new contamination source of Cr to the marine environment with unknown effects. The EFs of Cd and Pb, both listed as priority substances in the WFD, are 75 and 25 times higher, when using an open loop scrubber as compared to HFO and MGO combustion (Fig. 5).

For PAHs (Figs. 6–7), the EFs are always higher for HFO combustion, varying from 2 (fluoranthene (Fla), acenaphthylene (Acy) and pyrene (Pyr)) to 20 times higher (chrysene (Chr)) compared to EFs for MGO/MDO combustion. Similar results are found by others (e.g. Agrawal et al., 2008b; Moldanová et al., 2011) and Zhao et al. (2019) showed that the EFs of PAHs decrease with > 80% changing from HFO to MDO. The sum of the EFs for the 16 PAHs is 10 times higher from HFO combustion compared to MGO combustion. Also, the EFs of acenaphthene (Ace), Phe and fluorene (Flo) to water, from the use of HFO and open loop scrubbers, are 2 to 3 times higher than the

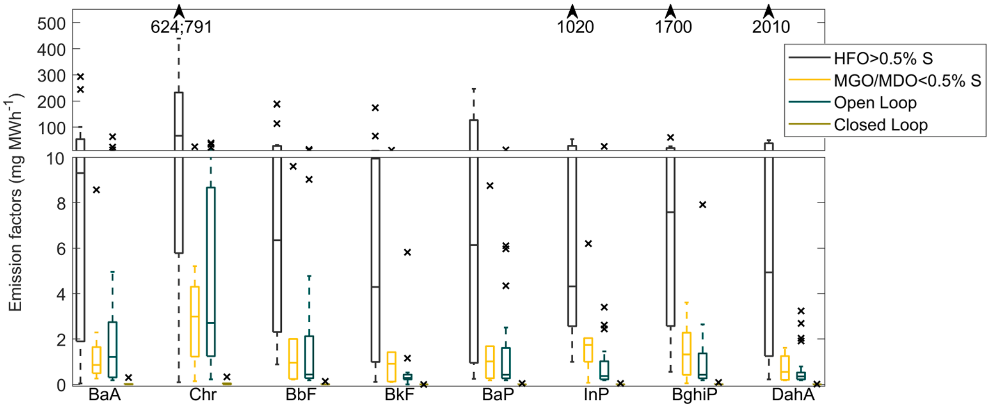

Fig. 7. Emission factors (EFs) of HMW PAHs where HFO and MGO/MDO represent EFs to the atmosphere while open and closed loop represent EFs to the water. The PAHs are listed in the order of molecular mass with the lowest molecular weight to the left. The box represents the 25th (bottom) and 75th (top) percentile with the mid-line being the median. The whiskers show the range of min and max values and the outliers are marked as crosses (if not visible within the range of the plot they are marked with an arrow and the corresponding value of the outlier). The scale of the Y-axis has been altered where the lower panel ranges from 0 to 10 mg/MWh and the top panel from 10 to 550 mg/MWh.

EFs of the same PAHs from the use of MGO/MDO, further supporting the statement that HFO combustion result in higher PAH emissions. The open loop system generates 100 (Fla) to almost 800 (Nap) times higher EFs to the water than the closed loop system (Figs. 6–7), even though the concentrations in the closed loop discharge water are higher (Table 2).

Nap and Phe have the largest contribution to the total emission of the 16 PAHs, in accordance with previous studies (Moldanová et al., 2011; Uhler et al., 2016), with the relative contribution of Nap EFs being on average 80% and the Phe EFs approximately 10% of the sum of the 16 PAHs EFs from combustion. Nap and Phe are also the most soluble PAHs which could also explain the elevated levels in open loop scrubber discharge water where Phe constitute 30% and Nap 50% of the sum of the emitted 16 PAHs. Flo and Phe appears to be most efficiently scavenged by the scrubber system (Fig. 6) with 30% and 60% remaining in the exhaust after combustion of HFO while > 80% remains for the other PAH species (Table A.5 of Appendix A).

The particle associated PAHs (Fig. 7) are emitted to a greater extent during HFO combustion. Summarising the EFs of the five PAHs grouped according to the WFD (BaP, benzo[*k*]fluoranthene (BkF), benzo[*b*]fluoranthene (BbF), indeno[*1,2,3-cd*]pyrene (InP), BghiP; Annex 1 DIRECTIVE 2008/105/EC), results show that HFO combustion (29 mg/MWh) generates almost 5 times higher emissions compared to MGO/MDO combustion (6 mg/MWh). For a medium sized vessel operating during 50% of the year, that difference corresponds to 1.8 kg of highly toxic PAHs entering the environment.

4.3. Scenario-based environmental load and fate of metals and PAHs

The total environmental load, with respect to most metals and all PAHs, is significantly higher in the Pre-2020 scenario compared to the MGO scenario (Figs. 8–9). For metals, the relative load from the Closed loop scenario and the MGO scenario are at similar levels while the Open loop scenario, which currently is the one preferred by the industry, will result in an increased environmental load for As, Cd, Cr, Cu, Hg and Pb (Fig. 8). This can be deduced from the high EFs connected to open loop scrubber-use in combination with the fact that the EFs of these metals from HFO and MGO/MDO combustion do not deviate significantly from each other (Figs. 4–5). The exceptions are V, Ni and Fe where all scenarios will result in a decrease compared to the Pre-2020 sulphur cap scenario. The decrease is however attributed to the increased use of MGO/MDO, from 20% to 77%, rather than the introduction of scrubbers.

The relative environmental load of all 16 PAHs will decrease moving away from an HFO-dominated market, also in comparison to the inclusion of scrubbers (Fig. 9). The effects of introducing scrubbers is difficult to evaluate, as it is known that the scrubber is not removing all the organic compounds from the exhaust and there are only a few studies that present exhaust concentrations, before and after the scrubber, on vessels operating in open and closed loop mode, respectively. In a study of the closed loop mode, it was concluded that the sum of the concentrations of the 16 US EPA PAHs decreased by 45% over the scrubber (Winnes et al., 2018; Winnes et al., 2020). In the same study, black carbon (BC) and organic carbon (OC), that could be used as proxies for HMW PAHs, were not reduced over the scrubber while elemental carbon (EC) was reduced by 30%. As EC and BC are both measures of soot content of the exhaust and both these analytical techniques are associated with substantial uncertainties, 30% difference might not be enough to suggest a significant decrease over the closed loop scrubber system (Aakko-Saksa et al., 2018). According to a study by Fridell and Salo (2016), the removal efficiency of many of the PAHs is greater with an open loop compared to a closed loop scrubber. In the exhaust after the scrubber, many of the LMW and HMW PAHs decrease by > 80%, the measurement uncertainty was however rather high ranging from 20 to 40%. When comparing the median EFs (HFO and open loop discharge) of this study (Table A.5 of Appendix A), results show that for all PAHs, except Phe and Flo, >80% of the PAHs will remain in the exhaust and are not collected by the scrubber, in contradiction with the results of Fridell and Salo (2016).

Using scrubbers results in a larger environmental load of PAHs compared to using MGO. The EFs of PAHs from closed loop scrubbers are several hundred times lower than from open loop scrubbers, one reason being the circular system where the sludge is collected. However, since a large fraction of the PAHs are still emitted to the atmosphere, assuming the same exhaust concentration irrespective of the operational mode of the scrubber, the bars in Fig. 9 look similar. The difference in relative load between the two scrubber scenarios can be interpreted as the fraction that is being collected by the closed loop sludge. In the Open loop scrubber scenario, the ships equipped with scrubbers corresponds to 22% of the bunker fuel demand of the entire fleet but contribute significantly to the total environmental load for most metals and PAHs and is responsible for > 80% of the environmental load of metals (Zn > 50%) and > 40% of the environmental load of most of the PAHs (Fig. A.1 of Appendix A). The relative environmental impact from scrubbers would decrease if the scrubber fleet changed to closed loop systems (Fig. A.2 of Appendix A). If the market would instead shift towards distilled fuels, both PAH and metal emissions would decrease.

In the calculations of the environmental load, it is assumed that the emitted compounds remain unchanged. In reality, once emitted to the atmosphere, there are several processes and reactions that will alter the properties and characterization of the parent compounds (Fig. 1). In the atmosphere, LMW PAHs are prevailingly in the gas phase and more likely to be removed through chemical reactions with radicals while HMW PAHs are associated with particle phase and are more prone to deposition (Atkinson and Arey, 1994). From the compilation of the EFs presented here (Fig. 6 and Table A.4-A.5), it can be assumed that approximately 40% of the Phe emissions will enter the marine environment in its parent form when a scrubber is used. For the atmospheric mode-of-entry, Phe are primarily present in the gas phase and will be subject to chemical transformation and degradation before deposition. The atmospheric lifetime of Phe is only a few hours (Atkinson and Arey, 2007; de Bruyn et al., 2012). Assuming that most of the atmospheric gaseous PAHs are transformed and degraded before deposition, the marine environment will thus receive a much larger load of for example Phe with the introduction of scrubbers. The same is true for other LMW PAHs (e.g. Nap) and even though most Nap (>95%) continues to be emitted as exhaust, the 5% that is scavenged by the scrubber and released as discharge water, constitutes a significant fraction (180 mg/MWh) of PAHs that will be emitted directly to the water.

Some of the semi-volatile compounds (e.g. Pyr, Ant and Fla) will partition between the phases while the 5–6 ringed PAHs (e.g. BaP,

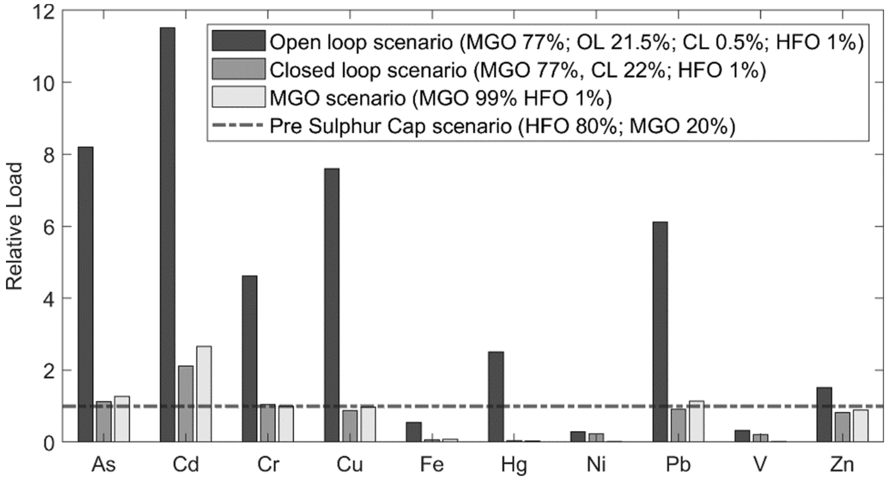

Fig. 8. The environmental load of metals from the different scenarios presented in table 1 relative to the Pre-2020 sulphur cap scenario (relative load = 1 (dashed line)).

BghiP and InP) are almost entirely found in the particle phase (Birgül et al., 2011; Friedman and Selin, 2012; EMEP, 2020). For particle-associated PAHs, heterogeneous reactions in the atmosphere are an important loss process before deposition. However, research show evidence of a fraction of PAHs unavailable for these reactions due to shielding by the particles (Atkinson and Arey, 1994; Lohmann and Lammel, 2004), turning PAHs into persistent compounds in the air with the potential of long-range transportation to pristine areas (Arey and Atkinson, 2003; Burgess et al., 2003; Lohmann and Lammel, 2004; Zimmermann et al., 2013). Similarly, shielding can prevent photochemical oxidation and biodegradation in the water column, making sedimentation the primary fate for these compounds (Burgess et al., 2003; Manzetti, 2013). In a study by Fridell and Salo (2016); BC, EC and OC, which all are associated with HMW PAHs, decreased by > 70% over the open loop scrubber which can be considered significant. Other studies report a BC removal from the exhaust by 25–70% by open loop scrubber systems (Lack and Corbett, 2012). BC can attain hygroscopic properties (Lack and Corbett, 2012), and the ions of the seawater could enhance this, making the scavenging of BC more efficient in open loop scrubbers. Increased hygroscopic properties are usually observed after aging of the particles (Lack et al., 2009) and Lieke et al. (2013) found that, after the scrubber, microscale soot particles were significantly altered, becoming smaller and denser, similar to ageing. The water in the scrubber also contributed to hygroscopic growth of these particles within minutes, compared to hours under normal atmospheric conditions. The overall marine environmental load for the particle-associated compounds might not change considerably with the change in mode-of-entry of the emissions but the dispersion and dilution will most likely change, from being more wide spread, with the conventional combustion, to becoming more local when using scrubbers. It is also worth noting that far from all particles that are emitted to the air will be deposited on the ocean surface.

In this study, focus is directed towards metals and the US EPA 16 PAHs. For future research, other harmful substances, known to be

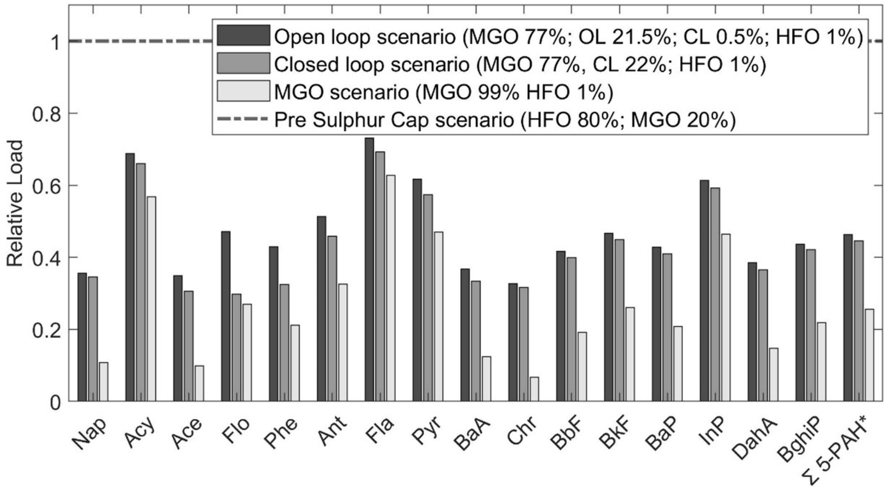

Fig. 9. The environmental load of PAHs from the different scenarios presented in table 1 relative to the Pre-2020 sulphur cap scenario (relative load = 1 (dashed line)).*The Σ 5-PAHs compares the relative load of the 5 PAHs grouped in the WFD (BaP, BkF, BbF, InP and BghiP).

Table 1
Scenarios, inspired by the forecasts of IEA, showing percentage of the world fleet running of different fuels with and without scrubber. OL = Open loop. CL = Closed loop.

	Pre-2020 scenario	Open loop scenario	Closed loop scenario	MGO/MDO scenario
HFO	80%	1%	1%	1%
MGO	20%	77%	77%	99%
HFO + Scrubber	–	22% (OL:99%; CL:1%)	(OL:0%; CL:100%)	–

present in ship emissions, should also be included such as dibenzothiophenes, related to the sulphur content of the fuel with known adverse estrogenic effects (Streibel et al., 2017); formaldehyde and acetaldehyde, that showcase toxic properties and represent a large fraction of the carbonyl compounds emitted from shipping (Reda et al., 2014) and monoaromatic compounds (e.g. benzene) being carcinogenic with the potential of forming phenolic compounds (Arey and Atkinson, 2003; Streibel et al., 2017). Also of importance are the degradation products of both gaseous and particulate PAHs that can be ring-retained products, e.g. nitro-PAHs (N-PAHs) as well as opened structures of phthalic acids, phthalaldehyde and phthalic anhydride (Arey and Atkinson, 2003; Keyte et al., 2013). Oxidized PAHs, e.g. O-PAHs and N-PAHs, are generally more mutagenic and carcinogenic compared to its parent, unoxidized form (Atkinson and Arey, 1994; Arey and Atkinson, 2003; Moldanová et al., 2011; Achten and Andersson, 2015; Zhao et al., 2020). O-PAHs are more persistent and mobile than its parent PAH (Moldanová et al., 2011) and will thus have a higher tendency to spread longer.

The results presented in this study suggests that allowing discharge of scrubber water to the marine environment is in direct conflict with the WFD's goals to achieve good environmental status in European waters. If 20% of the bunker fuel demand is covered by HFO with open loop scrubbers (Open loop scenario Fig. 8), the environmental load of three of the metals (Cd, Pb and Hg) that are included in the priority substance list (Annex 1 DIRECTIVE 2008/105/EC) are predicted to increase by 12, 2 and 6 times respectively as compared to the Pre-sulphur cap scenario. Also, the marine environmental loads of parent Nap, included in the priority substance list

Table 2
Average concentration and the 95% confidence interval (CI) of a selection of metals and PAHs in open loop scrubber discharge water, open loop inlet water and closed loop scrubber discharge water where N_{Tot} is the total number of samples and $N_{<LOD}$ are the number of measurements below limit of detection, included as ½ LOD. Pristine seawater, i.e. typical open ocean concentrations, are listed for comparison where the metal concentrations are based on general surface levels according to Bruland and Lohan (2003) and the PAH concentrations have been derived from Law et al. (1997), measuring PAH content in the North Sea surface water.

		Open loop scrubber discharge		Open loop inlet water		Closed loop scrubber discharge		Pristine seawater
		$\overline{X}$ ± 95% CI (μg/L)	N_{Tot} ($N_{<LOD}$)	$\overline{X}$ ± 95% CI (μg/L)	N_{Tot} ($N_{<LOD}$)	$\overline{X}$ ± 95% CI (μg/L)	N_{Tot} ($N_{<LOD}$)	(μg/L)
Metals	Arsenic (As)	6.8 ± 3.4	66 (42)	5.7 ± 1.4	57 (39)	22 ± 9.4	24 (5)	1.9
	Cadmium (Cd)	0.8 ± 0.3	64 (53)	0.9 ± 0.3	58 (50)	0.55 ± 0.19	24 (18)	0.07
	Chromium (Cr)	15 ± 6.5	57 (28)	17 ± 19	51 (37)	1300 ± 1700	15 (8)	0.21
	Copper (Cu)	36 ± 12	72 (18)	29 ± 13	62 (24)	480 ± 230	24 (1)	0.19
	Iron (Fe)	260 ± 250	9 (0)	37 ± 39	7 (0)	490 ± 82	3 (0)	–
	Lead (Pb)	8.8 ± 4.4	69 (36)	7.7 ± 4.6	59 (40)	7.7 ± 3.1	24 (14)	0.002
	Mercury (Hg)	0.09 ± 0.01	24 (19)	0.09 ± 0.02	21 (18)	0.07 ± 0.02	16 (11)	0.0002
	Nickel (Ni)	48 ± 12	67 (3)	11 ± 6.2	58 (32)	2700 ± 860	24 (0)	0.47
	Vanadium (V)	170 ± 49	63 (0)	9.0 ± 4.9	54 (32)	9100 ± 3200	24 (0)	1.7
	Zinc (Zn)	110 ± 59	72 (20)	160 ± 140	60 (29)	370 ± 200	24 (2)	0.33
LMW PAHS	Naphthalene (Nap)	2.81 ± 0.77	59 (1)	0.10 ± 0.07	53 (39)	2.08 ± 1.05	20 (0)	< 0.010
	Acenaphthylene (Acy)	0.12 ± 0.07	68 (24)	0.11 ± 0.10	65 (61)	0.09 ± 0.06	14 (2)	< 0.003
	Acenaphthene (Ace)	0.19 ± 0.07	68 (14)	0.01 ± 0.003	65 (61)	0.47 ± 0.31	14 (0)	< 0.002
	Fluorene (Flo)	0.46 ± 0.10	68 (4)	0.06 ± 0.05	65 (59)	1.32 ± 0.54	14 (0)	< 0.001
	Phenanthrene (Phe)	1.51 ± 0.29	68 (1)	0.09 ± 0.07	66 (36)	5.00 ± 2.30	14 (0)	< 0.008
	Anthracene (Ant)	0.08 ± 0.04	68 (17)	0.02 ± 0.02	65 (56)	1.55 ± 2.00	14 (3)	< 0.001
	Fluoranthene (Fla)	0.16 ± 0.04	68 (7)	0.03 ± 0.02	65 (48)	0.63 ± 0.41	14 (0)	< 0.001
	Pyrene (Pyr)	0.31 ± 0.11	68 (8)	0.05 ± 0.03	65 (41)	0.76 ± 0.59	14 (0)	< 0.001
HMW PAHs	Benzo[*a*]anthracene (BaA)	0.12 ± 0.05	68 (25)	0.03 ± 0.02	66 (50)	0.30 ± 0.29	14 (4)	< 0.002
	Chrysene (Chr)	0.19 ± 0.07	68 (17)	0.04 ± 0.03	65 (47)	0.50 ± 0.45	14 (3)	< 0.002
	Benzo[*b*]fluoranthene (BbF)	0.04 ± 0.02	68 (32)	0.01 ± 0.004	65 (56)	0.14 ± 0.12	14 (5)	< 0.001
	Benzo[*k*]fluoranthene (BkF)	0.01 ± 0.01	49 (40)	0.01 ± 0.005	47 (44)	0.02 ± 0.02	11 (9)	< 0.001
	Benzo[*a*]pyrene (BaP)	0.05 ± 0.02	68 (37)	0.01 ± 0.004	66 (57)	0.06 ± 0.05	14 (9)	< 0.001
	Indeno[*1,2,3-cd*]pyrene (InP)	0.07 ± 0.06	68 (50)	0.05 ± 0.05	65 (61)	0.04 ± 0.03	14 (9)	< 0.001
	Benzo[*ghi*]perylene (BghiP)	0.02 ± 0.01	68 (43)	0.01 ± 0.01	65 (61)	0.07 ± 0.07	14 (8)	< 0.001
	Dibenzo[*a,h*]anthracene (DahA)	0.03 ± 0.01	68 (54)	0.02 ± 0.01	65 (64)	0.03 ± 0.02	14 (9)	< 0.001

(Annex 1 DIRECTIVE 2008/105/EC), and Phe are also predicted to increase as the atmospheric degradation is by-passed when the scrubber scavenges some of the PAHs. The same could also be true for other priority substances such as anthracene (Ant) and Fla as these are semi-volatile, prone to efficient atmospheric degradation. The relative load of the sum of the 5 PAHs (far right in Fig. 9), grouped in Annex 1 of the WFD (DIRECTIVE 2008/105/EC), indicate that if 22% of the bunker fuel demand were covered by scrubbers instead of MGO the relative load of these priority hazardous compounds will almost double. The combined results show that installing scrubbers with a continued use of HFO implicate a higher environmental load, with respect to metals and PAHs, as compared to shifting towards less polluting fuels. Opting for a closed loop system instead of an open loop system would reduce the environmental impact, especially considering metals. But the results indicate that most PAHs will remain to be emitted to the air and, based on that, the environmental impact from closed loop scrubbers remain higher as compared to MGO/MDO combustion.

5. Conclusions

A continued use of HFO, with or without a scrubber, will result in a greater environmental load with respect to metals and PAHs as compared to a shift to MGO. Installing open loop scrubbers will not reduce the load, only change the primary recipient from the atmosphere to the marine environment, which will alter the distribution of the parent compounds and their derivatives. Shifting the emissions from air to water means that many of the compounds will not be susceptible to atmospheric chemistry reactions before entering the surface waters. This will also affect the dispersion of contaminants where atmospheric long-range transport might be reduced but that the local footprint of shipping will increase. To quantify the extent of the adverse effects on the marine environment is beyond the scope of this study and will require further investigations.

The installations of scrubbers might also introduce entirely new contamination sources such as Cr, shown by the enrichment of Cr in scrubber water. The reason for the elevated levels of Cr have not been fully understood but a possibility would be corrosion of stainless-steel pipes that are exposed to reactive and acidic scrubber water. The acidity will also affect the mobility and speciation of all metals, potentially increasing their bioavailability and thus their toxicity.

Based on the results from this study and in accordance with several others (e.g. Winnes et al., 2016; Wu et al., 2018), HFO should be replaced by less polluting alternatives. Emissions of SO_X and PM_{mass} are clearly not the only combustion related hazards and regulations should aim at targeting all pollutants to the entire environment. Shifting from residual fuels towards distillate fuels would reduce the environmental load. Installing open loop scrubbers, would not, and HFO should therefore be phased out as a marine fuel. Removing HFO from the market would also decrease the risk of ships being non-compliant. For future work, more information regarding low-sulphur residual fuels (VLSFO and ULSFO) is needed before these can be included in the evaluation.

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CRediT authorship contribution statement

Anna Lunde Hermansson: Methodology, Investigation, Writing - original draft, Writing - review & editing, Visualization. **Ida-Maja Hassellöv:** Conceptualization, Writing - review & editing, Supervision. **Jana Moldanová:** Writing - review & editing. **Erik Ytreberg:** Conceptualization, Investigation, Writing - review & editing, Supervision.

Declaration of Competing Interest

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

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.trd.2021.102912.

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